UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR DE INGENIEROS DE
CAMINOS, CANALES Y PUERTOS**

**Hybrid systems based on metal oxide and
nanocarbons: electronic properties and
applications for photocatalysis**

TESIS DOCTORAL

ALICIA MOYA CUENCA

Licenciada en Ciencias Químicas

2017

Departamento de Ciencias de Materiales

Escuela Técnica Superior de Ingenieros de Caminos,
Canales y Puertos

Universidad Politécnica de Madrid

**Hybrid systems based on metal oxide and
nanocarbons: electronic properties and
applications for photocatalysis**

TESIS DOCTORAL

Alicia Moya Cuenca

Licenciada en Ciencias Químicas

Director de Tesis

Juan José Vilatela

Dr. Ciencia de Materiales

2017

“Follow your interests, get the best available education and training, set your sights high, be persistent, be flexible, keep your options open, accept help when offered, and be prepared to help others”

Mildred Dresselhaus

Con todo mi cariño, a mis padres

ACKNOWLEDGEMENT

I would like to thanks to many people who supported me during the course of my PhD study.

First of all, I would like to thank to Dr. Juan José Vilatela for giving me the opportunity to perform my PhD study in a very interesting research field. I am grateful for the deep and fruitful discussions along my PhD study. This thesis is a mutual work, thanks for your guide and support as supervisor.

I also want to thank to IMDEA Materials Institute for allowing me to work in a very competitive research institute. It has been a pleasure to work in a really international environment. In particular, I want to express my gratitude to all the colleagues of Multifunctional Nanocomposites Group that have been around during these years and support me every day. Dr. Belén Alemán, Dr. Laura Cabana, Dr Juan Pedro Fernández, Juan Carlos Fernández, Bartolomé Más, Alfonso Monreal, Víctor Reguero, Evgeny Senokos, Yunfu Ou, Dr. Hangbo Yue and all the students, lot of thanks to all you for the discussion and great moments during these four years, especially those who I consider them my friends.

I acknowledge gratefully the European Union Seventh Framework Programme for the financial support of this work (project nº 310184) that has effectively allowed this PhD. The collaboration with all the members of the European project has provided me the opportunity to cooperate with other researchers of the same or complementary fields, which has resulted in a very rich scientific interactions. In particular, I would like to express my gratitude to Prof. D. Eder and Dr. Alexey Cherevan for all the discussion along the project. Also, I want to thank for the opportunity of visiting his lab and extend my knowledge in the photocatalysis field. As well, for their friendly welcome and their time during my stay in Münster. This acknowledgement can be extended to all the members of Prof. Eder's group.

I sincerely appreciate other collaborations that have considerably improved this work. Dr. Víctor de la Peña O'Shea, Dr. Fernando Fresno, Patricia Reñones, Dr. Avishek Saha, Prof. Dirk Guldi, Prof. Maurizio Prato, Dr. Silvia Marchesan, Daniel Iglesias, Dr. Reinhold Wannemacher, Dr. Andrés Castellanos, Dr. Aday Molina-Mendoza, Dr. Daniel

Granados and Dr. Manuel Rodríguez, thanks to all for the efforts that have complemented my knowledge.

I would like to extend my acknowledgements to many other people, some of them far away from science, but all of them close to me. For this, I take the confidence to write my next words in Spanish.

Quisiera extender mis agradecimientos a otras muchas personas, algunos de ellos alejados de la ciencia, pero todos cerca de mí. Me gustaría agradecer a muchísimos compañeros con los que he compartido muchos momentos en IMDEA o fuera de él. Tanto científicos como técnicos, administración, recepción o mantenimiento, gracias por convertir el día a día del trabajo en un dulce momento. En especial, Alberto, Eva, Irene y Luis, gracias por todos estos años de respaldo como grandes compañeros y amigos.

Por supuesto, no puedo olvidar a mis químicos con los que comparto mis andadas, y en especial, a Carmen y Lidia. Gracias por seguir tan de cerca cada uno de mis pasos y alegraros tanto de cada uno de ellos como yo. No importa dónde nos sitúe el destino, siempre estaremos unidas y compartiendo grandes momentos para el recuerdo.

No puedo dejar de lado a mis amigos taranconeros con los que comparto algo muy importante, mis raíces. Latiguillos y tripones, gracias por muchos momentos divertidos. También a los sanseros, con los que he compartido muchos momentos a lo largo de estos cuatro años. Y por supuesto, a la peña, quienes han vivido muy de cerca esta etapa de mi vida. Así, me gustaría nombrar especialmente a Cris, Fer, Gonza, Isa, Kata, Legi, Lore, Manu, Nuri, Raquel, Txule y Viole.

Finalmente a mi familia. A mis padres, Fernando y M^a Mar quienes siempre me apoyan incondicionalmente, depositan toda su confianza en mí y se ilusionan con mis retos. A mi hermana Coral, tan alegre, luchadora y valiente, no sabes cuánto te admiro. A mi prima Natalia, que siempre se preocupa por mí como prima y amiga. Y a Ivi, quién ha vivido de verdad el día a día de esta tesis, ayudándome y apoyándome en todo momento, lo cual ha hecho todo mucho más fácil.

Sin todos ellos, esta tesis no habría sido posible. Muchas gracias.

RESUMEN

Una más eficiente conversión de la energía solar es altamente demandada para la sostenibilidad de las fuentes energéticas mundiales. Actualmente, existe un incremento continuo en el interés de nuevos materiales híbridos inorgánicos/nanocarbonos para aplicaciones fotocatalíticas. Uno de los objetivos de esta tesis es el desarrollo de nuevas morfologías híbridas con estructuras mesoporosas mediante la combinación del método sol-gel y la técnica de electrohilado, la cual forma fibras híbridas unidimensionales con propiedades coloidales en suspensión. Además, el crecimiento *in situ* de óxidos metálicos sobre la superficie de nanocarbonos funcionalizados (nanotubos de carbono o grafeno) ha permitido formar grandes intercaras, las cuales facilitan procesos de transporte y transferencia de carga. Por tanto, el proceso de hibridación constituye un paso fundamental para crear un nuevo material, diferente de sus componentes individuales. En esta tesis, el estudio de efectos sinérgicos en la intercara entre el material inorgánico y los nanocarbonos ha sido ampliamente explotado, resaltando un fuerte acoplamiento entre ambos componentes como evidencia de la hibridación. La estrategia de la funcionalización química de los nanocarbonos ha permitido la formación de enlaces Ti-O-C, los cuales llevan a la aparición de estados electrónicos originados en las regiones de la intercara. La presencia de nuevos estados energéticos favorecen los procesos de transferencia de carga a través de la intercara óxido metálico/nanocarbón y así, retrasa la recombinación de los portadores de carga. Además, estudios electroquímicos han sido usados para estudiar los procesos de transferencia de carga a través de la intercara sólido/líquido. Esta intercara llega a ser muy importante en los procesos fotocatalíticos. Efectivamente, la eficiencia fotocatalítica ha incrementado hasta 14 veces más en la producción de hidrógeno que las puras nanopartículas inorgánicas. Finalmente, fotoelectrodos basados en el control del crecimiento de óxidos metálicos en la superficie de fibra de nanotubos de carbono, por ejemplo mediante deposición atómica por capas, han sido usados para demostrar los efectos de la intercara en las propiedades fotoelectroquímicas. Los resultados de esta tesis pueden ser aplicados a la formación de otros híbridos con diseño controlado de sus arquitecturas e intercaras, las cuales beneficiarán sus eficiencias fotocatalíticas.

ABSTRACT

A more efficient solar-to-energy conversion is highly demanded for the sustainability of the world energy sources. Nowadays, there is a continuously increasing interest in new inorganic/nanocarbon hybrid materials for photocatalytic applications. One of the objective of this thesis is the development of novel hybrid morphologies with mesoporous structure by combination of sol-gel and electrospinning technique, which forms one-dimensional hybrid fibres with colloidal properties in suspension. Furthermore, the *in-situ* growth of metal oxides on functionalised nanocarbon (CNTs or graphene) surface enables to form large interfaces, which facilitate charge transport and transfer processes. Therefore, the hybridisation process constitutes a fundamental step to create a new material, different from their individual components. In this thesis, the study of the synergetic effects at the interface between the inorganic and the nanocarbons has been widely exploited, highlighting a strong coupling between both components as evidences of the hybridisation. The strategy of chemical functionalisation of the nanocarbons has enabled the formation of Ti-O-C bonds, which leads to electronic states emerging from the large interfacial regions. The presence of new interfacial energy states favours the charge separation across the metal oxide/nanocarbon interface and thus, delays the photocarrier recombination. Moreover, electrochemistry studies have been used to study the charge transfer processes across the solid/liquid interface. This interface become more important under the photocatalytic process. Effectively, the photocatalytic efficiency has increased up to 14 times more in the hydrogen production than bare inorganic nanoparticles. Finally, photoelectrodes based on the control of the metal oxide growth on CNT fibre, i.e. atomic layer deposition, have been used to demonstrate the effects of the interface in the photoelectrochemical performance. The results of this thesis can be applied to the formation of other inorganic/nanocarbon hybrids with controlled design of their architectures and interfaces, which will benefit their photocatalytic efficiencies.

Contents

LIST OF ABBREVIATIONS	V
LIST OF FIGURES	VII
LIST OF TABLES	XVII
1. INTRODUCTION	1
2. LITERATURE REVIEW	3
2.1 Nanocarbon-based hybrids	4
2.1.1 Nanocarbons: structure and properties	4
2.1.2 Inorganic/nanocarbon hybrids	7
2.1.3 Interfacial effects in inorganic-nanocarbon hybrids.....	11
2.1.4 Applications of inorganic/nanocarbon hybrids.....	14
2.2 Photocatalytic water splitting	17
2.2.1 Bases of semiconductor photocatalyst for water splitting	20
2.3 Rational design of hybrid nanostructures for photocatalysis.....	23
2.3.1 Optimising the crystal structure and phase composition of TiO ₂	24
2.3.2 Optimising the morphology of TiO ₂	29
2.4 Summary	32
3. MATERIAL AND EXPERIMENTAL TECHNIQUES.....	33
3.1 Materials	33
3.1.1 Multi-walled Carbon Nanotube	33
3.1.2 Graphene	34

3.1.3 Macroscopic CNT fibre.....	35
3.1.4 Chemicals	36
3.2 Sample preparation	37
3.2.1 Synthesis of electrospun nanofibers	37
3.2.2 Synthesis of nanoparticles by sol-gel method	39
3.2.3 Synthesis of thin films by atomic layer deposition	39
3.3 Thermogravimetric analysis	41
3.4 Electron and Optical Microscopy.....	41
3.4.1 Optical Microscopy	41
3.4.2 Electron Microscopy	41
3.5 X-Ray Diffraction.....	44
3.6 Photoelectron Spectroscopy	46
3.7 Raman Spectroscopy.....	48
3.8 Physisorption.....	49
3.9 Absorption/emission spectroscopy	51
3.9.1 UV-Vis Diffuse Reflectance Spectroscopy	51
3.9.2 Fourier Transform Infrared Spectroscopy.....	52
3.9.3 Photoluminescence Spectroscopy.....	53
3.10 Conductivity.....	54
3.11 Electrochemical Methods	56
3.11.1 Open-circuit potential measurements	58
3.11.2 Chronoamperometry	59
3.11.3 Impedance Spectroscopy	60
3.12 Photocatalytic experiments.....	62
3.12.1 Photocatalytic Hydrogen Production	63
3.12.2 Photocatalytic CO ₂ Reduction.....	65

4. SYNTHESIS, MORPHOLOGY AND STRUCTURE OF ELECTROSPUN HYBRIDS..... 67

4.1	<i>In-situ</i> synthesis of TiO ₂ /nanocarbon hybrid.....	68
4.1.1	Sol-gel and electrospinning process.....	68
4.1.2	Heat treatment.....	72
4.2	Crystallisation into mesoporous fibre structure.....	74
4.2.1	Structure evolution of electrospun fibres	74
4.2.2	Morphology of electrospun TiO ₂ fibres and comparison with nanoparticles.....	76
4.2.3	Texture properties of electrospun fibres	81
4.3	New TiO ₂ /nanocarbon hybrid fibres.....	83
4.3.1	Morphology of TiO ₂ /nanocarbon hybrid.....	83
4.3.2	Structure of TiO ₂ /nanocarbon hybrid	84
4.3.3	Texture properties of TiO ₂ /nanocarbon hybrid.....	86
4.4	Evidence of hybridisation in TiO ₂ /nanocarbon hybrid.....	88
4.4.1	Interfacial study of TiO ₂ /nanocarbon hybrid	88
4.4.2	Electronic structure of TiO ₂ /nanocarbon hybrid.....	92
4.4.3	Optical properties of TiO ₂ /nanocarbon hybrid.....	98
4.5	Summary.....	101

5. PHOTOELECTROCHEMICAL AND PHOTOCATALYTIC PROPERTIES OF ELECTROSPUN HYBRIDS 105

5.1	Photoconductivity of electrospun samples.....	106
5.2	Photoelectrochemical studies of electrospun TiO ₂ and TiO ₂ /nanocarbon hybrid photoelectrodes.....	111
5.3	Photocatalytic hydrogen production.....	122
5.3.1	Photocatalytic reaction.....	123
5.3.2	Optimisation of photocatalytic reaction conditions.....	125

5.3.3 Structure-photoactivity relation of electrospun fibres	127
5.3.4 Morphological effect in photocatalytic activity	129
5.3.5 Photocatalytic activity of TiO ₂ -nanocarbon hybrids	130
5.3.6 Comparison of TiO ₂ -based photocatalyst	134
5.4 Photocatalytic CO ₂ reduction	137
5.5 Summary	140
6. NEW TiO₂/CNTf HYBRID MATERIAL.....	143
6.1 Morphology and crystal structure of new TiO ₂ /CNTf hybrid	144
6.2 Understanding the electronic structure of TiO ₂ /CNTf hybrid	151
6.3 Electrochemical properties of new TiO ₂ /CNT fibre hybrid	163
6.4 Summary	168
7. CONCLUSIONS AND FUTURE WORKS.....	171
7.1 Conclusions	171
7.2 Future work	175
A. ELECTROSPUN NIOBIUM/TANTALUM OXIDE FIBRES FOR PHOTOCATALYSIS.....	177
A.1 Synthesis of Nb ₂ O ₅ and Ta ₂ O ₅ by sol-gel and electrospinning	178
A.2 Highly crystalline mesoporous structure	180
A.3 Photocatalytic hydrogen production tests	184
A.4 Summary	186
BIBLIOGRAPHY	187

LIST OF ABBREVIATIONS

AC	Alternating Current
ALD	Atomic Layer Deposition
AQY	Apparent Quantum Yield
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CB	Conduction Band
CCD	Charge Coupled Device
CE	Counter Electrode
CEM	Controlled Evaporator Mixer
CNT	Carbon NanoTube
CNTf	Carbon NanoTube Fibre
CPE	Constant Phase Element
CVD	Chemical Vapour Deposition
DC	Direct Current
DFT	Density Functional Theory
DOS	Density Of States
DRS	Diffuse Reflectance Spectroscopy
DSSCs	Dye-Sensitizer Solar Cell
DWCNT	Double-Wall Carbon NanoTube
EC	Equivalent Circuit
ED	Electron Diffraction
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FFT	Fast Fourier Transform
FID	Flame Ionization Detector
FT-IR	Fourier Transform InfraRed
FTO	Fluorine Tin Oxide
FWHM	Full Width Half Maximum
GR	Graphene
HAADF	High Angle Annular Dark Field

HOPG	High Ordered Pyrolytic Graphite
HRTEM	High Resolution Transmission Electron Microscopy
HT	High Temperature
IR	InfraRed
LED	Light Emitting Diode
LT	Low Temperature
MWCNT	Multi-Wall Carbon NanoTube
NIR	Near InfraRed
OCP	Open Circuit Potential
OM	Optical Microscopy
PDMS	PolyDiMethylSiloxane
PEC	PhotoElectrochemical Cell
PL	Photoluminescence
PVP	PolyVinylPyrrolidone
RE	Reference Electrode
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
STEM	Scanning Transmission Electron Microscopy
SWCNT	Single-Wall Carbon NanoTube
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TGA	ThermoGravimetric Analysis
UPS	Ultraviolet Photoelectron Spectroscopy
UV	Ultraviolet
VB	Valence Band
VBM	Valence Band Maxima
WE	Working Electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

LIST OF FIGURES

Figure 2.1: Atomic models of a) monolayer (left) and bilayer (right) graphene[Bostwick et al. 2007] and b) single, double and multi-wall (from left to right) carbon nanotubes. Taken from http://www.physicsworld.com/	5
Figure 2.2: Functionalisation of CNTs through a) covalent and b) non-covalent interaction.	6
Figure 2.3: Schematic representation of a) nanocarbon composites formed by mixture of the two individual components and b) nanocarbon hybrids formed by coating the nanocarbon surface by the inorganic component.	8
Figure 2.4: Summary of synthetic methods used for hybridisation of a) nanocarbons (CNTs or graphene) either pristine or oxidised with functional materials by b) <i>ex-situ</i> and c) <i>in-situ</i> approaches.[Shearer et al. 2014]	10
Figure 2.5: Scheme of proposed mechanism of interfacial charge transfer in inorganic/nanocarbon hybrid with CNT acting as: a) electron acceptor, b) electron donor, c) sensitizer and d) impurity.....	13
Figure 2.6: Scheme of various applications of inorganic/CNT hybrid materials.	15
Figure 2.7: Photocatalytic hydrogen production from water using a powder photocatalyst. Adapter from [Kudo and Miseki 2009].....	18
Figure 2.8: Schematic energy diagram of a) photosynthesis by green plants and b) photocatalytic water splitting (artificial photosynthesis). Adapted from [Kudo and Miseki 2009]	18
Figure 2.9: Honda-Fujishima effect of photoelectrochemical water splitting process using TiO ₂ photoelectrode.....	19
Figure 2.10: Mechanism of water splitting process in a single-particle of a semiconductor photocatalyst.....	20

Figure 2.11: Band structure of several semiconductor and redox potential of water splitting.[Xiaoping CHEN 2013]	21
Figure 2.12: Particle size effect on photocarriers diffusion and recombination in photocatalytic water splitting process.	22
Figure 2.13: TiO ₆ octahedra in a) anatase and b) rutile, showing different connectivity between the octahedra.	25
Figure 2.14: Electronic structure of C-doped TiO ₂ photocatalyst. Adapted from [Schneider et al. 2014].....	28
Figure 2.15: a) Alignment of anatase nanoparticles in the fibre network. b) Interparticle charge transfer process within a nanofiber. [Choi et al. 2010]	31
Figure 2.16: Effect of the pH on the TiO ₂ agglomeration and on the increase of H ₂ production due to interparticle charge transport.[Lakshminarasimhan et al. 2008]	31
Figure 3.1: Schematic representation of the sulfonitric oxidation process employed for functionalisation of MWCNTs.	34
Figure 3.2: Schematic representation of the diazo-coupling reaction employed in the functionalisation process of graphene.....	35
Figure 3.3: Schematic representation of the CVD reactor for CNTf production.	36
Figure 3.4: Schematic representation of sol-gel + electrospinning process.....	38
Figure 3.5: General representation of the applied thermal treatment.....	39
Figure 3.6: Scheme of a cycle of ALD process using Ti(N(CH ₃) ₂) ₄ as inorganic precursor, N ₂ as purged gas and H ₂ O as oxygen source.	40
Figure 3.7: Interaction volume of the signals generated by interaction between electron beam and sample in SEM mode.....	42
Figure 3.8: Schematic representation of a Transmission Electron Microscope operating in image mode (left) and diffraction image mode (right).....	43

Figure 3.9: Schematic representation of Bragg's law.....	45
Figure 3.10: Schematic representation of photoelectron spectroscopy technique and resulting photoelectron spectra using two excitation sources: X-ray exciting core electrons and UV light exciting VB electrons.	46
Figure 3.11: Schematic representation of the electronic states of a general system where transitions between vibrational states show a) Anti-Stokes Raman scattering, b) Rayleigh scattering and c) Stokes Raman scattering.....	49
Figure 3.12: Representation of physical gas adsorption on a porous solid surface by increasing the gas pressure.	50
Figure 3.13: Scheme of the photoluminescence process, showing the main radiative recombination process that can occur in a semiconductor material	54
Figure 3.14: Optical microscope images and schematic electrode cross-section of the fabrication by <i>pick-up and drop technique</i> of a single fibre photodetector.....	55
Figure 3.15: Schematic representation of the three electrode electrochemical cell used in this report.	58
Figure 3.16: The simple RC circuit (Randles circuit) and its corresponding Nyquist plot.....	61
Figure 3.17: Photograph of water splitting reactor used for testing TiO ₂ photocatalysts.	63
Figure 3.18: Effect of the light power in the photocatalytic H ₂ evolution rate.....	65
Figure 3.19: Schematic reactor system for the photoreduction of CO ₂	66
Figure 4.1: Optical images showing the sequential optimisation of electrospinning process described in <i>Table 4.2</i>	71
Figure 4.2: a) Photograph of a typical mesh of electrospun fibres. b) Scanning electron micrographs showing the uniformity of the as-electrospun fibres.....	71

Figure 4.3: Thermogravimetric decomposition curves of a) the PVP fibre and b) the different type of nanocarbons.....	72
Figure 4.4: Thermogravimetric decomposition curves of the sol-gel precursor solution containing 3vol.% of ox-MWCNTs.....	73
Figure 4.5: XRD patterns showing the crystal structure of TiO ₂ fibres annealed between 400-800°C in: a) Ar atmosphere and b) air atmosphere	75
Figure 4.6: a) Anatase/rutile ratio and b) crystal size corresponding to the XRD patterns of <i>Figure 4.5</i> as a function of the annealing temperature.....	75
Figure 4.7: a) XRD patterns of TiO ₂ fibres obtained at 500°C and b) effect of the Ar flow in the phase composition and crystal size.....	76
Figure 4.8: Scanning electron micrographs of a) TiO ₂ nanoparticles produced by standard sol-gel and b) TiO ₂ fibres produced by sol-gel and electrospinning. Inset shows a high resolution image of an individual electrospun fibre.....	77
Figure 4.9: Transmission electron micrographs of a-c) TiO ₂ fibres at different magnifications with anatase planes highlighted in c) and d) TiO ₂ nanoparticles.	78
Figure 4.10: Electron diffraction pattern of a) TiO ₂ fibres and b) TiO ₂ nanoparticles. Characteristic diffraction of anatase and rutile are highlighted in the images.....	78
Figure 4.11: XRD patterns of TiO ₂ nanoparticles (black curve) and TiO ₂ fibres (red curve) obtained under the same annealing conditions: (a) 400°C for 2.5h in air and (b) 500°C for 1h in Ar.	79
Figure 4.12: a) Normalised Raman spectra highlighting the vibrational modes of anatase phase and b) zoom of the E _g mode at ~144cm ⁻¹ , including a representation of the vibration.....	80
Figure 4.13: a) N ₂ adsorption-desorption isotherms and b) Cumulative pore volume (dash line) and pore size distribution (scatter+line) of TiO ₂ nanoparticles and fibres, obtained from the adsorption branch.....	82

Figure 4.14: a) SEM and b) HRTEM images of TiO ₂ /ox-MWCNTs fibres showing the successful hybridisation of the <i>in-situ</i> approach.	84
Figure 4.15: XRD patterns of 1vol.% TiO ₂ /ox-MWCNTs hybrid showing a mixture of anatase and rutile phases. Referenced patterns of both phases are included below.	85
Figure 4.16: a) N ₂ adsorption-desorption isotherms and b) Cumulative pore volume (dash line) and pore size distribution (scatter+line) of TiO ₂ /ox-MWCNTs hybrid fibres.	86
Figure 4.17: Relation between crystal size and surface area of pure TiO ₂ and TiO ₂ /nanocarbon hybrids.	87
Figure 4.18: a) Raman spectra of electrospun TiO ₂ /ox-MWCNTs hybrid with the vibrational modes of anatase phase and nanocarbon highlighted.	88
Figure 4.19: a) Normalised anatase E _g mode at ~144cm ⁻¹ and b) D and G characteristic Raman features of nanocarbons before and after hybridisation.....	89
Figure 4.20: a-b) HR-TEM images of TiO ₂ /ox-MWCNTs hybrid showing the large interfaces formed between (101) atomic plane of anatase nanocrystals and the (002) atomic plane of MWCNTs, highlighted in the direct and inverse FFT image.....	90
Figure 4.21: FT-IR spectra of a hybrid with oxidised MWCNTs and reference samples of the ox-MWCNTs and TiO ₂ fibres.	91
Figure 4.22: a) XPS spectra of Ti2p state and deconvolution of b) TiO ₂ and c) TiO ₂ /ox-MWCNTs spectra using mixed Gaussian/Lorentzian curves.....	92
Figure 4.23: a) XPS spectra of O1s state and deconvolution of b) TiO ₂ and c) TiO ₂ /ox-MWCNTs spectra using mixed Gaussian/ Lorentzian curves.....	93
Figure 4.24: a) XPS spectra of C1s state and deconvolution of b) Ox-MWCNTs and c) TiO ₂ /ox-MWCNTs spectra using mixed Gaussian/ Lorentzian curves.....	94
Figure 4.25: a) XPS spectra of valence band region of TiO ₂ and TiO ₂ /ox-MWCNTs samples and b) zoom of the onset in the low energy region.	95

Figure 4.26: Full UPS spectra of a) TiO ₂ and TiO ₂ /nanocarbon hybrids samples and b) Ox-MWCNTs samples.....	96
Figure 4.27: UPS spectra of a) TiO ₂ and TiO ₂ /nanocarbon hybrids and b) Ox-MWCNTs represented at the high binding energy, where secondary electron cut-off energy provides the work function values of each material.	97
Figure 4.28: Valence band states observed at low binding energy in the UPS spectra for TiO ₂ and TiO ₂ /nanocarbon hybrids.....	98
Figure 4.29: UV-Visible diffuse reflectance spectroscopy of TiO ₂ and TiO ₂ /nanocarbon hybrid fibres.....	99
Figure 4.30: a) Photoluminescence spectra of TiO ₂ fibres and TiO ₂ /ox-MWCNTs hybrid. b) Fitting of PL spectra of both samples.....	101
Figure 4.31: Schematic representation of the structural evolution of the electrospun fibres during the thermal annealing.....	102
Figure 4.32: a) Schematic representation of CNT bonded to (101) anatase. b) Electronic band structure of the hybrid material.....	103
Figure 5.1: a) Optical image of fibre device together to a schematic cross-section of the device. b) SEM image of an individual fibre deposited between the metallic electrodes (inset shows a high resolution SEM image of this fibre).	107
Figure 5.2: Current-voltage curve of TiO ₂ fibre device in dark conditions.....	107
Figure 5.3: a) Current-voltage curves of TiO ₂ fibre device in dark conditions and under illumination of 455nm wavelength using different light power. b) Same curves but in logarithmic scale.	108
Figure 5.4: Photocurrent measured at different light power and showing a sub-linear relation, indicative of photogating.	109
Figure 5.5: Photocurrent response of TiO ₂ device over the time with illumination of 455nm of wavelength. The slow fall confirms that photogating is a major photocurrent mechanism in the material.....	109

Figure 5.6: Responsivity as a function of the wavelength to compare the optoelectronic properties between pure TiO ₂ fibre and TiO ₂ /ox-MWCNTs hybrid fibre devices.....	110
Figure 5.7: SEM image of TiO ₂ fibre sample deposited on FTO substrate.....	112
Figure 5.8: a) Open-circuit potentials under dark and illumination conditions and b) lifetime of injected electrons.	113
Figure 5.9: Chronoamperometry curves of TiO ₂ air, TiO ₂ Ar and TiO ₂ /ox-MWCNTs photoelectrodes, showing a rapid photoresponse for all the materials.....	114
Figure 5.10: Nyquist and Bode plots of the EIS data for TiO ₂ annealed in air, TiO ₂ annealed in Ar and TiO ₂ /ox-MWCNTs hybrid under dark and illumination conditions. Inset: magnification of the high frequency range.....	118
Figure 5.11: Proposed equivalent circuit for the mesoporous electrospun fibres photoelectrodes.....	119
Figure 5.12: Mott–Schottky plot at a frequency of 10 kHz in the dark.	121
Figure 5.13: a) TEM image of TiO ₂ fibre after photocatalytic test showing well dispersed Pt nanoparticles of 2-3nm size. b) Continuous H ₂ monitoring during a typical photocatalytic test.	124
Figure 5.14: H ₂ evolution rate a) curves and b) values, varying the sacrificial agent (methanol) content.	125
Figure 5.15: H ₂ evolution rate a) curves and b) values, varying the loading of co-catalyst (Pt nanoparticles).	126
Figure 5.16: H ₂ evolution rate a) curves and b) values, varying the amount of photocatalyst. Fit of the plot in b) shows that above 30mg a <i>plateau</i> in the H ₂ production is observed.....	127
Figure 5.17: a) H ₂ evolution rate curves of TiO ₂ fibres annealed at different temperatures and b) the effect of the crystal phase on the H ₂ production.....	128

Figure 5.18: a) H ₂ evolution rate curves of TiO ₂ fibres annealed at different Ar gas flow and b) the effect of the crystal phase and size on the H ₂ production.	128
Figure 5.19: H ₂ evolution rate curves of TiO ₂ nanoparticles (black curve) and TiO ₂ fibres (red curve), tested under identical conditions.	129
Figure 5.20: Hydrogen production curves over time. The maximum hydrogen production rate at the <i>plateau</i> is detailed in the graph.....	131
Figure 5.21: Hydrogen production of pure TiO ₂ and TiO ₂ /ox-MWCNTs hybrid fibres with different anatase/rutile ratio.....	132
Figure 5.22: Hydrogen production rate of the four different type of nanocarbons as a function of their volume fraction.....	133
Figure 5.23: Photocatalytic H ₂ production rate of electrospun TiO ₂ and hybrids with pristine and functionalised nanocarbons compared against data from literature (see Table 5.5).....	136
Figure 5.24: Temporal evolution rates of the photoreduction products: a) H ₂ b) CO, c) CH ₄ and d) CH ₃ OH under UV/Vis illumination.	138
Figure 5.25: Selectivity (%) of the main reaction products obtained with TiO ₂ nanoparticles and TiO ₂ fibres materials under UV irradiation and CO ₂ /H ₂ O atmosphere.....	139
Figure 6.1: a) Optical image of a CNT fibre electrode, b) SEM image showing the CNT bundles forming the CNT fibre and c) TEM image illustrating the entanglement of the CNTs in the bundles.	145
Figure 6.2: Schematic picture of a TiO ₂ /CNTf sample.....	145
Figure 6.3: SEM images of a) as-grown CNT fibre, b-f) CNT fibre with ALD deposition of 10, 20, 40, 60 and 80nm of TiO ₂	146
Figure 6.4: XRD pattern of TiO ₂ /CNTf sample after ALD process, showing the peaks of the graphite structure and the wide background of the amorphous TiO ₂	148

Figure 6.5: a) TEM image and b) HRTEM image of 20nm_TiO ₂ /CNTf sample showing the conformal coating of the CNT bundles. The FFT and HRTEM images of the inset demonstrate that the coating consists in anataseTiO ₂ . c) HAADF-STEM image of 80nm_ TiO ₂ /CNTf sample and d) corresponding EDS spectrum and Ti, O mapping images.	149
Figure 6.6: a) XRD patterns of the hybrid samples annealed at 400°C in Ar atmosphere and corresponding to anatase phase. b) Magnification in the range of 23-29° showing the deconvolution of the anatase and carbon peaks.....	150
Figure 6.7: Raman spectra of as-grown CNTf and TiO ₂ /CNTf hybrids a) before and b) after annealing at 400°C for 1h in Ar atmosphere.	152
Figure 6.8: Raman of pristine CNTf (black line) and CNTf treated by ALD without (red line) and with (blue line) pulses of inorganic precursor.....	153
Figure 6.9: Shift of the CNT Raman modes as a function of the TiO ₂ thickness in TiO ₂ /CNTf hybrids. Dash-dot lines represents the peak position for the CNTf exposed only to O ₂ plasma.	155
Figure 6.10: Intensity ratio of D and D' mode with respect to G mode as a function of the TiO ₂ thickness in TiO ₂ /CNTf hybrids. Dash-dot lines represents the peak position for the CNTf exposed only to O ₂ plasma.	156
Figure 6.11: Raman spectra of anatase active modes for the pure CNTf and TiO ₂ /CNTf hybrids. The inset shows a magnification of the most intense peak, where a shift to lower wavenumber is observed when the TiO ₂ layer increases.	157
Figure 6.12: C1s region of XPS spectra for a) 20nm_TiO ₂ /CNTf hybrid, b) pristine CNTf and c) pure TiO ₂ sample.....	158
Figure 6.13: a) Ti2p and b) O1s region of XPS spectra for 20nm_TiO ₂ /CNTf.....	160
Figure 6.14: a) Full UPS spectra and b) secondary electron cut-off of CNT fibre (black line), TiO ₂ (red line) and TiO ₂ /CNTf hybrid (blue line).....	161

Figure 6.15: UPS spectra showing the valence band region of a) CNTf, b) TiO ₂ and c) TiO ₂ /CNTf hybrid.....	162
Figure 6.16: Scanning electron micrograph of TiO ₂ /CNTf hybrid electrode with 40nm of inorganic deposition.....	163
Figure 6.17: Open circuit potential measurements of TiO ₂ /CNTf hybrid photoelectrodes.....	164
Figure 6.18: Chronoamperometry curves at OCP of TiO ₂ /CNTf hybrid photoelectrodes.....	165
Figure 6.19: a) Nyquist and b) Bode plots of the EIS raw data (scatter) and fit data (lines) of TiO ₂ /CNTf hybrids with 40nm of TiO ₂ coating after annealing in Ar at 400°C for 1h.....	166
Figure 6.20: Proposed equivalent circuit model for the TiO ₂ /CNTf hybrid photoelectrodes.....	167
Figure A.1: Scanning electron micrographs of a) PVP/Nb system and b) PVP/Ta system.....	179
Figure A.2: Scanning electron images of a) Nb ₂ O ₅ crystallised at 575°C/1h and b) Ta ₂ O ₅ at 700°C/10h.....	179
Figure A.3: X-ray diffraction patterns of a) Nb ₂ O ₅ and b) Ta ₂ O ₅ fibres.....	180
Figure A.4: HRTEM images of a-b) Nb ₂ O ₅ and c-d) Ta ₂ O ₅ fibres.	182
Figure A.5: Raman spectra of a) Nb ₂ O ₅ and b) Ta ₂ O ₅ fibres and nanoparticles for comparison of their Raman modes.	183
Figure A.6: UV-Vis DRS spectra of Nb ₂ O ₅ and Ta ₂ O ₅ nanoparticles and fibres.	184
Figure A.7: Hydrogen production rates of Nb ₂ O ₅ and Ta ₂ O ₅ photocatalysts tested with and without the use of Pt as co-catalyst.....	185

LIST OF TABLES

Table 2.1: Intrinsic properties of CNT and graphene.....	5
Table 2.2: Properties of anatase and rutile phases.[Hanaor and Sorrell 2011].....	25
Table 2.3: Synthetic methods for the formation of TiO ₂ . [Hanaor and Sorrell 2011]	26
Table 4.1: Schematic illustration of the four types of nanocarbons employed in the synthesis of electrospun hybrid samples (referred as p-MWCNTs, p-GR, ox-MWCNTs and isoft-GR).....	69
Table 4.2: Summary of parameters employed in the synthesis of electrospun fibres and the conclusions obtained from their combination.	70
Table 4.3: Anatase/rutile ratio and crystal size of TiO ₂ and hybrid fibres.	85
Table 4.4: Textural properties of the synthesised materials.....	87
Table 4.5: Summary of Ti-O-C evidences obtained from XPS data.....	95
Table 4.6: Band gap energy of TiO ₂ fibres and TiO ₂ /nanocarbon hybrids fibres....	100
Table 5.1: OCP values at dark, illumination and the difference between both.	112
Table 5.2: Description and features of equivalent circuit models used in the literature for fitting the impedance spectra of inorganic semiconductors.....	116
Table 5.3: Parameters obtained by fitting the impedance spectra of the photoelectrodes using the equivalent circuit R1+Q1/(R2+C3/R3).	120
Table 5.4: Flat band potential and donor density obtained from Mott-Schottky representation.....	122
Table 5.5: Literature data of photocatalyst for hydrogen production.....	135
Table 5.6: Comparison of cumulative production ($\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}$) in the CO ₂ photoreduction reaction over the catalysts after 20h of UV illumination.....	139

Table 6.1: Measurements of TiO ₂ thickness by SEM images of <i>Figure 6.3</i>	147
Table 6.2: Crystallite size and microstrain calculated from XRD patterns of <i>Figure 6.6b</i> , in particular, from the (001) anatase plane and (002) carbon plane.	151
Table 6.3: Raman peak position, I _D /I _G and I _{D'} /I _G ratios for hybrid with several TiO ₂ thickness and annealed at 400°C.	154
Table 6.4: FWHM of C1s contributions for the TiO ₂ /CNTf and CNTf spectra.	159
Table 6.5: Parameters obtained by fitting the EIS spectra of the hybrid photoelectrodes using the equivalent circuit R1+R2/Q2+R3/Q3.	168

CHAPTER 1

INTRODUCTION

Hybrids based on metal oxides and nanocarbons are new multifunctional materials with a growing interest for energy and environmental applications. The relevant contribution of the hybrids is that they are new materials, with properties that differs from its individual components. Through a rational synthesis design of the hybrid morphology, texture and crystallinity and very importantly, through a control of the interface between both components, a very attractive material can be obtained. The *Chapter 2* reviews the literature of the nanocarbon-based hybrids, a brief introduction of photocatalysis and photocatalyst material for water splitting and finally, preliminary considerations necessities to a rational design of hybrid nanostructures.

The materials used and synthesised in this work by sol-gel process, electrospinning technique and atomic layer deposition are detailed in *Chapter 3*. The experimental techniques used to characterise the structure and properties of the hybrids as well as the conditions of the photocatalytic tests are also available.

Fibre nanostructures of TiO₂/nanocarbon hybrids have been produced by combination of sol-gel and electrospinning technique and have resulted in crystalline mesoporous nanofibres. The optimisation of the synthesis parameters and the analysis of the morphology, texture and structure of the electrospun fibres are presented in *Chapter 4*. Furthermore, the electrospun materials are compared with corresponding

metal oxides formed by standard sol-gel method. Finally, evidences of hybridisation are provided by means of the study of the optical and electrical properties of the TiO₂/nanocarbon interface.

The features of the one-dimensional TiO₂/nanocarbon hybrids favour the charge transport and transfer processes, arising from the synthetic process. Furthermore, the electrospun fibres can be used as colloidal suspensions or as film electrodes, which makes them versatile materials as photo(electro)catalysts. The optoelectronic and electrochemical properties of the electrospun fibres, either in dark or illumination conditions, are discussed in *Chapter 5*. Additionally, the photocatalytic performance for hydrogen production and carbon dioxide photoreduction are presented. In the particular case of photocatalytic hydrogen production, the reactions conditions has been optimised. The photoactivities of electrospun fibres have been related to morphological and structural properties. Lately, they have been compared with literature photocatalyst.

A new type of hybrid material in which the interface is highly important has been designed by the controlled growth of TiO₂ on the surface of macroscopic carbon nanotube fibre. Thus, the *Chapter 6* describes the morphology and crystal structure of the TiO₂/CNT fibre produced by atomic layer deposition on carbon nanotube fibre substrate. In addition, the electronic structure of the new hybrid material and its (photo)electrochemical properties are presented.

The contributions of the studies commented above for the metal oxide/nanocarbon hybrids are concluding in the *Chapter 7*. Furthermore, future directions in the preparation and study of hybrids are also described for the creation of more efficient materials for energy applications.

Finally, *Appendix A* presents preliminary results of niobium and tantalum oxides produced by combination of sol-gel and electrospinning techniques. Crystal structure and photocatalytic hydrogen production tests of Nb₂O₅ and Ta₂O₅ oxide fibres are also presented in comparison with randomly nanoparticles produced by sol-gel method and confirming the enhancement of this synthesis strategy .and the feasibility for application for other inorganic compounds.

CHAPTER 2

LITERATURE REVIEW

Solar energy is an ideal alternative since it is the most powerful, affordable and richest renewable and sustainable source of energy. The conversion of solar energy into chemical fuels is one of the most important challenge of this century. Hydrogen (H_2) is expected to be a promising fuel candidate since it has a high energy density of 140MJ/Kg (exceeding that of gasoline or coal). Moreover, it is a product of the water combustion and then, it is free of carbon and nitrogen oxide emissions. [Turner 1999] The combination of solar energy and water for the hydrogen production can fulfil the global demand of energy. There are several methods for using the sunlight in the splitting of water such as photovoltaic, photobiological or thermochemical. However, these methods require of expensive membranes, biospecies with limit time of use or higher temperatures, respectively. Additionally, photoelectrochemical or photocatalytic reactions constitute a very attractive alternatives because they are cost-effective and very simple.

New materials are necessary to fulfil all the requirements for the development of new and clean energies. The emergency of nanomaterials as the new building blocks to build light energy harvesting assemblies has resulted in an attractive way to use renewable energy resources due to its wide variety of morphologies, large surface areas and abundant surface states. Further hybridisation of energy functional nanomaterials with nanocarbons has increased the interest within this field. The unique band structure of the nanocarbons enables a very fast charge mobility and exceptional

conductivity. Furthermore, nanocarbons present a very large surface area, which makes them ideal substrates to avoid agglomeration of nanoparticles and importantly, increasing the contact area between both components, leading to interfacial interactions for enhancing the photoelectrochemical/photocatalytic properties of the new nanocarbon-based hybrid material.

2.1 Nanocarbon-based hybrids

The hybridisation process is a powerful strategy towards next-generation of multifunctional nanocarbon-inorganic hybrid materials for environmental and sustainable energy applications. Hybridising nanocarbons with a functional material increases the performance of the latter, obtained by combination of the intrinsic properties of each material. But importantly, also by creating of synergetic effects as consequence of the strong interaction between the two materials. Effectively, a close proximity between them results in a narrow interface that can promote charge transfer processes. Thus, the optimisation of the interface between the two components is crucial toward maximising properties.

2.1.1 Nanocarbons: structure and properties

Nanocarbons are graphitic structures with sp^2 hybridisation that can be presented in different morphologies. Graphene is a two-dimensional carbon allotrope that can be briefly described as a few layers of graphite structure (*Figure 2.1a*). Generally, graphene is distinguished between single-layer, bilayer and a few-layer of graphene, which refers to graphene with a layer number less than 10 (structure with more than 10 layers can be considered as graphite thin film). [Bostwick et al. 2007] Carbon nanotubes (CNTs) are one-dimensional carbon allotrope with a tubular structure of graphitic carbon (*Figure 2.1b*). They are arranged in single-wall, double-wall and multi-wall carbon nanotubes (SWCNTs, DWCNTs and MWCNTs, respectively). [Iijima 1991]

Figure 2.1: Atomic models of a) monolayer (left) and bilayer (right) graphene [Bostwick et al. 2007] and b) single, double and multi-wall (from left to right) carbon nanotubes. Taken from <http://www.physicsworld.com/>

The advantage of the nanocarbons compared with bulk graphite is the enhancement of the intrinsic properties of a single crystal as well as low-dimensional effects at the nanoscale. The properties of the nanocarbon (CNTs and graphene) are summarised in *Table 2.1*. The exceptional mechanical, electrical and thermal properties together to an ultra-high surface area make the nanocarbons a great candidates for their hybridisation with functional inorganic materials.

Table 2.1: Intrinsic properties of CNT and graphene.

Property	CNT	Graphene	References
Electron mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)	$1 \cdot 10^5$	$2 \cdot 10^5$	[Dürkop et al. 2004; Xie et al. 2013]
Current density ($\text{A} \cdot \text{cm}^2$)	$1 \cdot 10 \cdot 10^9$	$1 \cdot 2 \cdot 10^8$	[B. Q. Wei et al. 2001; Moser et al. 2007]
Young's modulus (TPa)	1	1	[Peng et al. 2008; Liu et al. 2012]
Tensile strength (GPa)	100	130	[Peng et al. 2008; Liu et al. 2012]
Thermal conductivity ($\text{W} \cdot \text{mK}^{-1}$)	2000-5000	2000-5000	[Balandin 2011]
Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	1315	2630	[Serp et al. 2003; Xie et al. 2013]

2.1 Nanocarbon-based hybrids

Furthermore, hierarchical structures based on nanocarbons have been developed in the last years and they constitute a very interesting approach through the creation of macroscopic materials formed by nanocarbon units. Hence, CNT fibres or CNT arrays have been successfully developed and importantly, these materials preserve to some extent the intrinsic properties of the nanocarbons. [Li et al. 2004; Zhang et al. 2004; Koziol et al. 2007] The hybridisation of these materials with inorganic compounds is beginning to be investigated and it presents an interesting approach for the creation of highly engineering nanocarbon-inorganic hybrid materials. [S. Neocleus et al. 2011]

In general, nanocarbons are seen as good scaffolds and current collector. However, the hydrophobicity of the nanocarbons makes the hybridisation a challenging process. For instance, many synthesis require the use of polar compounds and consequently, pristine nanocarbons tend to aggregate under such conditions as consequences of the Van der Waals interactions between individual graphitic layers. This difficult the formation of a homogeneous hybrid material. A very common strategy to improve the chemical reactivity and solubility of the nanocarbons is the functionalisation (*Figure 2.2*). It can be carried out by covalent attachment of chemical groups or by non-covalent methods based on the adsorption of functional molecules, also known as linking agents.[Eder 2010] The presence of functional groups improve the interaction between components in a polar media and also provide active sites for subsequent hybridisation processes. Finally, it results in large inorganic/nanocarbon interfaces that can dominate the behaviour of the hybrid material and then, improve the hybrid performance.

Figure 2.2: Functionalisation of CNTs through a) covalent and b) non-covalent interaction.

The type and degree of functionalisation prior the hybridisation process will clearly affect the properties of the final hybrid. The most common functionalisation routes are the strong acid treatment ($\text{HNO}_3/\text{H}_2\text{SO}_4$) or plasma etching, which oxidise the nanocarbons.[Datsyuk et al. 2008; Huang and Dai 2002] The result is the creation of functional groups on the nanocarbon surface, which greatly enhance the reactivity and solubility of the nanocarbons. Additionally, it may enable the covalent interaction with the other component of the final hybrid material. Yet, the functionalisation routes provide a limited control over the amount, type and distribution of functional groups. Moreover, the functionalisation also introduces structural defects in the nanocarbons, which alter their structure.[Tobias et al. 2014] Alternatively, the addition of linking agents offers an interesting approach to avoid the damage in the nanocarbon structure while improves their solubility. This non-covalent route have been reported using aromatic compounds such as benzyl alcohol.[Cooke et al. 2010] In this case, the benzyl alcohol molecules can be attached to the nanocarbon surface by π - π interactions while hydroxyl groups remains at the surface, enhancing thus their solubility.

The use of different nanocarbons have been investigated, and in general, functionalised nanocarbons have been more suitable for the hybridisation process than the pristine nanocarbons. The higher solubility of functionalised nanocarbons enables the formation of a more uniform hybrid material, leading to higher efficiencies in many energy applications.[Yang et al. 2012]

2.1.2 Inorganic/nanocarbon hybrids

Since nanocarbons have been widely used in the world of composite materials, their hybridisation with functional inorganic materials is increasing interest in the recent years. However, structure-properties relation is not clear in the literature of inorganic/nanocarbon hybrids. Commonly, improvements in the hybrid performance are explained for example by increases of surface area and rarely takes into account the structure.[Miranda et al. 2014] Moreover, a very common explanation is the possible charge transfer process, considering the hybrid as semiconductor/metal junctions between planar electrodes.[Yu et al. 2012; Reza Gholipour et al. 2015] In this

2.1 Nanocarbon-based hybrids

context, it is of interest to distinguish between hybrid and composites and also, give evidences of hybridisation that can probe the charge transfer process. The main distinction between both is the interfacial contact formed between components. Nanocarbon composites are materials where a low content of nanocarbons (usually lower than 5wt.%) are mechanically mixed as filler into a polymeric or ceramic matrix (*Figure 2.3a*). [Vilatela and Eder 2012] In a composite material, its properties are the sum of the intrinsic properties of each component. However, it does not have the ideal properties due to poor interfacial area of the composite material. Emergence of properties are not derived from either component.

Figure 2.3: Schematic representation of a) nanocarbon composites formed by mixture of the two individual components and b) nanocarbon hybrids formed by coating the nanocarbon surface by the inorganic component.

In contrast, the hybrids are materials formed by combination of nanocarbons and the inorganic compound with a strong interaction between them. [Liang et al. 2013] The result is the creation of large interfacial contact that plays a key role in the properties of the hybrid material (*Figure 2.3b*). Importantly, instead of enhance a specific property, the hybrids behave as new compound, slightly different to its individual components and providing a wide variety of improvements in the final hybrid material. Additionally, a key difference between hybrids and composites, is the content of nanocarbons, which can be either minority or majority component of the final hybrid material and very low fraction of the composite.

The synthesis of hybrid materials can be achieved by nanocarbons coating or filling (in the case of the CNTs). The inner channel of the CNTs has been filled by metals, alloys or inorganic nanoparticles.[Gautam et al. 2010; Eliseev et al. 2009; Cabana et al. 2014] However, for energy application, the inorganic generally needs to have its surface accessible to gas or liquid molecules. Therefore, the deposition of the second compound on the nanocarbon surface (coating them) in general results more interesting for the formation of hybrid materials for energy applications. This can be achieved by two routes: *ex-situ* and *in-situ* synthetic approaches.[Vilatela and Eder 2012; Eder 2010; Shearer et al. 2014]

In the *ex-situ* route, also known as the building block approach, the two components are synthesised separately and then attached using covalent, non-covalent or electrostatic interactions (*Figure 2.4*). This strategy has been used to successfully link nanoparticles[Yeh et al. 2009], quantum dots[Das et al. 2014], polymers[Gegenhuber et al. 2015] and biomolecules, especially proteins[Kuila et al. 2010]. In contrast, in the *in-situ* route, one component of the hybrid is synthesised in presence of the other or sometimes both are synthesised at the same time. The attachment of, for example, inorganic precursor leads to the formation of the inorganic compound on the surface of pristine or functionalised nanocarbons.

The *in-situ* hybridisation of the nanocarbons with inorganic precursors can be achieved using many different synthetic methods (*Figure 2.4*). On the one side, techniques such as photoreduction[Tan et al. 2010], thermal reduction[Sheng et al. 2011], chemical reduction/oxidation[Larrude et al. 2014] or electrodeposition[Day et al. 2005] have been used for the formation of metal nanoparticles/nanocarbon hybrids. On the other side, metal oxide-nanocarbons hybrids can be achieved by chemical routes such as sol-gel[Chen et al. 2009], solvothermal[Muduli et al. 2009] or microwave assisted[Kim et al. 2010] synthesis but also by electrochemical[Liu et al. 2013] and physical routes[Huang et al. 2016].

Thus, the choice of the synthesis method constitutes a key parameter in the control of the hybridisation process. Among all the reported methods for inorganic/nanocarbon hybrids, chemical routes have been widely used in literature, especially the sol-gel method. The transition of metal precursors (colloidal sol) into a

2.1 Nanocarbon-based hybrids

solid gel phase enables the formation of nanoparticles, [Wang et al. 2005a] nanowires [Dam et al. 2014] or thin films [Akhavan et al. 2011] coating the nanocarbons that were dispersed in the reaction solution. Deposition techniques are also popular, especially using hierarchical nanocarbon structures since their use in liquid media is limited. For example, the potential attraction of atomic layer deposition (ALD) for the formation of hybrid materials is growing interest due to control of film composition on the nanocarbon surface but also control the conformability and size of the inorganic coating.[Jin et al. 2012]

Figure 2.4: Summary of synthetic methods used for hybridisation of a) nanocarbons (CNTs or graphene) either pristine or oxidised with functional materials by b) *ex-situ* and c) *in-situ* approaches.[Shearer et al. 2014]

Overall, the choice of the hybridisation route is a compromise between the type of nanocarbons and its surface modification, the synthesis method of the inorganic and the properties of the hybrid material for the chosen application.

2.1.3 Interfacial effects in inorganic-nanocarbon hybrids

The morphology, size and crystal structure of the inorganic is highly influenced by the presence of the nanocarbons in the case of the *in-situ* synthesis approach. The nanocarbons, with a very high surface area, act as templates for the nucleation and crystal growth of the inorganic, leading to new morphologies and structures.[Nie et al. 2010] Moreover, the nanocarbons act as dispersing agents and prevent the agglomeration of the inorganic nanoparticles. Thus, the study of the hybridisation process including crystallisation and phase transformation is itself of interest for the design of optimised and functional hybrid materials.

Various reports have demonstrated the formation of very small inorganic particles when they have grown on the nanocarbon surface. The heat produced by the exothermic crystallisation and phase transformation of the inorganic can be dissipated by the nanocarbons, owing to their high thermal conductivity. Otherwise, the excess of heat would be used in the grain growth. This effect, known as *heat-sink* effect, has been investigated for TiO₂ coating CNTs.[Eder and Windle 2008] Interestingly, they observed that the *heat-sink* effect is extended up to ~50nm from the CNT surface, which emphasise the effects of the interface between nanocarbons and inorganic compounds.[Hungria et al. 2009]

Another evidence for the presence of synergetic effects at the inorganic-nanocarbon interface has been proved by Aksel et al. They have investigated a wide variety of metal oxides hybridised with CNTs and have studied the catalytic effect of the inorganic in the oxidation of the CNTs in air atmosphere. [Aksel and Eder 2010] Different oxidation temperatures were found ranging from 330°C for oxides such as Bi₂O₃ or PbO up to 820°C observed for inert metal oxides such as Al₂O₃ or SiO₂. Importantly, this effect was not observed for the corresponding composites formed by simple mixing of both components, which suggests that the large interfaces formed in the hybrid are the key role for this catalytic effect.

Expected to the formation of a large interface in the hybrid material has influence not only on the morphology and crystal structure of the inorganic but also on the electronic properties of the final material. In particular, there is a view that interfacing

semiconductors with nanocarbons favour charge separation.[Cherevan et al. 2014] There is however little evidence that this is the case and in most cases it is assumed directly from photocatalytic activities. For example, the study of photoinduced processes by determination of band gap energy, the position of the Fermi level or the presence of intra-band gap states are crucial parameters to predict the efficiency in the photocarrier generation and separation, which results very attractive in energy harvesting, nanophotonic or photodetection applications.[Gaudreau et al. 2013] In this regard, successful reduction in charge recombination rate has been demonstrated in hybrid materials by favouring interfacial charge transfer processes. For example, multiple reports show interfacial charge transfer between CNTs and TiO_2 by a considerable decrease of photoluminescence intensity[Xie et al. 2012] as well as by a decrease of the charge transfer resistance obtained by impedance spectroscopy studies.[Jiang et al. 2010] However, the direction of this charge transfer is not easy to predict and depends on the hybrid electronic structure.

In general, charge transfer processes can occur through different routes depending on the interaction formed between the two components in the hybrid material. *Figure 2.5* shows a scheme of possible routes for charge transfer processes between a semiconductor and a nanocarbon (i.e. CNT) upon illumination. Most commonly reported, the inorganic/nanocarbon hybrids are considered as classical heterojunctions. Hence, the photoexcited electrons in the conduction band of the semiconductor are transferred to the space-charge region formed as consequence of the alignment between the Fermi level of the nanocarbon and that of the semiconductor. Then, these photoexcited electrons are injected into the CNT, which act as electron sink since they have a very large electron storage capacity (up to 1 electron per 32 carbon atoms).[Kongkanand and Kamat 2007] Meanwhile, the holes remain on the inorganic surface to take part of the oxidation reaction (*Figure 2.5a*).[Lin et al. 2010; Kilic et al. 2016] Similarly, nanocarbons can act as electron donor and thus, provide electrons to the valence band of the semiconductor, filling the photogenerated holes in the valence band (*Figure 2.5b*).[Banerjee and Wong 2002; Jung et al. 2002] The overall beneficial effect is the physical separation of the photogenerated electrons and holes in the semiconductor and the effective suppression of charge recombination, one of the major limitation of inorganic semiconductors.

Furthermore, nanocarbons can act as photosensitizer to enhance the visible light absorption. This mechanism was proposed by Wang et al. and it consists in the injection of photoexcited electrons from CNT into the semiconductor conduction band (*Figure 2.5c*). [Wang et al. 2005b] Simultaneously, an electron of the semiconductor valence band is transferred to the positively charged CNT, leaving a hole. Thus, electrons in conduction and holes in valence band of the semiconductor can, for example, react with adsorbed species at its surface. Interestingly, Du et al. have studied interfacial charge transfer in TiO₂/graphene hybrids upon visible irradiation and they have predicted that electrons from the valence band of graphene were directly excited to the conduction band of TiO₂. [Du et al. 2012]

Figure 2.5: Scheme of proposed mechanism of interfacial charge transfer in inorganic/nanocarbon hybrid with CNT acting as: a) electron acceptor, b) electron donor, c) sensitizer and d) impurity.

Most of the predictions treat hybrid as bulk, planar heterojunctions between perfect graphene and semiconductor. Finally, Pyrgiotakis et al. have suggested a more complex mechanism between TiO₂ and CNTs based on the formation of a chemical bond between them as consequence of their strong interaction. Hence, the CNTs provide inter-band gap states through the Ti-O-C bond and extend the absorption of the hybrid material towards the visible range, similar to the effects of carbon doping in TiO₂ (*Figure 2.5d*). [Pyrgiotakis et al. 2005]

In summary, different mechanisms are found in the literature to explain the beneficial role of the nanocarbons in the efficiency of the charge separation and consequently, in the performance of inorganic/nanocarbon hybrid materials. However, it is not clarified which mechanism prevail over the others or most probably, if each mechanism refers to different hybrid materials according to the quality of interaction (electrostatic, covalent, etc.) and to the quantity of interfacial area presented between the inorganic and the nanocarbons. Hence, a successful hybridisation process should be considered when a uniform dispersion of nanocarbons within the inorganic has been achieved and importantly, when the nanocarbons have been distorted upon interfacing with the inorganic semiconductor.

Recent studies in graphene/(101) anatase TiO_2 using density functional theory (DFT) with corrections for the Van der Waals forces have properly described the electronic structure of the hybrid material. Ferrighi et al. have proved that residual O atoms at the interface can lead to strong chemical interaction between both components through Ti-O-C bonds, which provides further electronic states within TiO_2 band gap, arising from the hybridisation of the electronic states of the graphene with those of the TiO_2 . [Ferrighi et al. 2016] Additionally, they present simulation results indicating preferential localisation of electrons in the conduction band of TiO_2 while holes are delocalised on graphene.

Overall, it should be emphasised that a real *hybrid* would be that with a new electronic structure, slightly different to that of its individual components. The new interfacial states will finally lead to a favoured interfacial charge transfer and importantly, the opposite direction of the photocarriers will improve the charge separation. As a result, experimental observations will show a superior performance of the inorganic/nanocarbon hybrids in energy applications such as photocatalysis or photovoltaics.

2.1.4 Applications of inorganic/nanocarbon hybrids

Nanocarbon hybrids have demonstrated an attractive potential in a wide range of applications, especially in the field of environmental and sustainable energy. *Figure*

2.6 shows different energy application where inorganic/nanocarbon hybrids result a promising materials. For instance, energy storage devices have an attractive potential since they are able to be coupled with renewable energy systems, which are intermittent in time and localised in space. Consequently, they cannot fulfil the global energy demand. Thus, the use of electrochemical energy storage systems such as batteries and supercapacitors enable the storage and transport of excess energy. For this propose, the storage devices based on inorganic/nanocarbon hybrids present a higher electrochemical performance with desired energy and power output characteristics.[Liang et al. 2013] Moreover, nanocarbons provide a high surface area and mechanical stability that enable to improve the efficiency in the energy storage, power delivery and durability.

Figure 2.6: Scheme of various applications of inorganic/CNT hybrid materials.

The current research in supercapacitors based on inorganic/nanocarbon hybrids have increasing interest due to the high power performance and excellent cycling stability.[Simon and Gogotsi 2008; Wang et al. 2012a; Inagaki et al. 2010] Similarly, Li-ion, Li-S and Li-O₂ batteries using inorganic/nanocarbon hybrids have demonstrated an increase of the specific capacity, charge-discharge rate and long cycling performance.[Zhou et al. 2010; Li et al. 2012; Wang et al. 2011] For example, Yang et al. have produced a Co₃O₄/GO hybrid with a specific capacity of $\sim 1100 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ for the first 10 cycles and $1000 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ after 130 cycles at a low current density of $74 \text{ mA} \cdot \text{g}^{-1}$. In

contrast, the mechanical mixing of Co_3O_4 nanoparticles with graphene oxide has produced a lower specific capacity ($832\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$) and lower cycling stability. [Yang et al. 2010]

Furthermore, hybrids have also increased the efficiency of solar-to-energy conversion by means of photovoltaic cells or dye-sensitizer solar cells (DSSCs). DSSCs are photoelectrochemical cells closely related to photocatalytic systems that comprise a dye that absorbs light (usually visible) and separately transfer the photoexcited electrons and holes to the semiconductor and electrolyte, respectively, something similar to classical p-n junction (bases of photovoltaic technology). The inorganic/nanocarbon hybrids are widely used in DSSC systems since only a small amounts of nanocarbons leads to larger efficiencies in the conversion of sunlight into electricity. For example, the hybridisation of $\sim 0.01\text{wt.}\%$ of MWCNTs with TiO_2 increases the photoconversion efficiency $\sim 9\%$ due to the increase of photocurrent and improved photocarrier lifetime.[Dembele et al. 2013]

In addition, inorganic/nanocarbon hybrids have been reported for electronic and electrochemical sensing devices with a very fast response. As an example, SnO_2 -CNT hybrids can work as H_2 sensor at ambient conditions in contrast to pure SnO_2 , which operates above 200°C . Importantly, the hybrid sensor can detect 1% of hydrogen at room temperature in only 2-3s.[Mao et al. 2012]

Finally, inorganic/nanocarbon hybrids are commonly used in heterogeneous catalysis[Dong et al. 2003], electrocatalysis[Wu et al. 2012:4], photocatalysis[Li et al. 2011] or photoelectrocatalysis[Ng et al. 2010], increasing its performance for many catalysed chemical reactions. The low recombination rate of photoexcited electron-hole pairs in the semiconductor material improves the catalytic performance. Alternatively, the nanocarbons can be used as scaffold or structural supports for other catalyst due to their mechanical stability and high surface area. Additionally, the nanocarbons provide excellent electron conductivity and low corrosion resistant for their used as electrodes.

For example, Eder et al. have hybridised TS-1 zeolite with CNTs and studied the photocatalytic degradation of 4-nitrophenol under ultraviolet (UV) illumination, in-

creasing the efficiency up to 6 times more for hybrids than pure zeolite.[Krissana-saeranee et al. 2010] But interestingly, the corresponding composite material slightly increases the photoactivity of the pure inorganic catalyst. To probe the effects of the interface in the hybrid, the latter was destroyed via ball-milling and that affects to an enormous reduction of the photoactivity. Thus, the enhancement of the photocatalytic activity in the hybrid material strongly depends on the synergetic effects originated at the inorganic/nanocarbon interface.

Therefore, a rational strategy for the design of a hybrid photocatalyst must include the optimisation of the interface between both components of the hybrids as well as the morphology and crystal structure of the semiconductor. In this regard, Cherevan et al. have recently reported a Ta₂O₅-CNTs hybrid with large control of the inorganic growth on the CNT surface, which has resulted in about 35 time higher photocatalytic hydrogen production than pure inorganic. [Cherevan et al. 2014] The very high photoactivity is ascribed to the single crystal layer formed covering the CNTs, which facilitates the charge transport between at the interface and consequently, the photo-carrier separation.

2.2 Photocatalytic water splitting

Nowadays, clean energies such as hydrogen as fuel play an important role to solve the global energy demand and environmental issues. Hydrogen can be obtained from the splitting of water using natural energies sources such as sunlight by electrolysis, reforming biomass or photocatalytic/phoelectrochemical water splitting. Briefly, the UV illumination of powdered photocatalyst (*Figure 2.7*) immersed in a reactor containing water produces H₂ and O₂. Thus, the photocatalytic hydrogen production results a promising sustainable energy source.

Similar to photosynthesis by green plants, in a photocatalytic water splitting process, the photon energy is converted to chemical energy (*Figure 2.8*) through a largely positive change in the Gibbs free energy of 237.2kJ/mol according to *Equation 2.1*, which corresponds to 1.23eV per electron transferred. [Kudo and Miseki 2009]

2.2 Photocatalytic water splitting

Figure 2.7: Photocatalytic hydrogen production from water using a powder photocatalyst. Adapter from [Kudo and Miseki 2009]

Thus, the photocatalytic water splitting process is known as artificial photosynthesis and the photocatalyst system is represented by Z-schemes similar to those used in the photosynthesis mechanism. Yet, the water splitting process is a challenging reaction in contrast to other photocatalytic processes based on degradation of organic compounds, which have a negative Gibbs energy. [Michal et al. 2014]

Figure 2.8: Schematic energy diagram of a) photosynthesis by green plants and b) photocatalytic water splitting (artificial photosynthesis). Adapted from [Kudo and Miseki 2009]

In the last years, investigations have paid attention to the hydrogen production by photo(electro)catalysts since in 1970s Honda-Fujishima discovered the effect of TiO₂ for splitting water to H₂ and O₂ using sunlight as energy source. [Fujishima and Honda

1972] They developed a photoelectrochemical cell (PEC) for water splitting as illustrated *Figure 2.9*, it consists in an electrochemical cell with a working photoanode for O_2 evolution, a counter photocathode such as Pt for H_2 evolution, an electrolyte solution and an external circuit that connects both electrodes. The photogenerated electrons in the TiO_2 working electrode are driven by an external bias to the counter electrode where the water reduction takes place at the Pt surface. Simultaneously, the hole originated in the valence band of the working electrode oxidises the water at the photoanode surface.

Figure 2.9: Honda-Fujishima effect of photoelectrochemical water splitting process using TiO_2 photoelectrode.

The photoelectrochemical H_2 production can be aided by the external bias, which can provide an additional energy that facilitates the reaction. However, the use of an external bias potential is undesirable for technological applications. Also, a good stability of the photoelectrode in aqueous solution is necessary.

Different from photoelectrochemical water splitting using immobilising semiconductors, photocatalytic H_2 generation using powder semiconductors dispersed in an aqueous solution was reported by Bard as simple and cheap method to produce H_2 . [Bard 1979] Both systems are based on the same physical phenomena and thus, the features of the inorganic semiconductor either powder or film electrode must satisfy the necessary requirements of the water splitting process.

2.2.1 Bases of semiconductor photocatalyst for water splitting

The photocatalysis is defined as photochemical process where species in contact with the catalyst surface are reduced (or oxidised) under irradiation. *Figure 2.10* shows the simplest schematic photocatalytic process produced in an ideal single-particle of a semiconductor. Briefly, semiconductor photocatalysts present an electronic structure that consists on a filled valence band and an empty conduction band, both separated by a band gap energy. Through illumination with photons of energy equal or higher than the band gap of the semiconductor, electron-hole pairs are generated in the semiconductor material. The absorption of the light promotes electrons from the valence band (VB) to the conduction band (CB) of the semiconductor, leaving a hole in the VB. Both photocarriers migrate towards the active sites at the catalyst surface. Simultaneously, recombination of electrons with holes can occur, leading photons or heat and consequently, limiting the catalyst efficiency. Finally, electrons (or holes) that have reached the semiconductor surface, reduce (or oxidise) acceptor (or donor) species adsorbed on its surface. Thus, a large number of active sites will reduce the probability of charge recombination.

Figure 2.10: Mechanism of water splitting process in a single-particle of a semiconductor photocatalyst.

In order to design a superior semiconductor material for photocatalysis, several requirements need to be fulfilled. One of the best advantages of photocatalytic process is the use of clean and cheap energy such as sunlight energy. However, the 42% of the sunlight corresponds to the visible range (2.43-3.2eV) and usually, semiconductor metal oxides need higher energies (UV light) to overcome the band gap energy and produce electron-hole pairs. Thus, the photocatalytic process using sunlight is limited

to the 4% of its energy spectrum. In this regard, band gap engineering is being used to tune the electronic band structure of semiconductor. For example, the use of different dopants will incorporate states within the semiconductor band gap, being able to extend its use in the visible light.[Ishii et al. 2004; Niishiro et al. 2005] Also, oxysulfides[Ishikawa et al. 2002; Ishikawa et al. 2004] and oxynitrides[Hitoki et al. 2002b; Hitoki et al. 2002a] are being investigating for H₂ production because of its narrow bandgaps.

The photocatalytic process also requires a certain position of the valence and conduction band of the semiconductor, depending on the potential of the specie that will be reduced or oxidised. In the specific case of water splitting, the valence band should be lower than the water oxidation potential (1.23V vs SHE) and the conduction band should be higher than the water reduction potential (0V vs SHE). Furthermore, the pH of the solution is an important parameter to establish the band levels diagrams, which follows the Nernst equation with a change of -0.059V/pH.[Chen et al. 2013] *Figure 2.11* shows the band position and band gap energy of various inorganic semiconductor materials at pH 0. This requirement restricts the use of many semiconductors.

Figure 2.11: Band structure of several semiconductor and redox potential of water splitting.[Xiaoping CHEN 2013]

In addition, the semiconductor needs to separate efficiently the photocarriers through diffusion within the material and then, transfer the electrons and holes to the surface. *Figure 2.12* shows the importance of the particle size of nanomaterials in the charge separation and consequently, in the photocatalytic process. The small size of

2.2 Photocatalytic water splitting

nanoparticles reduces the distance to the surface and thus, the photogenerated electrons and holes can easily diffuse to the surface reaction sites. Subsequently, the probability of electron-hole recombination decreases. Finally, nanomaterials provide a high surface area that enables a more abundant adsorption of reactants. A high density of surface states can originate a depletion layer at the interface between the liquid and the semiconductor surface and this will provide beneficial charge separation. As a consequence the photochemical reactions will be enhanced.[Osterloh 2013; Maeda and Domen 2010]

Figure 2.12: Particle size effect on photocarriers diffusion and recombination in photocatalytic water splitting process.

Importantly, a large number of active sites in nanomaterials are necessary to favour photocatalytic rather than recombination process. In this sense, co-catalysts such as Pt or Ru_2O are used to increase the amount of active sites for H_2 evolution due to the conduction band of the most oxides are not high enough to reduce water.[Chen et al. 2014] The modification of the semiconductor surface with noble metal, for example by photodeposition method, enables a continuous driving force of the photo-generated electrons to the surface reaction sites due to the high work function of the noble metals. [Khanna 1980] In contrast, the valence band of the most oxides are deep enough to catalyse the water oxidation to form O_2 and therefore, no co-catalyst materials are needed. However, the water oxidation reaction involve four electrons and needs more reaction sites to occur.

Finally, the backward reaction can easily occur since it is energetically favourable and then, the use of sacrificial agents is often used as strategy for impeding the spontaneous formation of water.[Schneider and Bahnemann 2013] The use of electron donor compounds such as alcohols mixed in water can scavenge holes from the valence

band of the semiconductor to be oxidised instead of water. Thus, only half-reaction of the water splitting process is really performed (water reduction), increasing the hydrogen production by means of inhibiting the formation of water from the molecular components (H_2 and O_2). Nevertheless, although a semiconductor behaves as very photoactive material for some of the half-reaction, an active photocatalyst for water splitting should be that able to produce H_2 and O_2 in a stoichiometric amount.

2.3 Rational design of hybrid nanostructures for photocatalysis

The emergence of new materials for energy production, storage and transport has opened up a new way for the rational design of hybrid materials based on the assembly of inorganic/organic nanostructures. For example, the photocatalytic splitting of water into H_2 and O_2 using sunlight is a very promising strategy to obtain clean energy, however it is a challenging photocatalytic reaction.

Titanium dioxide is a fascinating material for solar energy conversion and environmental processes, such as water splitting to generate hydrogen and treatment of polluter air and water by means of photoelectrochemical or photocatalytic processes.[Fujishima et al. 2000] TiO_2 is a very interesting material because it fulfils common aspects from technological point of view such as large availability, high chemical stability and low price.

The original use of the titania was as white pigment due to its high refractive index, in which results high reflectivity from the surfaces.[Pfaff and Reynnders 1999] Lastly, nanoparticles of TiO_2 have been widely used for photocatalytic applications, which improve the surface properties of the material. The TiO_2 surface provide many reaction sites where the presence of adsorbed species such as water or hydroxyl groups is favoured. Thus, the photogenerated charges may be transferred to these adsorbates to catalyse the splitting of water. In comparison with other semiconductors, TiO_2 provides a high density of donor states and has a relatively slow rate of photocarrier recombination.[Linsebigler et al. 1995]

2.3 Rational design of hybrid nanostructures for photocatalysis

As a result, nanoparticles of TiO_2 are considered a promising photocatalyst material for water splitting. Yet, an optimised morphology, crystal structure and phase composition of the TiO_2 is necessary to increase its photocatalytic efficiency.

Recent improvements have been done with strategies such as hybridisation. The current research in inorganic-nanocarbon hybrids has been focused on TiO_2 because it is so far the best photocatalyst material. TiO_2 -nanocarbons have been investigated for sacrificial and non-sacrificial photocatalytic water splitting, mainly under UV light but also with visible light, showing an increasing of the hydrogen production.[Rawalekar and Mokari 2013; Eder 2010]

2.3.1 Optimising the crystal structure and phase composition of TiO_2

Titanium dioxide, also known as titania, presents three main polymorphs: anatase, rutile and brookite.[Linsebigler et al. 1995] Rutile is the stable phase since it presents the lowest Gibbs energy but the highest surface free energy. The other phases are metastable and tend to transform into rutile at high temperature.[Zhang and F. Banfield 1998] Anatase and rutile are the most common phases used in the literature, especially in photo(electro)chemistry and this work only investigates the properties of these two phases.

The crystallisation of TiO_2 into anatase or rutile forms TiO_6 octahedra with different distortion of the octahedral and thus, their assembly in chains is different. Whereas anatase phase share four edges, rutile shares two edges of the TiO_6 octahedra (*Figure 2.13*).[Carp et al. 2004] Thus, the anatase-to-rutile transformation involves the rearrangement of the octahedral by contraction of the unit cell, especially along the *c*-axis. The differences of each polymorph lead to different physical properties as summarises the *Table 2.2*.

Figure 2.13: TiO₆ octahedra in a) anatase and b) rutile, showing different connectivity between the octahedra.

Table 2.2: Properties of anatase and rutile phases.[Hanaor and Sorrell 2011]

Property	Anatase	Rutile
Crystal structure	Tetragonal	Tetragonal
Atoms per unit cell	4	2
Space group	I4/amd	P4 ₂ /mm
Lattice parameter (nm)	a= 0.3785 c= 0.9514	a= 0.4594 c= 0.29589
Unit cell volume (nm ³)	0.1363	0.0624
Density (Kg·m ⁻³)	3894	4250
Band gap energy (eV)	3.2	3.0
Refractive index	2.54	2.79
Hardness (Mohs)	5.5-6	6-6.5
Bulk modulus (GPa)	183	206

The formation of the anatase or rutile phase depends on the synthetic method. *Table 2.3* summarises common synthetic routes for the formation of TiO₂. Usually, the solution-based synthesis at room temperature and pressure promote the formation of amorphous TiO₂, which needs to be crystallised into the desired structure. For instance, in a sol-gel process titanium alkoxides as inorganic precursor is hydrolysed towards agglomerated of $[Ti(OH)_x(OH_2)_{6-x}]^{(4-x)+}$ octahedra.[Aruna et al. 2000] By controlling the pH, the formation of agglomerations leads to amorphous particles.

2.3 Rational design of hybrid nanostructures for photocatalysis

However, solvothermal synthesis and gas-based synthesis enable the formation of crystalline structures as consequence of the use of moderate temperatures and/or pressures. Firstly, the initial crystalline phase obtained is anatase but the transformation to rutile is dependent on the temperature and the time. Importantly, the anatase-to-rutile transformation is gradually produced, being quite common the co-existence of both.

Table 2.3: Synthetic methods for the formation of TiO₂. [Hanaor and Sorrell 2011]

Synthetic method	Phase formed
Hydrolysis of TiCl ₄	Amorphous
Sol-gel route	Amorphous
Solvothermal synthesis	Anatase
	Rutile
	Anatase + Rutile
Flame pyrolysis of TiCl ₄	Anatase
	Anatase + Rutile
Chemical vapour deposition	Amorphous
	Anatase
	Rutile
	Anatase + Rutile
Physical vapour deposition	Amorphous
	Anatase
	Rutile
	Anatase + Rutile

Although anatase is a metastable phase, it is considered the kinetically stable phase since it is formed at relatively low temperatures, owing to the less constrained structure of anatase. Importantly, the anatase-to-rutile transformation is an irreversible process, that is, a non-equilibrium process. Therefore, it does not occur at a unique temperature/pressure and thus, the conditions for the phase transformation are not established by the typical thermodynamic phase diagram. In contrast, the anatase-to-rutile transformation occurs gradually and a wide range of phase transition temperatures (400-1000°C) have been reported. [Al-Homoudi et al. 2004; Hirano et al. 2003] This wide temperature range indicates that the nucleation and growth of rutile depends on multiple factors during the synthesis such as particle size, surface area, atmosphere annealing, presence of impurities, etc.

In general, the transformation of anatase to rutile requires a thermal energy for the rearrangement of the atoms, which can be promoted or impeded and consequently, it enables the modification of the phase transformation temperature. For instance, the presence of defects in the oxygen sub-lattice significantly affects to the phase transformation.[Bak et al. 2003] The defects (oxygen vacancies) facilitate the relaxation of the lattice and therefore, the rearrangement of the atoms in the anatase lattice to the rutile one. This effect has been reported through annealing the TiO_2 at different atmospheres.[Gamboa and Pasquevich 1992] The results confirm that the phase transformation is favoured in the presence of inert (noble gases) or reduction (H_2) atmosphere, where oxygen vacancies are formed and these play an important role in the phase transformation. In contrast, air or O_2 atmospheres enable the filling of the oxygen vacancies, reaching a complete oxidation of the TiO_2 and delaying the phase transformation to bulk temperatures.[Gennari and Pasquevich 1998] This is particularly relevant for nanocarbon hybrids because the crystallisation of inorganic compounds typically occurs at high temperatures and consequently, it must be carried out in inert atmosphere either to prevent the damage or to avoid the removal of the CNTs.

These defects (mainly oxygen vacancies) can be understood as unpaired electrons. Their presence has an important effect on the photochemical properties of the TiO_2 . Under illumination condition, the charge transfer process to surface species is highly enhanced by n-type TiO_2 semiconductors, which presents many defects at surface levels. DFT studies of a variety of TiO_2 surface were investigated by Martinez et al. and confirm that electrons can flow from or to the surface adsorbate depending on the oxygen vacancies at the surface and the redox potential of the adsorbate.[Martinez and Hammer 2011] As consequence, accumulation or depletion layer can be formed due to the alignment of the Fermi level between the n-type semiconductor and the species adsorbed at its surface. But importantly, the chemistry of the TiO_2 surface can be regulated by controlling the oxidation state of the surface. For example, experimental studies have also reported that water predominantly dissociates at the oxygen vacancies.[Pei et al. 2013]

Similar effects in the phase transformation have been observed with intentional dopants and unintentional impurities, which produce alterations of its lattice.[Bak et

2.3 Rational design of hybrid nanostructures for photocatalysis

al. 2003; Reidy et al. 2006] For instance, carbon impurities can be a strong reducing agent during annealing in inert atmosphere, promoting the formation of defects such as oxygen vacancies and finally, favouring the transformation to rutile. This has been demonstrated in TiO₂ nanowires doped with carbon under oxygen-deficient atmosphere using DFT calculation.[Di Valentin et al. 2005] Additionally, many studies have used doping as strategy to improve the efficiency in photoinduced process of TiO₂, since they can tune the band gap, provide intra-band gap states and/or reduce the photocarriers recombination.[Leary and Westwood 2011; Ranjit et al. 1999; Serpone 2006; Chen et al. 2011] The doping of TiO₂ with C atoms, which has similar atomic radius than the O atoms, has demonstrated to modify the visible light absorption and the photoactivity of TiO₂. Nagaveni et al. successfully prepared C-doped TiO₂ by sol-gel method and observed a high photodegradation activity for methylene blue under visible and UV light irradiation.[Nagaveni et al. 2004] The presence of carbon atoms within the TiO₂ lattice modifies the TiO₂ electronic structure by providing new energy states within the TiO₂ band gap: two occupied and one empty states (*Figure 2.14*). Importantly, the C atoms also facilitates the formation of oxygen vacancies and consequently, the presence of defect states below the conduction band. Finally, the photoinduced process of the inorganic semiconductor are enhanced. [Schneider et al. 2014] This is especially relevant for hybrids containing functionalised nanocarbons, which can strongly interact with the metal oxide and act similar to the C impurities in terms of modifications of the electronic band structure.

Figure 2.14: Electronic structure of C-doped TiO₂ photocatalyst. Adapted from [Schneider et al. 2014]

Overall, the annealing of amorphous TiO_2 into anatase or rutile crystalline phases increases the mobility of the photocarriers and reduce the charge recombination rate. However, crystallisation processes at high temperature or long times produce the increase of the particle size, which will reduce the surface area of the material.[M. Hatherly et al. 2004] Furthermore, anatase phase presents a higher density of electronic states and adsorbed species at surface level.[Sumita et al. 2002] Sclafani and Herrmann have studied the photoactivity of anatase and rutile phases in terms of density of adsorbed species at the surface[Sclafani and Herrmann 1996] and the results confirm that anatase phase presents higher photocatalytic performance than rutile phase.

Nevertheless, a certain amount of rutile mixed with anatase presents better photocatalytic performance than a single phase TiO_2 photocatalyst, either anatase or rutile. The reason is plausible since the alignment of their band structure facilitates the charge separation at the interface between both phases.[Scanlon et al. 2013] This may be directly related to the fact that Degussa P25 (reference material formed by mixed $\sim 80:20$ anatase:rutile phases) exhibits very high photoactivities. Further, this material present a small particle size ($\sim 20\text{nm}$) and thus, a relatively high surface area ($35\text{--}65\text{m}^2/\text{g}$).[Ohtani et al. 2010; Hurum et al. 2003] The key of this photocatalyst is the combination of the nanosized, the surface area and the mixture of anatase and rutile phases that act as homojunction, effectively leading to low recombination rates. This type of homojunction has been also reported in literature for other semiconductor such as $\alpha/\gamma\text{-Bi}_2\text{O}_3$, which improves the photocarrier separation at the interfaces between both phases and subsequently, improves the photocatalytic efficiency.[Sun et al. 2012] Overall, the phase composition of the material has significant influences in its properties and consequently, in its performance. Therefore, the control of the phase composition to give a particular phase or a phase mixture is necessary in the design of an optimum semiconductor material.

2.3.2 Optimising the morphology of TiO_2

The morphology design of nanomaterials is increasing interest because it can be a key for the optimisation of the photocatalyst material. Quantum confinements at the

2.3 Rational design of hybrid nanostructures for photocatalysis

nanoscale modify the electronic band structure of the semiconductor with respect to that of the bulk. The development of nanostructures with well-engineered composition, geometry, crystal and electronic structures enables the enhancement of electron and hole transport processes. For example, one-dimensional nanorod, nanowire or nanofibers present a high surface-to-volume ratio with a large number of reaction sites. Importantly, they serve as channels for the electron transport, reducing their recombination with holes.[Wang et al. 2014]

In particular, nanofibres formed by electrospinning technique, a simple and versatile approach that further can be easily scaled-up, results to be a very attractive morphology for the benefit of many applications such as catalysis[Regonini et al. 2013:2], solar cells[Ramakrishna et al. 2006] or batteries.[Self et al. 2015] Although electrospinning technique has commonly used in the formation of polymer fibres, ceramic fibres can be also obtained through its combination with the sol-gel process. The presence of a polymer during the sol-gel process acts as a template for the transformation of inorganic precursor into a gel network. Finally, a posterior annealing for removal of the polymer and sintering of the inorganic results in ceramic mesoporous nanofibres[Macías et al. 2005], core/shell structures[Pan et al. 2012], hollow nanofibres[Hou et al. 2015] or aligned nanofibres[Xu et al. 2012].

The growth of crystalline TiO₂ nanoparticles confined in a one-dimensional structure produces a network of nanocrystals that shares atomic planes at their interface. For instance, anatase phase is usually constituted by trunked octahedrons that exhibits the lowest surface energy facets, the (101) facets with surface energy of 0.35J/m² as is illustrated in *Figure 2.15a*. [Barnard et al. 2005] *Figure 2.15b* shows a schematic representation of the charge transfer between nanoparticles until reaching an active site to react with the adsorbate. This is known as the *antenna effect* and describes a new concept developed for the photocatalytic mechanism of the one-dimensional semiconductors.[Wang et al. 2006] The overall effect is the improvement of the photocatalytic activity through a cooperative effect in the charge transport between the nanocrystal network within the fibre.[Park et al. 2013; Choi et al. 2012]

Figure 2.15: a) Alignment of anatase nanoparticles in the fibre network. b) Interparticle charge transfer process within a nanofiber. [Choi et al. 2010]

Thus, the network of nanocrystals in the fibre can be considered as a continuous agglomerations that favour the photocarriers separation through the multiple grain boundaries between the agglomerates, resulting in a critical factor for high efficient photocatalysts. For example, it has been observed that a change of pH until reaching the isoelectric point of the TiO_2 produces agglomerations of TiO_2 nanoparticles and then, the photocatalytic hydrogen production considerably increases (*Figure 2.16*). Photocurrent measurements using methyl viologen in the colloidal suspension of TiO_2 have demonstrated effective charge separation through electron transfer between agglomerated nanoparticles of TiO_2 . [Lakshminarasimhan et al. 2008]

Figure 2.16: Effect of the pH on the TiO_2 agglomeration and on the increase of H_2 production due to interparticle charge transport. [Lakshminarasimhan et al. 2008]

2.4 Summary

In summary, crystal size, phase composition, growth orientations and a high surface-to-volume ratio are the most interesting aspects for the design of a superior photocatalyst. In addition to structural effects, the morphological control of the inorganic semiconductor, for example, by using one-dimensional nanostructures provides a more versatile optoelectronic properties of the semiconductor. Further hybridisation of one-dimensional TiO_2 with nanocarbons, especially with CNTs (1D-nanocarbons) enhances photoinduced processes such as photocarrier generation and separation. The structural effects of the nanocarbon on the TiO_2 as a consequence of the intimate contact between both can induce defects that alters the structure of both. This reveals the importance of the interface in the modification of the semiconductor electronic structure. Also, it evidences that the control of the interface during the synthesis is a promising strategy to favour strong interfacial interactions between both components of the hybrid, facilitating charge transfer processes. Finally, this leads to the decrease of photocarrier recombination rate, which is a limiting factor in the photoactivity of TiO_2 . Therefore, the hybridisation results in a significant improvement of the photocatalytic activity of H_2 production of the TiO_2 .

CHAPTER 3

MATERIAL AND EXPERIMENTAL TECHNIQUES

This chapter describes the complete procedure of the experiments in detail, including synthesis, characterisation techniques and photocatalytic experiments used in the final results discussed in this thesis.

3.1 Materials

3.1.1 Multi-walled Carbon Nanotube

Good quality of pristine MWCNTs employed in this report were supplied by Thomas Swan Ltd. MWCNTs were produced by a vertical chemical vapour phase reactor (CVD process) using Fe as catalyst and methane as carbon feedstock. The reaction takes place at high temperature (800°C). MWCNTs have a high purity related to the low catalyst content as well as the low carbon impurities. These MWCNTs consist of a few layers of CNTs resulting in a diameter of 11 ± 2 nm and a length mainly ranging between 100 nm and a few microns. Consequently, high surface area is presented in the pristine material ($230\text{ m}^2/\text{g}$).

Due to the hydrophobicity of the pristine MWCNTs in polar solvents, they were functionalised following the typical route of sulfonitric oxidation of the surface, which creates carboxylic acid groups at external walls and at the end of the MWCNTs (*Figure*

3.1 Materials

3.1).[Tasis et al. 2006] Briefly, the MWCNTs were treated with a 3:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ with the aid of ultrasonication at room temperature for 5h. Following the treatment, the mixture was extensively washed in water until neutral pH, then methanol and finally, the nanocarbons were filtered and dried. The oxidised MWCNTs, referred as ox-MWCNTs, display a $8\pm 2\text{wt.}\%$ of functional groups, which regarding theoretical studies, correspond to $1.8\pm 0.5\text{mmol}$ of COOH/g of MWCNTs. After the treatment, their length was considerably decreased to 100-500nm and only a $<5\%$ exceeding the micron while diameter range is constant. As a result, the material could be easily dispersed as individual nanotubes yielding dispersions in polar solvents, which is useful for further hybridisation process. MWCNTs were functionalised and characterised by Dr. Silvia Marchesan and Daniel Iglesias from Trieste University, Italy.

Figure 3.1: Schematic representation of the sulfonitric oxidation process employed for functionalisation of MWCNTs.

3.1.2 Graphene

Graphene (GR) based materials of this report were supplied by Thomas Swan Ltd. Briefly, graphene was produced using a liquid-phase exfoliation process, followed by separation and washing techniques. As a result, a good quality graphene nanoplatelets in dispersion and graphene powder were received. Using this production method, carbon sp^2 layers were substantially undamaged and non-oxidised, the impurity levels are low ($8\pm 2\text{ wt.}\%$) and the graphene sheets were uniform in the range 200-500nm.

Similar to MWCNTs, chemical modification of graphene was successfully carried out using the aromatic diazo coupling reaction, which introduces isoftalic groups on

the graphene surface (*Figure 3.2*).[Criado et al. 2015] Thus, samples using this functionalised graphene are referred as isoft-GR. Before chemical functionalisation process, graphene was treated with microwaves at 80°C for 90min in order to remove impurities (surfactant presence) and avoiding the damage of the graphene structure. Then, aromatic primary amines (bearing carboxyl groups) and isoamyl nitrite were added and heated to 80°C for 1-2 hours. Diazonium salts are *in-situ* formed and subsequent, coupled through their aromatic rings to the graphene layer. Finally, graphene was filtered and washed with deionised water, methanol and ethanol. Analysis of the isoftalic groups introduced in graphene revealed a successfully achievement of a $14\pm 2\text{wt.}\%$ of functional groups, which corresponds to $0.43\pm 0.07\text{mmol}$ of isoftalic groups/g of graphene. Functionalised graphene was provided by Dr. Silvia Marchesan and Daniel Iglesias from Trieste University, Italy.

Figure 3.2: Schematic representation of the diazo-coupling reaction employed in the functionalisation process of graphene.

3.1.3 Macroscopic CNT fibre

CNT fibre (CNTf), was employed as macroscopic carbon material that presents the properties of CNTs such as mechanical properties, surface area and electrical and thermal conductivity. The fibres were produced by direct spinning method from the gas phase during the synthesis of CNTs by CVD.[Reguero et al. 2014] The reaction involves the use of butanol (97.7wt.%) as carbon source, ferrocene (0.8wt.%) as catalyst and thiophene (1.5wt.%) as promoter. The process was carried out in a vertical CVD reactor at 1200°C in hydrogen atmosphere with a precursor feed rate of 5mL/h. Fibres were produced by drawing from the CNT aerogel and collected in a winder with a rate of 5mL/min as is represented in *Figure 3.3*. These parameters set the production of continuous and homogeneous CNTf consisting in a few walls MWCNTs with an average diameter of $3.2\pm 1.7\text{nm}$ and several millimetres of length. The MWCNTs

3.1 Materials

are entangled forming bundles of CNTs, which remain porous in the meso-scale. Additionally, CNT bundles are also entangled forming the macroscopic fibre structure with porosity in the macro-scale. Finally, the available surface area results $\sim 250\text{m}^2/\text{g}$. The fibres were produced in our research group at IMDEA Materials Institute with the assistance of Víctor Reguero.

Figure 3.3: Schematic representation of the CVD reactor for CNTf production.

3.1.4 Chemicals

All the chemicals were purchased from Sigma-Aldrich and they were used without any modification. For the synthetic route, titanium (IV) ethoxide (85% purity), niobium (V) ethoxide (99.95% purity), tantalum (V) ethoxide (99.98% purity), absolute ethanol and acetic acid were used for the sol-gel process and polyvinyl pyrrolidone (PVP, $M_w=360000\text{g/mol}$) were employed for the use of electrospinning technique. Furthermore, for the atomic layer deposition, tetrakis(dimethylamido)titanium (IV) was used as inorganic precursor.

3.2 Sample preparation

3.2.1 Synthesis of electrospun nanofibers

Fibre nanostructures of metal oxides and metal oxides/nanocarbon hybrid were synthesised by combination of sol-gel method and electrospinning technique. The electrospinning technique consists in three main components: the power supply, a spinneret and a metallic collector. Hence, a polymer solution containing the inorganic precursors is electrified and the charges are distributed over the surface until the repulsive electrostatic forces overcome the surface tension. At this moment, a Taylor cone is originated, leading to the evaporation of the solvent whereas spinning continuously fibres of small diameter on the metallic collector.[Bhardwaj and Kundu 2010] The solution injected in the electrospinning set-up was an alcoholic solution containing the polymer and the inorganic precursor with controlled pH. An appropriate viscosity, conductivity and surface tension of the precursor solution are needed to be able to electrospun uniform fibres. For this, parameters such as polymer and inorganic concentration need to be controlled.

In a typical synthesis, a polymer solution of high molecular weight polyvinylpyrrolidone (PVP) in ethanol (10wt.%) was stirred until homogeneity. Then, the polymer solution was mixed with the precursor solution, consisting in metal (Ti, Nb or Ta) ethoxide dissolved in ethanol (63.5, 39.2 and 63.7wt.%, respectively) and a few drops of acetic acid to catalyse the sol-gel reaction. In the case of the metal oxide/nanocarbon hybrids, a dispersion in ethanol of different volume fractions (0.35-10vol.%) of pristine and functionalised nanocarbons was added to the previous mixture and kept it stirring vigorously to obtain a uniform dispersion. Before gelification process, the solution was loaded in a syringe of 5mL and fed into an electrospinning set-up (*Nanon 01A, MECC Co., Ltd.*). Many parameters have influence in the production of fibres such as voltage, tip-to-collector distance, flow rate as well as ambient factors (these supposed to be similar along the experimental procedures). The three parameters were optimal for a flow rate of 2mL/h, a distance of 10cm from the tip to the aluminium foil collector and an applied voltage of 18kV for TiO₂ and 30 kV for Nb₂O₅ and Ta₂O₅. A schematic representation of the process is shown in *Figure 3.4*.

Figure 3.4: Schematic representation of sol-gel + electrospinning process.

A randomly oriented electrospun fibres were collected containing the polymer and the metal-oxygen network. Further treatment at high temperature was performed in order to remove the polymer and crystallise the inorganic, taking into account that nanocarbons could be damage or even removed at high temperature. Thus, in a tubular furnace (*Nabertherm, RHTH 120/600/16*), the electrospun samples were annealed following the thermal treatment shown in *Figure 3.5*. Samples were heated up to 400°C (T_1) at 3°C/min during 2.5h (t_1) and under high air flow (400mL/h) to remove the polymer. The crystallisation of the metal oxides into the expected crystal structure requires higher temperatures and due to the thermal stability of the nanocarbons, this second step was done under inert atmosphere (Ar 99.99999% purity). Thus, several cycles of vacuum-Argon were applied to remove air, finally leaving the furnace filled with Ar (different Ar flows were used to study its effects in the crystal structure of the metal oxide, see *Section 4.2.1*). After that, the sample was heated to crystallisation temperature (T_2 : 500, 575 and 700°C for TiO_2 , Nb_2O_5 and Ta_2O_5 , respectively) for a certain time (t_2 : 1h for TiO_2 and Nb_2O_5 and 10h for Ta_2O_5) at the same heating ramp. Finally, after a slow cooling, fibres of metal oxide and metal oxide/nanocarbon hybrids were obtained.

Figure 3.5: General representation of the applied thermal treatment.

3.2.2 Synthesis of nanoparticles by sol-gel method

Nanoparticles (NPs) of metal oxides (Ti, Nb or Ta oxides) were synthesised by standard sol-gel method and reproducing the synthesis conditions that were employed for the electrospun fibres. Thus, an acidic solution of inorganic precursor (63.5, 39.2 and 63.7wt.% of Ti (IV), Nb (V) and Ta (V) ethoxides, respectively) and absolute ethanol was vigorously stirred at 80°C during a day. After a complete evaporation of the ethanol, a powder consisting in a network of metal-oxygen was obtained, which was further crystallised into the desired crystal structure of each metal oxide. Consequently, annealing of sol-gel samples was performed following the same heat treatment than that used for electrospun samples.

3.2.3 Synthesis of thin films by atomic layer deposition

Atomic layer deposition is a deposition technique of a gas phase on a certain substrate by surface reactions. ALD is a very versatile process for the deposition of thin layer of metal oxide.[Johnson et al. 2014] This technique has been used for the formation of hybrids based on macroscopic CNT fibre and thin TiO₂ coating with the aim of creating a macroscopic heterojunction between both nanomaterials (TiO₂/CNTf). Ideally, a monolayer of inorganic precursor is deposited on the nanocarbon surface and then, an oxidising agent forms the metal oxide atomic layer. A general scheme of

3.2 Sample preparation

the ALD process is represented in *Figure 3.6*. The application of several ALD cycles until the desired thickness of the inorganic can enable a conformal coating and can reduce the agglomeration of the inorganic.

Figure 3.6: Scheme of a cycle of ALD process using $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ as inorganic precursor, N_2 as purged gas and H_2O as oxygen source.

Two methods were used to produce TiO_2/CNTf hybrids, differentiated mainly by the oxidising agent. In both cases, a film of CNTf was deposited in fluorine-tin oxide (FTO) glass substrate and it was used as substrate of the ALD process. The first one was carried out by Nina Kemnade in the Prof. D. Eder group, in a reaction chamber of a Savannah 100 ALD system (*Cambridge Nanotech*). The metal precursor ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$, previously heated at 75°C to reach a vapour pressure of 1.2torr) was injected into the chamber, which was set at 150°C , in pulses of 0.5s followed by 10s of N_2 exposition, 0.03s of oxidising agent (water) and 15s of N_2 purging. This cycle was repeated during 400 times for the formation of 20nm of TiO_2 as the process follows a growth rate of 0.05nm/cycle. The other method was developed by Manuel Rodriguez at IMDEA Nanoscience Institute. The titanium precursor was the same but the oxidising agent was O_2 plasma of 300W. Also, the chamber temperature was slightly different, 135°C in this case. The cycle consisted in inorganic pulse of 0.1s, 35s of purging and 20s of plasma. The growth rate is also 0.05nm/cycle but this time, different ALD cycles were applied to study the effect of the TiO_2 thickness in the hybrid material. Under the experimental conditions used in both routes, the layer of TiO_2 was still amorphous. Therefore, the samples were annealed at 400°C for 1h in order to obtain crystalline

anatase phase. The heat treatment was carried out in Ar atmosphere to prevent the damage in the CNT fibre.

3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) were used to study the degradation of the polymer, the thermal stability of the nanocarbons and the conversion of sol-gel precursors into metal oxide under air and inert (N₂) atmospheres. Finally, a single heat treatment was designed to remove the polymer and crystallise the metal oxide while preserving the nanocarbons.

The TGA measurements were performed using a *TA Instruments Q50*, which consists in a high-precision balance and a platinum sample pan. Around 5mg of sample were heated at slow ramp, 3°C/min (reproducing conditions of the heat treatment in the tubular furnace), from room temperature to 800°C under controlled gas flow (90mL/min for both gases, air and N₂). The weight changes were recorded and plotted as a function of temperature and time.

3.4 Electron and Optical Microscopy

3.4.1 Optical Microscopy

Optical microscope (OM) images were captured in reflection and transmission modes on a microscope (*Olympus BX51*) equipped with a camera *Olympus ColorView* and acquired by the built-in system (*analySIS auto*) at different magnifications, in black&white and colour modes. The image resolution is limited by the wavelength of the photons (white light, $\lambda = 1000\text{\AA}$), resulting in a resolution of a few microns.

3.4.2 Electron Microscopy

Electron microscopes allow to study the material at higher magnifications than an optical microscope by the use of electron beam focused with magnetic lenses instead

3.4 Electron and Optical Microscopy

of light focused with optical lenses. The resolution is now limited by the wavelength of the excitation source, that in the case of electrons, the wavelength mostly depends on the accelerated voltage by

$$\lambda = h/[2m_0E(1 + E/2m_0c^2)]^{-1/2} \quad (3.1)$$

where h is the Planck's constant, m_0 is the rest mass of an electron, E is the energy of the accelerated electrons and c the speed of the light. Thus, resolution has been considerably increased (to nanoscale) compared to optical micrographs.

In scanning electron microscopes (SEM), images are produced by scanning the specimen with a focused electrons beam in a range of 0.2-40keV. The interaction of the electron beam with the atoms of the specimen produces different signals: secondary electrons, back-scattered electrons, X-rays and light by cathodoluminescence as is illustrated in *Figure 3.7*. These signals can be detected and contain information such as topography or chemical composition. The most common SEM mode is the detection of inelastic scattering of the secondary electrons from atoms in the surface, which forms an image with information about the topography and morphology of the sample. Also, elastic scattering reflects the back-scattered electrons whom intensity is proportional to the atomic number (Z) of the specimen, resulting in an image of the topography and composition of the sample.

Figure 3.7: Interaction volume of the signals generated by interaction between electron beam and sample in SEM mode.

In transmission electron microscopes (TEM), the beam of electrons are accelerated at high voltages, 200-300keV. The electrons of the beam can pass through a very

thin sample and the transmitted or diffracted electrons are detected by a charge-coupled device (CCD). Thus, TEM microscopes operate in two modes. TEM image observation mode (*Figure 3.8a*) forms an image that after few time of beam exposition, could be magnified and focus in an imaging device such as a fluorescent screen or detected by a CCD camera. The image contains information in a sub-nanometric scale, which enables to study the crystal structure of the specimen. Furthermore, the periodic structure of a crystalline sample can act as diffraction grating for the accelerated electrons. As result, a diffraction pattern is formed with information of the crystal structure. In order to acquire the diffraction pattern, the microscope operates in Diffraction image observation mode (*Figure 3.8b*). It forms a diffracted electron image focused at the back focal plane of the objective lens, which is projected onto the screen by the imaging lens system and finally, detected by a CCD. Usually, a Selected Area Electron Diffraction (SAED) aperture is employed to restrict the area of analysis.

Figure 3.8: Schematic representation of a Transmission Electron Microscope operating in image mode (left) and diffraction image mode (right).

3.4 Electron and Optical Microscopy

Finally, energy-dispersive X-ray spectroscopy (EDS) can be also used in electron microscopes and provides information about the chemical composition of the specimen. The electron beam interacts with the specimen and excites an inner electron, leaving a hole where the electron was. An outer electron fills this hole and the energy difference is released in the form of X-ray. The number and energy of the X-rays are detected and thus, an elemental analysis of the specimen can be obtained.

For this thesis, a scanning electron microscope (*EVO MA15, Zeiss model*) were used at 4-10keV at various magnifications. A dual beam with field-emission SEM (*FIB-FEGSEM, Helios NanoLab 600i FEI*) was employed for a greater detail of the sample using voltages ranged between 4-15keV. High resolution transmission electron microscope was performed on a *JEOL JEM 3000F* operating at 300kV and a *JEOL JEM 2100HT* and a *Talos F200X FEI*, both operating at 200kV. Analysis of the electron micrographs was carried out by using *ImageJ software*.

3.5 X-Ray Diffraction

X-ray diffraction (XRD) is a characterisation technique used for phase identification of a crystalline material. X-rays can be considered as waves with a wavelength similar to the crystallographic planes that follows the Bragg's law:

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \quad (3.2)$$

where n is a positive integer, λ wavelength of incident wave, d_{hkl} the distance between the crystallographic planes with Miller index (h,k,l) and θ_{hkl} the corresponding scattering angle. As is shown in *Figure 3.9*, when the x-rays interact with the periodicity of the atom in a crystal, electrons of the sample are elastically scattered forming X-rays. Regarding to the Bragg's condition, the electrons are scattered in a few specific directions, in a few specific angle, θ_{hkl} . The angles and intensities of the diffracted beams are detected, which enable to the identification of the atomic structure of a crystal and its orientation.

Figure 3.9: Schematic representation of Bragg's law.

Furthermore, this technique can provide information of the size and distortions presented in the material such as microstrain. When the size of the crystalline particles is reduced, the diffraction peaks become broader and they enable to determine the average size of crystal domains (D) by using Scherrer equation[Patterson 1939]:

$$D = k\lambda/(\beta \cos \theta) \quad (3.3)$$

where k is a shape factor (0.9 for spherical crystallites), β is the broadening at the full width half maximum (FWHM) of the analysed maximum diffraction and θ the scattering angle of the corresponding family planes. Also, the microstrain can be calculated by the following equation[Deane K. Smith and Frank H. Chung 1999]:

$$\varepsilon = \beta/(4 \tan \theta) \quad (3.4)$$

In addition, the ratio between TiO_2 phases can be determined. In particular, the anatase-to-rutile ratio of TiO_2 were estimated according to Spurr's equation [Spurr and Myers 1957]:

$$F_R = 1/[1 + \{0.8I_A/I_R\}] \quad (3.5)$$

where F_R is the weight fraction of rutile, I_A the intensity of the (101) anatase peak and I_R the intensity of the (110) rutile peak.

Samples were tested on a X-ray powder diffractometer (*Empyrean, PANalytical*) with $\text{Cu K}\alpha$ radiation ($\lambda=0.154\text{nm}$, 45k, 40mA) using a θ -2 θ geometry. The patterns

3.5 X-Ray Diffraction

were recorded in the 2θ region of $10-80^\circ$. The analysed materials were finely homogenized and average bulk composition was determined. The identification of the phase composition was done using the PDF database in *HighScore Plus software*. This software was also used for the refinement of some XRD patterns and importantly, the crystal size and microstrain provided by the software agree quite well with the values obtained using *Equation 3.3* and *3.4*.

3.6 Photoelectron Spectroscopy

Photoelectron Spectroscopy is a surface-sensitive spectroscopic technique that illuminates the material with monochromatic light generating emission of electrons by photoelectric effect. The kinetic energy of these electrons and the number of those are measured, which finally enable the determination of the chemical and elemental composition as well as the electronic state of the elements presented in the material.

As illustrates *Figure 3.10*, X-ray Photoelectron Spectroscopy (XPS) spectra are obtained by irradiating the material with a beam of X-rays of high energy (200-2000eV) that could excite electrons from the outer (valence band) and inner electrons (core levels) under ultra-high vacuum conditions. Similarly, Ultraviolet Photoelectron Spectroscopy (UPS) uses ultraviolet light, which is considerably low in terms of energy (10-45eV), and it only excites electrons from the valence band region. Each technique produces different spectra (*Figure 3.10*) with complementary information about the sample.

Figure 3.10: Schematic representation of photoelectron spectroscopy technique and resulting photoelectron spectra using two excitation sources: X-ray exciting core electrons and UV light exciting VB electrons.

In this sense, photoelectron spectra could be used to study the density of occupied states by assuming Koopman's theory (the emission of an electron does not change the energy of the other electrons).[T. Tsuneda et al. 2010] Measuring the kinetic energy of the photoelectrons, one can calculate the binding energy according to the following equation:

$$E_k = h\nu - E_b - \Phi \quad (3.6)$$

where E_k is the kinetic energy of the emitted photoelectrons, $h\nu$ the photon energy, E_b the binding energy of the emitted electron and Φ the work function of the detector. In our case, we use the Fermi level instead vacuum level as reference energy level and thus, the previous equation is simplify to:

$$E_k = h\nu - E_b \quad (3.7)$$

The range of E_b values gives information about the elemental composition, chemical environment and electronic states of the material. For instance, in the case of a metal oxide, the valence electrons of the metal are partially transferred to the oxygen, which is a more electronegative element. Thus, the attractive force of these electrons by the oxygen core is higher and the emitted photoelectron will escape with lower kinetic energy, that is, the binding energy increases. This effect is known as *chemical shift* and enables to know the oxidation states of the atoms in the solid. The NIST database contains information about the chemical shift of a huge variety of chemical compounds, including metal oxides.

Using UV photons as the excitation source we probe photoelectrons emitted from the valence band region of our materials of interest. In a typical UPS spectra, the work function of the sample could be calculated by subtracting the energy from the incident beam from the difference between the first electron detected coming from Fermi edge and the low energy cut-off of secondary electrons (w) according to:

$$\Phi = h\nu - w \quad (3.8)$$

The XPS spectra were performed in a *SPECS GmbH* system provided with ultra-high vacuum (10^{-10} mbar) and *PHOIBOS 150 9MCD* energy analyser at Instituto de Catálisis y Petroleoquímica (ICP-CSIC). The light source was monochromatic X-ray

3.6 Photoelectron Spectroscopy

(Al/Ag double anode). *CasaXPS software* was employed for the XPS/UPS data analysis. Additionally, XPS/UPS measurements were carried out in a *Multilab System 2000 Thermo Fisher* at Málaga University, using monochromatic light source (Mg and Al anode) for XPS data and UV (He I, 20.22eV) for UPS data. For UPS, a bias voltage of 0.75V was applied to the sample of analysis after calibration, which allows the separation of the secondary electrons signal of the sample from that of the analyser. The spectra are calibrated and represented with respect to Fermi level (binding energy of 0eV). Finally, the spectra are represented in decreasing binding energy, which was calculated from the original kinetic energy data by using *Equation 3.7*.

3.7 Raman Spectroscopy

Raman spectroscopy is a non-destructive technique based on the analysis of the inelastic scattering light from the material, also known as Raman scattering. A monochromatic light interacts with vibration modes, phonons or other excitations in the system and produce the excitation of electrons, usually from ground state to a determined excited state, that rapidly leave emitting a photon. If the electrons come back to the initial state, the difference between the initial ($\tilde{\nu}_1$) and final ($\tilde{\nu}_2$) energy level is none, and this is the elastic scattering (Rayleigh scattering, *Figure 3.11b*). When the system produces inelastic scattering, electron in excited state leave to a vibrational state different to the initial one that may be at higher energy ($\tilde{\nu}_2 + \omega_v$, called anti-Stokes Raman scattering shown in *Figure 3.11a*) or at lower energy ($\tilde{\nu}_2 - \omega_v$, called Stokes Raman scattering and shown in *Figure 3.11c*). The difference in energy between the initial and final states is a frequency (ω_v), commonly referred as Raman shift.

A laser of visible light is commonly used as excitation light. The light interacts only with atoms near to the surface of the material, providing very sensitive information about them. Thermal vibrations, stress, size or structural and compositional defects, all of them produce a frequency changes (Raman shift) and therefore, this technique gives a very useful information about the structure and composition of the materials.

Raman spectra were obtained using a micro-Raman spectrometer Renishaw PLC equipped with a laser of 532nm of wavelength and a micron of spot size. Laser power was ranged between 5-10mW depending on the sample.

Figure 3.11: Schematic representation of the electronic states of a general system where transitions between vibrational states show a) Anti-Stokes Raman scattering, b) Rayleigh scattering and c) Stokes Raman scattering.

3.8 Physisorption

The physical adsorption properties of a sample can be determined by the isotherms of gas molecules adsorbed on a solid surface. By recording the amount of gas that is adsorbed for the sample, the specific surface area and pore volume could be determined. As illustrates *Figure 3.12*, gas molecules begins to cover isolated sites on the surface at low pressures. By increasing the gas pressure, coverage of adsorbed molecules increases until they form a monolayer (Langmuir monolayer). Further increasing of gas pressure causes the multi-layer coverage where Brunauer-Emmett-Teller (BET) method can be used to calculate the specific surface area of the samples by:

$$S_{BET} = V_m N_{av} s / Vm \quad (3.9)$$

where V_m is the molar volume of the adsorbate gas in a monolayer, N_{av} the Avogadro number, s the adsorption cross section of the adsorbed gas molecule, V the molar

3.8 Physisorption

volume of the adsorbate gas and m the mass of the solid sample. The molar volume of the gas absorbed in a monolayer can be determined by applying the BET equation:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \frac{p}{p_0} \quad (3.10)$$

where p and p_0 is the equilibrium and saturation pressure of adsorbate gas at the temperature of the experiment and c a BET constant related to the adsorption enthalpy. To obtain the molar volume of a monolayer, this equation must be applied in a pressure region (p/p_0) where linearity is fulfilled, that is, at low relative pressure, before that multi-layer adsorption process starts and capillary condensation would occur. [Brunauer et al. 1938] BET method has been applied at P/P_0 from 0.06 to 0.2, which gives a linearity with a correlation coefficient r^2 of 0.99999.

Figure 3.12: Representation of physical gas adsorption on a porous solid surface by increasing the gas pressure.

Increasing the relative pressure, saturation is reached (last stage of *Figure 3.12*). The sample is completely covered by gas molecules and all the pores are filled. The relation between the relative pressure and the volume of condense capillary enables the determination of pore diameter, volume and distribution, by using Barrett-Joyner-Halenda (BJH) method and assuming cylindrical porous. [Barrett et al. 1951] Pore volume is the amount of gas adsorbed by the solid and pore diameter can be estimated from the derivative $[dV(\log d)]$ of total pore volume as a function of logarithmic pore diameter.

Adsorption-desorption isotherms of solid samples (50mg) were carried out on *Micrometrics ASAP 2020* at 77.3K with N₂ as adsorbate (N₂ molecule area of 0.162mm²). [Rouquerol et al. 1999] Previously, samples were outgassed at 300°C for 3 hours under vacuum. Specific surface area and pore size distribution were calculated by analysing isotherm data with BET and BJH method, respectively.

3.9 Absorption/emission spectroscopy

Optical spectroscopy techniques are based on the interaction of the matter with photons from UV, visible and near infrared (NIR). Mainly, two main processes are studied: absorption and emission processes. In this thesis, UV-Vis Diffuse Reflectance Spectroscopy (DRS) was used to study the absorption properties of the metal oxides and their hybrids, Fourier Transform Infrared Spectroscopy (FT-IR) was employed to study the vibrations of the samples when they are excited with infrared light and Photoluminescence Spectroscopy (PL) was used to study the emission properties of the samples of interest after the absorption of photons.

3.9.1 UV-Vis Diffuse Reflectance Spectroscopy

The UV-Vis spectroscopy consists in the measurement of absorption, transmission or reflectance of a sample as a function of a wavelength region (from visible to near ultraviolet light). Specifically, DRS technique is based on the illumination of a flat surface of the solid sample since light cannot penetrate in an opaque solid. The reflected light from the solid surface is measured, which follows the Lambert- Absorption law:

$$I = I_0 e^{-Kx} \quad (3.11)$$

where I is the intensity of the reflected light from an initial intensity (I_0) passing through a layer of thickness x of a medium with an absorption (or extinction) coefficient K .

For a homogeneous crystal orientation, the incident light is reflected back symmetrically with respect to the sample surface, called as *normal reflection*. However,

3.9 Absorption/emission spectroscopy

for randomly orientation of particles, light is reflected in different directions due to the different orientation of the sample surface, called as *diffuse reflection*. The diffuse reflected light could be detected and analysed giving information about optical absorption properties of the solid sample. Specifically, for semiconductor materials, light produces the excitation of electrons from filled energy states (valence band) into empty energy states (conduction band). Consequently the amount of reflected light decreases, which enable the determination of the semiconductor bandgap energy (E_g). The semiconductor band gap energy can be calculated by fitting the Tauc law:

$$[\alpha(h\nu)]^m = A(h\nu - E_g) \quad (3.12)$$

where α is the absorption coefficient, h the Planck's constant, ν the light frequency (or wavenumber), A the absorbance of the sample and m a parameter depending on the nature of the bandgap semiconductor, which takes values of 1 or $\frac{1}{2}$ for direct or indirect bandgap, respectively. Finally, E_g is the bandgap energy and it can be calculated from the tangent of the linear fitting of *Equation 3.12*.

Absorption studies were obtained in *Lambda 1050 PerkinElmer* by means of a diffuse reflectance module containing an integrated sphere. Samples were placed in a holder with 2mm diameter and they were measured in the wavelength range of 250-800nm using BaSO_4 as standard sample. Bandgap energy was calculated by implementing the Tauc equation for indirect semiconductors.

3.9.2 Fourier Transform Infrared Spectroscopy

Conventional infrared (IR) spectroscopy is a vibrational spectroscopy that studies the absorption of infrared light by a solid, liquid or gas sample. The frequency range of the IR light is in resonance with the frequency of vibrations in covalently bonded atoms, which allows the identification of the chemical structure of the sample. A molecule can vibrate in different modes (stretching, rocking, scissoring, etc.), called as vibrational modes. But not all of them are *IR active*, that means, not all produce an IR signal. A necessary condition for a specific vibrational mode would be *IR active* is that a change in the molecule dipole occurs (permanent dipoles are not required).

Thus, the IR spectrum consists in the measurement of the intensity of the transmitted light as a function of wavelength (or frequency), which provides information about the amount of energy absorbed by a molecule at a certain frequency. In contrast to conventional IR spectroscopy where sample is illuminated with a monochromatic light (as in UV-Vis absorption spectroscopy), Fourier Transform Infrared Spectroscopy uses a broadband IR light (containing all the wavelength range in the same beam). For this, the FT-IR spectrometer contains a Michelson interferometer and a moving mirror in such a way that the moving of the mirror produces the block or the transmission of specific wavelengths. The detector measures the amount of light as a function of the mirror position, known as FT-IR interferogram. Finally, a Fourier transform algorithm converts the raw data into the final spectra (transmittance of light vs frequency). Therefore, this technique presents several advantages such a higher sensitivity and speed.

In this report, FT-IR spectra were carried out in a *PerkinElmer 2000* spectrometer. The frequency range was $400\text{-}4000\text{cm}^{-1}$ with a resolution of 4cm^{-1} . A KBr disk containing the sample was employed in transmission mode.

3.9.3 Photoluminescence Spectroscopy

The Photoluminescence Spectroscopy consists in the study of light emission process after the absorption of photons by the sample. Various relaxation processes can occur after excitation and only the radiative process are measured by a photodetector. The PL signal is produced when a photogenerated electron-hole pair is recombined emitting light. Typically, for semiconductor materials, they are illuminated with light of higher energy than bandgap, resulting in photon emission of ultraviolet, visible or infrared range. Spectra analysis enables to study the luminescence process of the semiconductor material. After excitation of semiconductor and consequently, generation of electron-hole pairs, different radiative relaxation process can occur as illustrates *Figure 3.13*.

Figure 3.13: Scheme of the photoluminescence process, showing the main radiative recombination process that can occur in a semiconductor material

A direct electron-hole recombination is also known band-to-band recombination (from CB to VB), which further provides information about the bandgap energy. Additionally, indirect recombination processes can occur by relaxation of the electron in CB to an energy level placed above the valence band. Similarly, electrons can be relaxed to a defect states below the conduction band and combine with holes hosted in or above the valence band. Subsequently, the photoluminescence spectra can be very useful to determine intra-band gap states associated to distortions in the crystal structure, presence of defect or dopants in the sample.

Photoluminescence spectroscopy was recorded using a pulsed laser of 355nm wavelength and repetition rate of 235Hz for excitation. A cut-off filter at 370nm was employed to discriminate the laser light and laser-induced luminescence. All the measurements were carried out at room temperature.

3.10 Conductivity

The conductivity of a single electrospun fibre was measured by depositing it in a photodetector device with collaborators from IMDEA Nanoscience Institute. For such a study, electrospun fibres were transferred onto pre-patterned electrodes by *pick-up and drop* technique.[Castellanos-Gomez et al. 2014] The steps of this process are illustrated in *Figure 3.14* by optical micrographs together to a schematic representation of the electrode cross-section. *Picture 1* shows the electrode consisting in two

bridging Ti/Au (5/50nm) electrodes pre-patterned on a SiO₂/Si substrate. *Picture 2* shows the Si wafer with the nanofibres, which were deposited from an alcoholic dispersion by spray coating. *Picture 3* shows the polydimethylsiloxane (PDMS) stamp (*Gelfilm, Gelpak*) in a close proximity to the electrode, which enables the alignment of the substrate and the sample to place the fibre in the gap between electrodes. In *picture 4*, a change in the colour evidences the contact between the stamp and the substrate. The *pictures 5-9* show the peeling off the stamp, leaving the fibre deposited between the metallic electrodes. The fibres used for the device preparation have a selected dimensions determined by the optical microscope resolution ($>400\text{nm}$ diameter) and the gap between electrodes ($>10\mu\text{m}$ in length).

Figure 3.14: Optical microscope images and schematic electrode cross-section of the fabrication by *pick-up and drop technique* of a single fibre photodetector.

3.10 Conductivity

The electronic (current-voltage) measurements were carried out with a source-meter unit (*Keithley 2450*). The response to the light of the electrospun fibres were also measured with 8 light emitting diodes (LEDs) with wavelength between 375-1020nm (*LEDD1B – T-Cube LED driver*) and coupled to a multimode optical fibre with a light spot of 200 μm . The time-dependent measurements were carried out by modulating the light intensity with a function generator (*Yokowaga*).

3.11 Electrochemical Methods

Electrochemistry is a physical-chemical method that study the behaviour of a chemical compound under electrical perturbation. The electrochemistry is based on the reduction-oxidation (redox) reactions, a type of chemical reactions that involve the transfer of electrons between two species, which change their chemical oxidation state by gaining or losing electrons. Mainly, it could be two types of electrochemical process: those that by applying an external current produce a chemical reaction as in electrolysis or those that through a spontaneous chemical reaction originates a current as in batteries.

The electrochemical process takes into account the overall process that occurs in an electrochemical cell including reduction and oxidation reactions, which occur in separated electrodes but connected through an electrolyte and an external electrical circuit. Classically, electrochemical cells were known as Galvanic cells, which consists in two conductive electrodes: anode or working electrode (WE) and cathode or counter electrode (CE) where the oxidation and reduction reactions take place, respectively. Between both electrodes, an electrolyte with free ions can transport the electric charges generated in the electrodes. However, the main limitation of the electrochemical cells with two electrodes configuration is the voltage control over the working electrode while a current is being produced in the counter electrode. In order to solve this problem, three electrode cells were developed. The third electrode is the reference electrode (RE) and simulates a half cell with a well-known electrode potential. The reference electrode measures and controls the potential of the working electrode since a current passes through it to balance the current of the working electrode.

The most common reference electrode is the standard hydrogen electrode (SHE), whom potential is defined as 0.00V at 1atm of pressure, 25°C and pH=0. This potential refers to the following reduction reaction:

The chemical potential of the rest redox reactions are tabulated as reference of SHE and always for the reduction reaction (the oxidation reaction will take the same potential but with opposite sign). Thus, the cell potential can be calculated by:

$$E_{cell}^{\circ} = E_{red}^{\circ}(cathode) - E_{red}^{\circ}(anode) \quad (3.14)$$

For example, the splitting of water by an external voltage (electrolysis) to its elemental components, hydrogen and oxygen, follows the next reactions:

Thus, the electrolysis of water needs -1.23V at 25°C, 1atm and pH=0 (or [H⁺]=1M). For other solution pH, the potential must be adapted using the Nernst equation.[Chen et al. 2013]

Electrochemistry is thus an analytical tool to determine electrochemical properties of the semiconductor and in particular, the semiconductor/electrolyte interface. The study of the electrochemical and/or photoelectrochemical properties of the nanomaterials is gaining importance due to relevant processes such as generation, separation and recombination of photocarriers can be studied. Subsequently, the enhanced electrochemical properties can be related with the ability to drive efficiently water splitting. But importantly, it can be also used to improve the performance of water splitting by separation of the redox reaction in the anode and cathode electrodes with further possibility of applying an external bias voltage to improve the catalytic efficiency.

Electrochemical measurements were carried out in a standard three-electrode cell as illustrates *Figure 3.15*. The potential is applied to the working electrode and it is

3.11 Electrochemical Methods

stabilised with a Ag/AgCl reference electrode, which presents a standard potential of $E_{Ag/AgCl}^0 = 0.235V$ vs. SHE for pH=0 at 25°C and 1atm. The current passes from the working to the counter electrode through an ionic electrolyte. Samples were deposited by spray coating from a dispersion solution onto clean conductive substrate (FTO with resistivity of $7\Omega/cm^2$) forming the WE. Pt wire was used as CE, Ag/AgCl/KCl saturated as RE and the electrolyte solution was 0.1M Na_2SO_4 adjusted to pH=2 with H_2SO_4 . Finally, a *SP-200 Bio-Logic* potentiostat was used to apply the voltage and measure the current.

Figure 3.15: Schematic representation of the three electrode electrochemical cell used in this report.

3.11.1 Open-circuit potential measurements

Open-circuit potential (OCP) is a technique very used in DSSC systems for analysing the electron lifetime and the photovoltage of the cell. This technique is based on the measurement of the OCP in the dark and upon illumination conditions, when the photogenerated electrons and holes are separated under the influence of the electric field within the semiconductor space charge region. Under these conditions, the measured voltage represents an idea of the flat band potential (E_{fb} , flow of electrons that occurs until the Fermi level of the semiconductor and the redox potential of the electrolyte are equalled). This approach is only accurate if the illumination is suffi-

ciently intense to completely remove the band bending at the surface and the recombination rate is slow. In addition, the change of the potential between both conditions enables the determination of the photovoltage. However, the photovoltage measured at OCP may not be the same than that under operating conditions since it is necessary to include the overpotential of the reaction. Finally, after the light is switched off, the electrons and holes recombine and the kinetic of this process can be studied by the electron lifetime following the next equation:

$$\tau_n = -\frac{K_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (3.15)$$

where K_B is the Boltzmann constant, T the temperature, e the electron charge, V_{oc} the voltage at open circuit conditions and t the time. The OCP measurements were carried out in dark and illumination conditions (150W Xe lamp, *Newport*). The wavelength of the light was lower than 400nm and the power density that reaches the surface of the electrode is 530mW/cm².

3.11.2 Chronoamperometry

Chronoamperometry is an electrochemical technique in which a constant potential is applied to the working electrode and the resulting current is monitored as a function of time. The photoresponse of the electrode will provide an idea of the efficiency of the photoinduced processes at a given potential. This leads to a very rapid comparison of the electrochemical response of different photoelectrode materials in terms of charge separation and/or accumulation upon illumination. Furthermore, the behaviour of the photoelectrodes can be determined by the difference in current density between dark and illumination conditions. Hence, if this difference is higher than zero, the photoelectrode behaves as photoanode and if it is lower than zero, it behaves as photocathode. During the experiments of this thesis, the photoelectrodes were set at fixed potential and intermittently illuminated by using a manual chopper and a light source (Xe lamp, *Newport*) of 150W in the UV range ($\lambda < 400\text{nm}$).

3.11.3 Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a characterisation technique for kinetic studies of electron transfer at the solid/liquid interface. In general, this technique consists in the measurement of the alternating electrical current $I(\omega)$ at a certain radial frequency ω when a small sinusoidal voltage $V(\omega)$ is applied to the system. Similar to Ohm's law, impedance $Z(\omega)$ can be written as:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} \quad (3.16)$$

EIS technique is applied to a solid material with two contacts being one of them an external electrical circuit and the other an electrolyte (liquid ionic conductor). When a small sinusoidal alternating current (AC) voltage signal over a continuous bias potential is applied in a range of frequencies, the voltage signal follows the expression:

$$V(\omega) = V_A \sin(\omega t) = V_A \sin(2\pi f t) \quad (3.17)$$

where V_A is the amplitude of the voltage, which should be low enough to keep the system in the linear limit. Thus, the corresponding current is recorded and can be expressed as:

$$I(\omega) = I_A \sin(\omega t) = V_A \sin(\omega t + \Phi) \quad (3.18)$$

As the current signal presents a phase shift Φ with respect to the input voltage signal, the complex impedance has the form:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_A \sin(\omega t)}{I_A \sin(\omega t + \Phi)} = |Z| \frac{\sin(\omega t)}{\sin(\omega t + \Phi)} \quad (3.19)$$

Impedance is therefore a function of $|Z|$ and Φ . This technique could be expressed as a complex function using the Euler's relationship:

$$Z = Z' + iZ'' = |Z|(\cos \Phi + i \sin \Phi) \quad (3.20)$$

where the real part Z' corresponds to resistance phenomena (R) as the ones measurable in direct current (DC) and the imaginary part iZ'' corresponds to other processes such as capacitance (charge accumulation in an electric field, $Z_C = 1/i\omega C$) or

inductance (charge accumulation in a magnetic field, $Z_L = i\omega L$). The impedance is measured in a frequency range due to different processes occur at different frequencies due to their different time constants. The low frequency range can be considered an approximation to the DC regime due to the corresponding time constant is slow enough to stabilise the measurement. Overall, EIS technique allows a separately determination of the different electron transfer processes.

Nyquist plot is a common representation of the impedance spectra by plotting the imaginary part of the impedance $-Z''$ as a function of its real part Z' . As shows *Figure 3.16*, the Nyquist plot of the simplest RC circuit (resistance in parallel to a capacitor) results in a semicircle with diameter R , characteristic angular frequency ω_L at the apex of the semicircle, $|Z|$ the vector length between the origin and the impedance value at the apex and phase shift Φ the angle between $|Z|$ and the corresponding point in the abscissa axis.

Figure 3.16: The simple RC circuit (Randles circuit) and its corresponding Nyquist plot.

In order to analyse the impedance spectra, the concept of equivalent circuit (EC) model is required, which consists is an electrical circuit whom electrical components represent charge transfer processes in the solid/liquid interface (electrode/electrolyte) and/or within the solid. The fit of the Nyquist plot with an appropriate EC provides values of the electrical components of the circuit, which can be ascribed to electron transport, transfer and accumulation processes in the electrode. Hence, EIS results in a non-destructive technique for the kinetic study of the different process that occurs at the electrode. For example, the Nyquist plot of *Figure 3.16* represents the impedance spectra of a RC circuit, which describes a very basic electrochemical system: an electrode in contact with an electrolyte. In particular, this circuit is ascribed

3.11 Electrochemical Methods

to the resistance (R) of the electron transfer between electrode/electrolyte interface. The capacitance (C) of the double-layer formed between the electrode and electrolyte. For non-ideal capacitance effects, the Nyquist plot presents a depressing semicircle. In such a case, a constant phase element (CPE) is used in the equivalent circuit model instead of a capacitance.

In addition, EIS could be applied in a voltage range in order to study the capacitance as a function of the applied potential. When the Fermi level of the electrode is higher than that for the electrolyte, the Mott-Schottky equation can be used to determine the flat band potential by:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 e N_D} \left(E - E_{fb} - \frac{k_B T}{e} \right) \quad (3.21)$$

where C is the double-layer capacitance, ϵ the dielectric constant of the semiconductor, ϵ_0 the electric permittivity in vacuum, A the interface area, e the electron charge, N_D the donor density, E the applied potential, E_{fb} the flat band potential, k_B the Boltzmann's constant and T the temperature of the experiment. From the Mott-Schottky plot, one can extract the flat band potential from the intersection of two linear region with the x-axis and donor density from the slope. This method presents more accurate values than the flat band potential estimated by OCP measurement.

3.12 Photocatalytic experiments

Photocatalytic tests of the samples were carried out in collaboration with research groups, which host photocatalytic reactors of H_2 production (D. Eder group at Technical University of Wien) and CO_2 reduction (V. de la Peña group at IMDEA Energy Institute). Briefly, the design of the photocatalytic reactors, the preparation of the photocatalytic material, the employed light source and the gases detection system are described below.

3.12.1 Photocatalytic Hydrogen Production

The photocatalytic hydrogen production test were performed in flow-type reactors designed by Dr. Alexey Cherevan. Two types of reactors have been used for the water splitting process. One was used for the test of TiO_2 photocatalysts and the other for the test of Nb_2O_5 and Ta_2O_5 photocatalysts. The former consists in a cylindrical glass container with a quartz cap that allows the illumination from the top of the reactor (*Figure 3.17*). The light source was a Lumatec *SUV-DC-P Deep UV* equipped with a super pressure mercury lamp of 200W, which enables its use in the UV (240-500nm) and visible (400-700nm) range separately. In order to keep constant the temperature, a water cooling in the outer part of the cylindrical reactor was used, avoiding the overheating due to the powerful light irradiation.

Figure 3.17: Photograph of water splitting reactor used for testing TiO_2 photocatalysts.

The second reactor is an extended version of the previous one but with an inner irradiation, which enables a better efficiency in the light absorption of the photocatalyst and thus, higher absolute values of H_2 production. Furthermore, the light source is much powerful than the previous one. It is a 700W Hg *TQ 718* lamp (*UV Consulting*), emitting light in the range of 200-600nm. Consequently, an advanced water cooling system from *Lauda (Variocool 1200W)* was used to keep constant the temperature of the photocatalytic reaction. In addition, the reactor design has an inlet for the addition

3.12 Photocatalytic experiments

of the co-catalyst during the reaction instead to prior the reaction as occurs in the first described reactor.

In both cases, the catalyst was dispersed in the reaction medium and then, the reactors were purged with Ar gas (99.998% purity) before experiments to remove oxygen in the reactor. Furthermore, the Ar gas was used during the experiments as carrier gas of the photocatalytic reaction products. A mass flow controller *Q-Flow 140 Series* from *MCC-Instruments* was used to control the Ar flow (30 and 100mL/h for the first and the second described reactors, respectively). The difference of the carrier gas flow arises from the different reaction volume, which are 200 and 850mL, respectively. CaCl₂ trap was placed to remove impurities before gases arrives to analyser.

The gas detection system was the same in both reactors: a *X-Stream* gas analyser from *Emerson Process Management* that enables the simultaneous detection up to four gases over 60 candidates by combination of four channels of thermal conductivity detector (TCD), non-dispersive infrared/ultraviolet/visible photometers (ND-IR/UV/VIS), trace moisture (tH₂O), paramagnetic and electrochemical oxygen (pO₂/eO₂) detectors and sensors. In the case concerning this report, oxygen, hydrogen, chlorine and carbon dioxide were monitoring by using the pO₂/eO₂, TCD, ND-UV and ND-IR detectors, respectively. Finally, the gas flow in ppm is continuously collected over time and it could be converted to H₂ evolution rate in µmol/h by assuming that 1ppm is equal to 1/1000000 volume of carrier gas (30 or 100mL/h) and then volume is converted to mol/h using the ideal gas equation ($PV = nRT$), resulting:

$$H_2 \text{ evolution rate (mol.h}^{-1}\text{)} = \frac{H_2 \text{ flow (ppm)}}{1000000} * Ar \text{ flow (mL.min}^{-1}\text{)} * \frac{60(\text{min.h}^{-1})}{1000(\text{mL.L}^{-1})} * \frac{P(\text{atm})}{(T(K)*R(\text{atm.L.K}^{-1}.\text{mol}^{-1}))} \quad (3.22)$$

In the case of TiO₂ photocatalyst, more than 50 samples have been tested in the photocatalytic reactor under the same experimental conditions for 3 years. Along this time, differences in absolute values of the hydrogen production have been observed. Subsequently, we have noticed a hydrogen production dependence with the light intensity, which decreases along its lifetime. *Figure 3.18* shows the hydrogen evolution

rate using a lamp with many hours of use, resulting in a light power of 1.32W and, a new lamp with 3.2W of power. The increase in hydrogen generation correspond to the power ratio (0.41), establishing the importance of the lamp power in the final hydrogen production rate.

Figure 3.18: Effect of the light power in the photocatalytic H₂ evolution rate.

3.12.2 Photocatalytic CO₂ Reduction

CO₂ photoreduction experiments were conducted in continuous flow mode in a gas-phase stainless steel photoreactor of cylindrical shape and effective volume of 190mL with a borosilicate window of 98.2% transmittance for top-irradiation (*Figure 3.19*). The powdered catalysts (0.1g) were deposited on a glass microfibre filter from aqueous suspensions. Then, the filter containing the sample photocatalyst was dried at 100°C for 3h and placed inside the reactor. The reactor was firstly degassed at 50°C under vacuum and purged with Ar (100mL/min) for 1h in order to remove any residual compounds weakly adsorbed on the surface of the catalyst. Then, a pure carbon dioxide (99.9999 %, *Praxair*) and water (Milli-Q) mixture was fed into the reaction system with a CO₂:H₂O molar ratio of 7.25 by means of a Controlled Evaporator Mixer (CEM). The flow was kept in the dark for 1h in order to establish an adsorption-desorption balance at the reaction temperature. Prior to illumination, the reactor was pressurised and kept at the reaction flow rate for another 1h. Finally, the reaction conditions were set at 2 bar and 50°C. The photocatalytic measurements were performed using four UV lamps of 6W ($\lambda_{\text{max}} = 365 \text{ nm}$). In-line analyses of the reactor outlet gas were performed every 22 minutes, using a *Bruker 450* gas chromatograph

3.12 Photocatalytic experiments

equipped with three columns (*BR-Q Plot*, *BR-Molsieve 5A* and *CP-Sil 5B*), three detectors (2 *FID* and 1 *TCD*) and a methanizer. All photocatalytic tests were investigated over a period of 20 h of irradiation.

Figure 3.19: Schematic reactor system for the photoreduction of CO₂.

Apparent Quantum Yields (AQY) were calculated according to *Equation 3.23*, considering the number of electrons required to obtain each product, and measuring the incident spectral irradiance on the surface of the catalyst below 400 nm by means of an optical fibre *StellarNet UVNb-50* spectrometer.

$$AQY(\%) = \frac{\text{reacted electrons}}{\text{incident photons}} * 100 \quad (3.23)$$

The selectivity of the catalyst was calculated to determine the trend to the formation of a certain product. The selectivity calculated for each product was determined using the following equation, considering the cumulative production:

$$S(\%) = \frac{\mu\text{mol of product}}{\mu\text{mol in total}} * 100 \quad (3.24)$$

The converted carbon or hydrogen was calculated to easily compare the photocatalytic production in terms of μmol of C or H in the total products. Thus, the conversion was determined, for the cumulative production, by:

$$C_{\text{converted}} = (\mu\text{mol of product}) * (C \text{ atom number}) \quad (3.25)$$

$$H_{\text{converted}} = (\mu\text{mol of product}) * (H \text{ atom number}) \quad (3.26)$$

CHAPTER 4

SYNTHESIS, MORPHOLOGY AND STRUCTURE OF ELECTROSPUN HYBRIDS

The Chapter 4 contains details of experimental results in terms of strategy and optimisation of the *in-situ* growth of metal oxides with nanocarbons. The main goal is to create a new hybrid material whose properties differ from those of the individual components. At first, *Section 4.1* provides information about the parameters used for the sol-gel synthesis in combination with electrospinning technique. Different approaches were employed to hybridise the metal oxide and the nanocarbons (CNTs or graphene); i.e. the use of linking agents or chemically functionalise nanocarbons. Finally, the heat treatment was designed and optimised to produce hybrids under conditions compatible with the individual phases.

In *Section 4.2*, a morphological, structural and textural characterisation of the electrospun materials is detailed in comparison to reference nanoparticles produced by standard sol-gel method. This reveals important information about the nanofibre morphology in their characteristic porosity and crystal structure. *Section 4.3* is focused in the general structural characterisation of the different hybrid materials to gain more insight into the nanocarbon effect, altering the structure of the metal oxide. Finally, *Section 4.4* presents results on the optical and electronic properties of TiO₂/CNT hybrids, providing experimental evidences of strong coupling between the two phases and improved interfacial properties.

4.1 *In-situ* synthesis of TiO₂/nanocarbon hybrid

TiO₂ has been extensively studied as a promising material for energy applications. The simplicity and low cost of its synthesis together to large specific surface area and the possibility to obtain different morphologies at the nanoscale makes TiO₂ a great candidate for its hybridisation with nanocarbons. In order to favour the synergy between both materials, a rational synthesis is implemented with the aim of creating an optimum morphology and tight TiO₂/nanocarbon interfaces. Hence, among all possible synthetic methods, sol-gel method combined with electrospinning technique was chosen. It enables the synthesis of sufficiently large amounts of the material for further studies as photocatalyst or nanostructured electrodes.

4.1.1 Sol-gel and electrospinning process

A standard sol-gel process consists in two main reactions: hydrolysis and condensation of the metal alkoxide precursor. During the first reaction, molecules of precursor form a colloidal solution (*sol*) that evolve towards a network of particles similar to a polymer network (*gel*), which contains solid and liquid phases. The drying of the liquid, mainly solvent, is necessary to complete the condensation process and the densification of the solid. For the specific case of combined sol-gel and electrospinning, the drying process is forced to occur immediately when the solution is electrospun under the applied voltage. Afterwards, annealing process is necessary for crystallisation of the inorganic.

The sol-gel method results a very interesting approach because it is a low temperature synthesis method with fine control of morphology and composition. Also, sol-gel route enables the incorporation of small amounts of other materials such as dopants, dyes or nanocarbons. In the case of CNTs or graphene, they can be added to the initial precursor solution to embed them into the metal oxide network, where they can be uniformly disperse if their concentration is low. Furthermore, the nanocarbon surface can provide nucleation sites for the formation of the TiO₂. However, the incorporation of nanocarbons to the sol-gel solution is a challenge due to their hydrophobicity. Two types of functionalisation strategies are presented in this chapter, used to

modify the chemistry of the nanocarbons surface before they are mixed with the inorganic sol-gel solution: covalent and supramolecular. The first type includes an oxidation process or a diazo-coupling reactions (see details in *Section 3.1*). For the second functionalisation, pristine nanocarbons are dispersed in a polar solvent with benzyl alcohol used as linking agent. Its aromatic groups form π - π interactions with the nanocarbons while the hydroxyl groups remain on the surface, making thus the nanocarbons less hydrophobic while avoiding damage of their structure.[Eder 2010] The different functionalisations employed in the formation of TiO₂/nanocarbons hybrids studied here are illustrated in *Table 4.1*.

Table 4.1: Schematic illustration of the four types of nanocarbons employed in the synthesis of electrospun hybrid samples (referred as p-MWCNTs, p-GR, ox-MWCNTs and isoft-GR).

	Covalent functionalisation	π - π interactions <i>via</i> linking agent
MWCNTs	<p>ox-MWCNTs</p> <p>isoft-GR</p>	<p>p-MWCNTs</p> <p>p-GR</p>
Graphene		

In a typical experiment, the hybrid fibres were prepared by combining sol-gel chemistry and electrospinning technique as described in detail the *Section 3.2*. The precursor solution is prepared under acidic conditions to accelerate the hydrolysis reaction and favour the formation of a continuous network during condensation reaction. In this work, the pH is controlled by adding drops of acetic acid to the alcoholic solution containing titanium ethoxide (63.5wt.%). Then, an alcoholic dispersion of nanocarbons of different volume fractions, usually ranged between 0.35-5vol.%, is added to the sol-gel solution immediately after the addition of acetic acid. Finally, a polymer solution of PVP in ethanol is added. The resulting mixture has enough viscosity for the electrospinning of continuous fibres.

4.1 In-situ synthesis of TiO₂/nanocarbon hybrid

There are several parameters during electrospinning that need to be optimised to enable continuous fibre spinning of fibres free of beads, drops and other defects. *Table 4.2* summarises the effect of the polymer concentration and electrospinning parameters such as feed rate, tip-to-collector distance or applied voltage. *Figure 4.1* shows the morphology of fibres obtained during sequential optimisation of electrospinning parameters. First, polymer concentration was adjusted until fibre were observed (10wt.%, *Figure 4.1a*). Then, the fine tune of the electrospinning parameter (*Figure 4.1b-d*) enable the formation of uniform TiO₂ fibres without any defects at 18kV, 2mL/h and 10cm.

Table 4.2: Summary of parameters employed in the synthesis of electrospun fibres and the conclusions obtained from their combination.

Parameter	Wt (%)	V _{app} (kV)	Φ (mL/h)	D (cm)	Conclusions
Polymer (PVP) concentration (Wt.%)	5	18	1	10	10wt.% of PVP provides the best properties for the fibre formation, still drops appear (<i>Figure 4.1a</i>).
	10	18	1	10	
Applied voltage (V _{app}), kV	10	12	1	10	High voltages produce a decrease in the fibre diameter. Beads are formed at too low and too high voltages; best voltage at 18kV. (<i>Figure 4.1b</i>).
	10	15	1	10	
	10	18	1	10	
	10	23	1	10	
Flow rate (Φ), mL/h	10	18	0.5	10	The best density and uniformity of fibres occur for 2mL/h because it leads to faster solvent evaporation. (<i>Figure 4.1c</i>).
	10	18	1	10	
	10	18	2	10	
Tip-to-collector distance (D), cm	10	18	2	5	An intermediate tip-to-collector distance is necessary to give time for solvent evaporation before fibres reach the collector. 10cm was the optimum distance; lower and higher distances produce beads. (<i>Figure 4.1d</i>).
	10	18	2	10	
	10	18	2	12.5	
	10	18	2	15

Figure 4.1: Optical images showing the sequential optimisation of electrospinning process described in *Table 4.2*.

The resulting as-electrospun material produced under optimised parameters forms a mesh of fibres (*Figure 4.2a*) containing typically a 50wt.% polymer, the inorganic gel and, in the case of the hybrid material, the nanocarbons embedded inside. *Figure 4.2b* shows that fibres of hundreds microns length and diameter ranged between 350-950nm are homogeneous and suggest that the nanocarbons are well dispersed in the electrospun matrix.

Figure 4.2: a) Photograph of a typical mesh of electrospun fibres. b) Scanning electron micrographs showing the uniformity of the as-electrospun fibres.

4.1.2 Heat treatment

The following step after electrospinning consists in heat treating the fibres to 1) remove the polymer by calcination in air without loose of the fibre morphology and 2) crystallise the inorganic, which in the case of TiO₂ requires temperatures about 500°C to form anatase. Whereas the latter treatments are normally carried out in air, in this study the treatments are performed in Ar to prevent the oxidation damage to the nanocarbons, especially those chemically modified with functional groups, which contain surface defects. This leads to densification and crystallisation conditions distinct from those used in traditional sol-gel, which affects on the structure and composition of the metal oxide and also the hybrid.

The thermal stability of the polymer and the different nanocarbons used in this thesis were studied using thermogravimetric analysis. The degradation in air of the electrospun PVP fibre is represented in *Figure 4.3a* and occurs between 350-480°C. The nanocarbons decomposition curves are shown in *Figure 4.3b* and their removal is observed between 100-300°C above the PVP degradation, depending the type of nanocarbon. The pristine nanocarbons, MWCNTs and graphene, are oxidised at 600 and 725°C, respectively; however, the functionalised MWCNTs and graphene have their oxidation temperature shifted down to 570 and 600°C, respectively. Interestingly, the chemical modification of the graphene surface produces higher decrease of its oxidation temperature than that of the MWCNTs. This is related to a more significant degradation of the graphene crystal structure.

Figure 4.3: Thermogravimetric decomposition curves of a) the PVP fibre and b) the different type of nanocarbons.

Based on the thermal decomposition of the PVP and the nanocarbons (*Figure 4.3*), the first heat treatment of as-electrospun fibres was fixed at 400°C in air, which should complete the removal of PVP while preserving the nanocarbons. The compositional evolution of the metal oxide was analysed by recording thermograms of the sol-gel precursor solution without polymer but with 3vol.% of MWCNTs (*Figure 4.4*). Weight loss is constant until 300-350°C, which corresponds to the densification process involving the removal of solvents, organic compounds and inorganic precursors. An abrupt change in the weight loss appears at 350-500°C, which comes from the sintering and crystallisation of TiO₂. Further increase of the temperature does not change the weight, confirming that the reaction has finished. Crystal growth continues and reaches the phase transformation from anatase to rutile without change of sample weight.

Figure 4.4: Thermogravimetric decomposition curves of the sol-gel precursor solution containing 3vol.% of ox-MWCNTs.

Crystallisation for bulk TiO₂ into anatase phase is around 500°C.[Hanaor and Sorrell 2011] However, this temperature is just 70°C below the oxidation of functionalised MWCNTs for the samples in this work, and TiO₂ is known to further catalyse the oxidation of CNTs.[Aksel and Eder 2010] Therefore, the crystallisation stage was carried out in inert atmosphere. Thus, the complete heat treatment consists in a first stage at 400°C in air for 2.5h to remove the polymer, and subsequent annealing at 500°C in Ar or vacuum for 1h. For the synthesis of other metal oxides and their hybrids, crystallisation was still carried out in inert atmosphere, but the temperature was adjusted accordingly (see *Appendix A*).

4.2 Crystallisation into mesoporous fibre structure

The combination of sol-gel and electrospinning results in a fibre architecture, which has influences on the inorganic composition and surface properties. In this section, the characterisation of the morphology, crystal structure and porosity of TiO₂ fibres, are compared with reference material produced by standard sol-gel process.

4.2.1 Structure evolution of electrospun fibres

Structure analysis of the electrospun samples was performed using X-ray diffraction in order to determine crystalline phases, crystal size and degree of crystallinity, important parameters for subsequent applications of the material, e.g. as photocatalyst. At relatively low temperatures such as 500°C, the kinetically most stable phase, anatase TiO₂ is obtained. However, their transformation into rutile phase is thermodynamically favoured and could be facilitated during the synthesis. For instance, the presence of the polymer in addition to the inert atmosphere are expected to affect the crystallisation process, particularly the onset of the anatase-to-rutile transformation and/or the crystal size.

The XRD patterns of *Figure 4.5* show the crystal evolution of TiO₂ fibres annealed in Ar (*Figure 4.5a*) in comparison with those annealed in air (*Figure 4.5b*), both in the temperature range of 400-800°C. At the lowest temperature, 400°C, only anatase diffraction peaks are observed for both atmospheres. The presence of rutile at only 500°C in Ar whereas they appear at 650°C in air, demonstrates the early phase transformation using the inert gas. The position and relative intensity of the anatase (JCPDS No. 00-021-1272) and rutile (JCPDS No. 00-021-1276) diffraction peaks are included in the *Figure 4.5*. The absence of oxygen in an inert atmosphere promotes the formation of a non-stoichiometric oxide. These O vacancies have been already obtained by a partial reduction of the oxide through annealing in reducing atmospheres (e.g. CO₂/H₂) [Nakade et al. 2002] or by incomplete oxide synthesis in an inert atmosphere (e.g. in Ar). [Eder and Windle 2008] Subsequently, O vacancies favour repositioning of Ti and O atoms in the rearrangement of Ti-O octahedral from anatase to rutile.

Figure 4.5: XRD patterns showing the crystal structure of TiO₂ fibres annealed between 400-800°C in: a) Ar atmosphere and b) air atmosphere

It is well-known that there is a competition between the crystal growth and the phase transformation during the crystallisation process of TiO₂. The influence of the atmosphere in favouring those processes is analysed from the XRD patterns of *Figure 4.5*. From the peak intensities and width, the anatase/rutile ratio and the crystal size were calculated using the Spurr and Scherrer equation, respectively.[Spurr and Myers 1957; Patterson 1939] Those calculated parameters are represented in *Figure 4.6* as a function of the annealing temperature using both atmospheres: Ar and air. The formation of rutile in the TiO₂ fibres annealed in Ar occurs at temperatures below 500°C whereas in air, it occurs about 650°C (*Figure 4.6a*). However, crystal sizes are lower than those obtained in air for temperatures lower than 650°C (*Figure 4.6b*).

Figure 4.6: a) Anatase/rutile ratio and b) crystal size corresponding to the XRD patterns of *Figure 4.5* as a function of the annealing temperature.

4.2 Crystallisation into mesoporous fibre structure

Furthermore, the role of the inert gas flow in the phase transformation was studied for a TiO₂ fibres annealed at 500°C. *Figure 4.7a* shows the XRD patterns using an Ar flow varied between 0 to 400 L/h. It illustrates the larger content of rutile with the increase of the Ar gas flow. *Figure 4.7b* presents the corresponding anatase/rutile ratio and crystal size parameter as function of the gas flow and shows that both, crystal size and phase transformation are facilitated. Overall, this confirms that the effect of the inert atmosphere is the facilitation of the rutile nucleation through a non-complete oxidation of the TiO₂ fibres.

Figure 4.7: a) XRD patterns of TiO₂ fibres obtained at 500°C and b) effect of the Ar flow in the phase composition and crystal size.

In summary, the Ar atmosphere has influence on the crystal structure by means of limiting the oxygen content during crystallisation. A rearrangement of the structure favour the transformation of anatase into rutile phase while limits particle coarsening. The crystallisation of the electrospun fibres are fixed to 500°C for 1h and without use of continuous gas flow, rate of 0 L/h. These parameters lead to the formation of a highly crystalline material with a certain amount of rutile and small particle size (~11.5 nm).

4.2.2 Morphology of electrospun TiO₂ fibres and comparison with nanoparticles

The synthesis of TiO₂ through annealing of electrospun fibres constitutes an approach that is substantially different from TiO₂ nanoparticles. TiO₂ nanoparticles produced and annealed under the same conditions as the inorganic fibres but without the

polymer, result in aggregates of nanoparticles (*Figure 4.8a*). For electrospun samples, the removal of the polymer results in the formation of inorganic porous fibres with reduction in diameter around 150-500nm, although with some reaching ~800nm. The inset of the *Figure 4.8b* shows a high magnification electron image of a fibre where its complex structure is observed. The fibre consists of TiO₂ nanocrystals interconnected and forming a 1-dimensional structure. Importantly, the fibres present a rough surface and a large porosity that facilitates, for example, the adsorption of reactants species for a photocatalytic reaction.

Figure 4.8: Scanning electron micrographs of a) TiO₂ nanoparticles produced by standard sol-gel and b) TiO₂ fibres produced by sol-gel and electrospinning. Inset shows a high resolution image of an individual electrospun fibre.

Figure 4.9a-c display TEM images of TiO₂ fibres obtained by combination of sol-gel process and electrospinning technique. Effectively, the fibre structure is formed by a network of TiO₂ nanocrystals that have grown along the fibre and forms a mesoporous structure (*Figure 4.9a*). Whether in hybrids or pure inorganic, the crystal size ranges between 4-28nm (*Figure 4.9b*). The crystals are interconnected along the mesoporous fibre structure and give rise to a large interface between them similar to grain boundaries (*Figure 4.9c*). In contrast, TEM image of individual nanoparticles (*Figure 4.9d*) shows randomly distributed agglomerations of nanoparticles. The particle size is in the range 5-20nm and is therefore comparable to the crystal sizes in electrospun samples.

Figure 4.10 presents electron diffraction patterns of the TiO₂ fibres (*Figure 4.10a*) and TiO₂ nanoparticles (*Figure 4.10b*). Both display diffraction rings, which reveal their polycrystalline nature. Diffraction from anatase crystals is observed for both

4.2 Crystallisation into mesoporous fibre structure

samples. In addition, diffraction spots associated to rutile phase, even when the annealed treatment was identical, are observed in TiO_2 fibres, but not in the particles.

Figure 4.9: Transmission electron micrographs of a-c) TiO_2 fibres at different magnifications with anatase planes highlighted in c) and d) TiO_2 nanoparticles.

Figure 4.10: Electron diffraction pattern of a) TiO_2 fibres and b) TiO_2 nanoparticles. Characteristic diffraction of anatase and rutile are highlighted in the images.

Further analysis of the fibre structure in comparison with the nanoparticles was performed by XRD after each annealing step. *Figure 4.11a* shows the XRD patterns

after polymer removal in air (400°C for 2.5h). The electrospun TiO₂ fibres already present the typical diffraction peaks of the anatase phase such as a well-defined (101) anatase plane and other less intense diffraction peaks. However, the TiO₂ nanoparticles still present an amorphous pattern. The implication is that the increased density of the gel network in the fibre accelerates the crystallisation process in the fibre with respect to dispersed nanoparticles.

Similarly, *Figure 4.11b* shows the XRD patterns of both samples after the crystallisation process at 500°C (1h in Ar). At this temperature, both materials are highly crystalline and consist mainly of anatase. However, the electrospun TiO₂ fibre presents also rutile diffraction peaks, in agreement with electron diffraction observations. These results show that the fibre morphology accelerates crystallisation due to the large interfaces between anatase nanoparticles, which decrease the activation energy for the rutile nucleation at the interfaces. The kinetics of phase transformation of 6nm diameter anatase particles haven been studied in details by Zhang and Banfield.[Zhang and Banfield 2000] Their work shows that phase transformation in nanostructured systems are dominated by the amount of anatase-anatase interface and thus by the “number of particles”. In the case of the TiO₂ fibres in this work, annealing in Ar further enhances this effect by providing sites for the transformations in the form of oxygen vacancies.

Figure 4.11: XRD patterns of TiO₂ nanoparticles (black curve) and TiO₂ fibres (red curve) obtained under the same annealing conditions: (a) 400°C for 2.5h in air and (b) 500°C for 1h in Ar.

4.2 Crystallisation into mesoporous fibre structure

The vibrational structure of the TiO₂ fibres was further studied by Raman spectroscopy in comparison with reference TiO₂ nanoparticles. In contrast to XRD where the x-rays interact with the atomic planes of the crystal lattice, Raman spectroscopy provides information about the vibrational modes of the material arising from their interaction with light (photons) via inelastic scattering. Furthermore, the interaction depends on the light wavelength and their electronic structure. In this study, a laser of 532nm was used due to it is in the gap energy of the inorganic, avoiding Raman resonance signals of the inorganic.

Figure 4.12a illustrates a representative spectra for electrospun TiO₂ fibres and TiO₂ nanoparticles. For both, the Raman spectra correspond to vibration modes of the anatase crystal structure at 144 (E_g), 196 (E_g), 396 (A_{1g}), 515 (A_{1g}) superimposed on 519 (B_{1g}) and 639 (E_g) cm⁻¹ in the bulk.[Antony et al. 2015] For electrospun fibres, shoulders at the high energy side of the band at 396cm⁻¹ and the low energy side of the band at 639cm⁻¹ evidences the presence of rutile phase, previously observed by XRD. Whereas the intensity of the diffraction peaks is proportional to volume fraction of crystal phases, Raman is not and their modes are slightly evidenced.

Figure 4.12: a) Normalised Raman spectra highlighting the vibrational modes of anatase phase and b) zoom of the E_g mode at ~144cm⁻¹, including a representation of the vibration.

Figure 4.12b shows the most intense band, the E_g mode at ~144cm⁻¹, which is assigned to the O-Ti-O (181° bond angle) bending vibrations.[Frank et al. 2012] The inset of the Figure 4.12b represents a [TiO₆] octahedron with arrows indicating the vibration of the E_g mode. Interestingly, a displacement of 2.2cm⁻¹ in the E_g band position

to higher wavenumber is observed for the electrospun fibres in comparison with TiO₂ nanoparticles. Also, the band width increases for the fibres. A phonon confinement effect in small particles is often the origin of the broadening and the displacement of the E_g vibrational mode.[Zhu et al. 2005a] However, both samples present similar average crystal size (~12nm) and thus, this effect is discarded. Furthermore, it is not clear that such confinement would be present in nanocrystals joined as a mesoporous structure rather than individualised. Instead, defects such as oxygen vacancies can also produce disorders in the crystal structure of the metal oxide.[Eder et al. 2010] The vibrational structure of the TiO₂ fibre and especially, the E_g mode sensitive to O bonds, can be shifted as consequence of the oxygen vacancies. For instance, Liu et al. have shown a Raman shift of 4cm⁻¹ associated to oxygen defects in TiO₂. [Liu et al. 2009]

4.2.3 Texture properties of electrospun fibres

The texture properties of samples with fibre and nanoparticle morphology was analysed by N₂ adsorption-desorption isotherms. The BET surface area and BJH pore size distribution were determined from this measurement. *Figure 4.13a* shows that the isotherms are type IV according the IUPAC classification for adsorption isotherms.[Sing K. S. W. 2009] At low relative pressures, the adsorption occurs in a monolayer that enables determination by BET method of the surface area of the samples. Interestingly, the BET surface area of the electrospun TiO₂ fibre is 41.4m²/g, about 50% lower than our control sample of TiO₂ nanoparticles, which presents 95.5m²/g of surface area.

Increasing the relative pressure, the adsorption occurs by stacking of a finite number of layers and a typical hysteresis loop appears between the adsorption and desorption curves. This indicates capillarity condensation in meso and macropores (below and above 50nm pore size, respectively) because of the difference in vapour pressure between the adsorbed and the released gas. Hysteresis loop at relative pressure (P/P₀) greater than 0.4 are observed in *Figure 4.13a*, which corresponds to pores in the mesoscale for both samples, fibres and nanoparticles. Yet, clear differences in the shape of the hysteresis loops are observed due to the different type and size of the

4.2 Crystallisation into mesoporous fibre structure

pores. Applying the Barrett-Joyner-Halenda method, their pore size distributions were determined and represented in *Figure 4.13b*. A narrow pore size distribution (2-10nm) is observed in the TiO₂ nanoparticles whereas the TiO₂ fibres present a wide pore size distribution ranged between 2 and 60nm.

The lower surface area of the nanofibres compared with nanoparticles, in spite of a similar crystal size, is due to the very large interface formed between the TiO₂ nanoparticles in the fibre, as observed by SEM and TEM. During synthesis, the immiscibility of the polymer solution with the inorganic precursor solution produces an agglomeration of the Ti units dispersed in the polymer matrix. During the heat treatment, the densification and sintering of the inorganic evolves into a network of interconnected TiO₂ nanoparticles that share atomic planes at their interface. Thus, the large interfacial area reduces significantly the porosity of the fibre structure, roughly by half in comparison with randomly agglomerated nanoparticles. However, the fibres present larger pore sizes as a result of the presence of the polymer after electrospinning. During its removal, the polymer leaves large pores within the fibre.

Figure 4.13: a) N₂ adsorption-desorption isotherms and b) Cumulative pore volume (dash line) and pore size distribution (scatter+line) of TiO₂ nanoparticles and fibres, obtained from the adsorption branch.

In summary, the combination of sol-gel and electrospinning technique produces not only a different morphology, also significant differences in the crystal structure and porosity of the metal oxide. This method was originally developed for TiO₂ but

later adopted to produce other metal oxides, e.g. Nb₂O₅ and Ta₂O₅, whose results are presented in the *Appendix A*.

4.3 New TiO₂/nanocarbon hybrid fibres

The *in-situ* hybridisation of TiO₂ with small amount of nanocarbons using the combination of sol-gel and electrospinning, allows to create a new hybrid material with superior properties and substantially different than their individualised component. In contrast to *composite* materials, a *hybrid* material requires a strong interaction between both components. The morphology, texture and structural characterisation of the hybrid material are shown in this section in comparison with bare TiO₂ fibres previously characterised in *Section 4.2*.

4.3.1 Morphology of TiO₂/nanocarbon hybrid

The addition of nanocarbons to form hybrid fibres has not major influence on the general morphology of the TiO₂/nanocarbon hybrid. Using the same synthesis conditions than that used for the TiO₂ fibres except the loading of nanocarbon dispersion, the hybrid material consists in fibres with similar diameter than bare TiO₂ fibres sample (*Figure 4.14a*). The observation of nanocarbons was a challenge since the fibres are too thick for transmission electron microscopy and the nanocarbon are fully covered by TiO₂ nanoparticles. Yet, location of nanocarbons protruding from the fibres was only possible in TiO₂/ox-MWCNTs hybrid fibres with high content of ox-MWCNTs (10-40vol.%). These samples were purposely synthesised to study the structure of the hybrid upon addition of CNTs. *Figure 4.14b* shows the intimate contact between the TiO₂ nanoparticles and the CNTs. Furthermore, high resolution TEM (HRTEM) observation confirms that the ox-MWCNTs were not degraded during the annealing treatment. Thus, a successful hybridisation has been achieved through the *in-situ* synthesis from molecular precursors on the CNT surface.

Figure 4.14: a) SEM and b) HRTEM images of TiO₂/ox-MWCNTs fibres showing the successful hybridisation of the *in-situ* approach.

4.3.2 Structure of TiO₂/nanocarbon hybrid

The effect of the nanocarbons in the crystallisation of the inorganic was studied by XRD. *Figure 4.15* shows a representative XRD pattern of a hybrid with 1vol.% of ox-MWCNTs, as well as the theoretical position and relative intensity obtained from the corresponding JCPDS cards. The pattern is indexed as a mixture of anatase and rutile phases. However, the diffraction peaks of the nanocarbons are not observed. The most intense peak of graphite structure, corresponding to the interlayer (002) atomic plane at $2\theta = 26.56^\circ$, is expected to be masked by the broad peak of (101) anatase plane at $2\theta = 25.28^\circ$. The broadening of TiO₂ peaks because of their nanosize, combined with the low content of the nanocarbons difficult the detection of nanocarbons and analysis of their crystallinity by powder XRD.

Table 4.3 presents the anatase to rutile ratio and the average crystal size for pure TiO₂ fibres and the different types of TiO₂/nanocarbon hybrids. Although a similar phase composition is observed in all hybrids, the use of functionalised nanocarbons increases the rutile content in comparison with those hybrids with pristine nanocarbons. Presumably, better interfaces can be formed through the chemical compatibility between the nanocarbon functional groups and the inorganic precursor. These interfaces can thus facilitate the nucleation and phase transformation.

Figure 4.15: XRD patterns of 1vol.% TiO₂/ox-MWCNTs hybrid showing a mixture of anatase and rutile phases. Referenced patterns of both phases are included below.

Table 4.3 also contains values of the anatase and rutile crystal sizes calculated from their (101) and (110) diffraction peaks and using the Scherrer equation. Crystallites between 10-15nm were calculated for the anatase phase and between 9-17nm for rutile phase. The crystal size of hybrids with pristine nanocarbons is very similar to that of pure TiO₂, however, the functionalised nanocarbons show small variations. A decrease of the crystal size would increase the surface area of the material, which could benefit for example the photocatalytic activity.

Table 4.3: Anatase/rutile ratio and crystal size of TiO₂ and hybrid fibres.

Samples	Anatase/rutile ratio	Anatase crystal size (nm)	Rutile crystal size (nm)
TiO ₂	0.82	12.38	13.34
TiO ₂ /p-MWCNTs	0.85	12.47	12.43
TiO ₂ /ox-MWCNTs	0.8	9.73	9.18
TiO ₂ /p-GR	0.83	12.44	13.89
TiO ₂ /isoft-GR	0.73	14.65	17.04

4.3.3 Texture properties of TiO₂/nanocarbon hybrid

The textural properties of the four types of hybrids were analysed from their N₂ adsorption-desorption isotherms. A representative isotherm of a TiO₂/ox-MWCNTs hybrid sample is shown in *Figure 4.16a*. Similar to pure TiO₂ fibres, the hybrids present type IV of isotherm and hysteresis loop characteristic of the mesoporous material. Their relatively wide pore size distribution, *Figure 4.16b*, indicates that the hybrids contain pores in the whole range of the mesoporosity with similar cumulative pore volume than the TiO₂ fibres.

The cumulative pore volume and the average pore size obtained from the BJH method of the four types of hybrids are reported in *Table 4.4* together with pure TiO₂ fibre for comparison. The hybrid samples do not present important differences in the total pore volume with respect to the pure TiO₂ fibre. However, their pore size distribution is slightly narrower than that of TiO₂ fibres.

Figure 4.16: a) N₂ adsorption-desorption isotherms and b) Cumulative pore volume (dash line) and pore size distribution (scatter+line) of TiO₂/ox-MWCNTs hybrid fibres.

Furthermore, the *Table 4.4* presents the BET surface area values. In contrast to simple composites where the nanocarbons would increase the total surface area; the *in-situ* hybridisation produces a hybrid material with surface areas similar to pure TiO₂ fibres. This is due to the most of the nanocarbons are fully covered by TiO₂ nanopar-

ticles, exposing thus similar surface areas than pure inorganic. Nevertheless, the hybrids present huge interfaces between TiO₂ and nanocarbon with an interfacial area that approximately corresponds to the surface area of the nanocarbons.

Table 4.4: Textural properties of the synthesised materials

Samples	BET surface area (m ² /g)	Cumulative Pore volume (cm ³ /g)	Pore diameter (cm ³ /g)
TiO ₂	41.4	0.095	9.6
TiO ₂ /p-MWCNTs	40.7	0.074	5.3
TiO ₂ /ox-MWCNTs	48.4	0.092	6.1
TiO ₂ /p-GR	32.1	0.096	9.8
TiO ₂ /isoft-GR	24.9	0.051	4.3

Although the overall mesoporosity of the hybrid is similar to the pure inorganic, higher available surface area is obtained using MWCNTs compared with graphene. A direct relation of the crystal size, either anatase or rutile, with the BET surface area can be observed in *Figure 4.17*. The lower crystal size of the samples results in a higher surface area.

Figure 4.17: Relation between crystal size and surface area of pure TiO₂ and TiO₂/nanocarbon hybrids.

4.4 Evidence of hybridisation in TiO₂/nanocarbon hybrid

The structure of the TiO₂/nanocarbon samples was investigated and reveals significant changes as a result of the hybridisation process. In particular, the chemistry of the functional groups of the nanocarbons appeared crucial to form a real hybrid material with emerging properties. The close proximity of the components suggests a strong interaction between both materials. The interaction at the interface can be probed by Raman and FT-IR spectroscopy and, the electronic structure of the hybrid, e.g. Fermi energy level (E_F) and valence band electrons, by photoelectron spectroscopy. Finally, optical absorption and emission studies can provide additional features of the hybrid materials such as band gap energy (E_{gap}) and presence of inter band gap states.

4.4.1 Interfacial study of TiO₂/nanocarbon hybrid

The vibrational modes of the hybrid material were studied by Raman spectroscopy and compared with that of pure inorganic fibres as well as reference nanoparticles. Because of the different structure of the inorganic/organic hybrids, vibrations of both components appear at different frequency range, facilitating thus the complete characterisation of the hybrid material. A representative spectrum of 1vol.% TiO₂/ox-MWCNTs is presented in *Figure 4.18*. Bands at low wavenumber correspond to anatase TiO₂ in addition to a small amount of rutile. At higher wavenumber, Raman features of the sp³ (referred as D band at about 1350cm⁻¹) and sp² (referred as G band at about 1580cm⁻¹) nanocarbon structure are observed.

Figure 4.18: a) Raman spectra of electrospun TiO₂/ox-MWCNTs hybrid with the vibrational modes of anatase phase and nanocarbon highlighted.

Figure 4.19a shows the sharp intense peak, the E_g mode at $\sim 144\text{cm}^{-1}$ for the TiO₂/ox-MWCNTs hybrid, TiO₂ fibres and TiO₂ nanoparticles samples for comparison. The blue shift of 2.2cm^{-1} is observed for the TiO₂ fibres and increases up to 6.8 cm^{-1} for the hybrid fibres in comparison with the nanoparticles. As discussed before, this shift is partly due to the presence of oxygen vacancies as a result of annealing in Ar. But the additional upshift in the hybrid is attributed to a strong coupling with the C atoms of the nanocarbons, possibly through a Ti-O-C bond, which leads to an enhancement of the interfacial interactions. In order to evaluate changes in the graphitic structure of the nanocarbons, Figure 4.19b shows the Raman spectra for the D and G peaks in the TiO₂/ox-MWCNTs in comparison with the raw ox-MWCNTs material. The intensity ratio between the D and G peak is quite similar, indicating that the overall graphitic structure has not dramatically changed due to the hybridisation process. Quantification of the peak parameters are not reliable in the hybrid spectrum due to their low and wide bands. But in summary, the interfacial interactions created during the densification and crystallisation of inorganic have resulted in noticeable shifts in the Ti-O vibration.[Lee et al. 2012a]

Figure 4.19: a) Normalised anatase E_g mode at $\sim 144\text{cm}^{-1}$ and b) D and G characteristic Raman features of nanocarbons before and after hybridisation.

High resolution TEM images in Figure 4.20 confirm the close interfaces between TiO₂ nanoparticles and CNTs and reveal the ability to disorder the structure of both, inorganic and nanocarbon materials. Analysis of the crystallinity at the interface between CNTs and TiO₂ suggests a preferential growth of the TiO₂ nanoparticles. In Figure 4.20 is also included the Fast Fourier Transform (FFT) of a selected area of the

4.4 Evidence of hybridisation in TiO₂/nanocarbon hybrid

micrograph, the latter highlighted with a white square. Then, applying a mask on certain spotlight (highlighted in the FFT images) and doing the inverse FFT operation, one can obtain a clearer image of the atomic planes at the TiO₂/CNT interface. Interestingly, the interface most commonly found and showed in *Figure 4.20* is that formed between the (101) anatase atomic planes and the (002) atomic plane of the CNT, both corresponding to atomic distance of about 0.35nm.

Figure 4.20: a-b) HR-TEM images of TiO₂/ox-MWCNTs hybrid showing the large interfaces formed between (101) atomic plane of anatase nanocrystals and the (002) atomic plane of MWCNTs, highlighted in the direct and inverse FFT image.

In this sense, FT-IR spectroscopy has been a useful tool to analyse the vibrations of functional groups of the nanocarbons and thus, determine the chemical structure of the hybrid material. *Figure 4.21* presents the FT-IR spectra of ox-MWCNTs, TiO₂ fibres and a hybrid with high amount of functionalised CNTs (40vol.%) to increase the signal intensity from interfacial FT-IR modes.

Signals at the region 1630-1400cm⁻¹ in the hybrid material confirm the presence of CNTs and indicate that the polymer removal process does not produce extensive damage to the CNTs. Additionally, the hybridisation process lead to a loss of the functional groups of the nanocarbons, as confirmed by the absence of the C=O signal at 1730cm⁻¹, and also the notable reduction in the asymmetric and symmetric C-H stretching modes at 2930 and 2860cm⁻¹, respectively. These effects on the functional groups of the MWCNTs are typical of an annealing in inert atmosphere.

Figure 4.21: FT-IR spectra of a hybrid with oxidised MWCNTs and reference samples of the ox-MWCNTs and TiO₂ fibres.

More importantly, the hybrid presents signals at 1160, 1090 and 1030cm⁻¹, which are assigned to rocking and stretching modes of Ti-O-C.[Urlaub et al. 2000; Finnie et al. 2000] CNTs also present weak signals arising from C-O vibrations in this region; however, in the hybrid IR spectrum, we can rule out such peak assignment to the CNT themselves, in light of the expected intensity relative to the CNT fingerprint and of the absence of the C=O signal in the IR hybrid spectra. Ti-O-C bond from Ti precursor is also discarded, as it is not observed in the pure TiO₂ fibre and would not survive the annealing process. Therefore, the FT-IR data point to the formation of a covalent Ti-O-C bond at the TiO₂/ox-MWCNT interface. Such covalent bond, formed during the *in-situ* growth process, could enhance the spatial charge separation.

4.4 Evidence of hybridisation in TiO₂/nanocarbon hybrid

In summary, both materials, TiO₂ and nanocarbons, are in close contact to interact and produce changes (defects) in their structure. More importantly, the large interface formed between TiO₂ nanocrystals and nanocarbon results in a strong coupling that is expected to favour electron transfer, particularly in the case of use functionalised nanocarbons. Their functional groups can easily react with the inorganic precursors and form covalent Ti-O-C bonds. The existence of this covalent bond can further explain the large displacements obtained in the Raman bands.

4.4.2 Electronic structure of TiO₂/nanocarbon hybrid

The electronic structure and the chemical composition of the hybrid materials have been studied by X-Ray Photoelectron Spectroscopy. The high sensitivity of this technique enables identification of chemical elements and their environment, determining thus their coordination and oxidation state. Moreover, combining XPS and UPS spectroscopies, information about the electronic structure of the hybrid material can be accurately determined. However, these are surface techniques, which probe ~10nm (XPS) and ~2-5nm (UPS) of the materials. XPS spectra were calibrated taking the C1s peak as referenced energy (284.5eV) to avoid charge accumulation effect in the semiconductor during the measurement. The XPS spectra are represented as decreasing binding energy because these states are localised below the Fermi level (E_F corresponds to BE of 0eV). XPS spectra of TiO₂ fibres and TiO₂/ox-MWCNTs hybrid were analysed in separate energy region according to the observed elements (Ti, O, C), as well as the valence band region.

Figure 4.22: a) XPS spectra of Ti2p state and deconvolution of b) TiO₂ and c) TiO₂/ox-MWCNTs spectra using mixed Gaussian/Lorentzian curves.

The region of Ti2p in *Figure 4.22a* shows the characteristic band of Ti⁴⁺ in TiO₂ states for the TiO₂ fibres and TiO₂/ox-MWCNTs samples. *Figure 4.22b* y *Figure 4.22c* present the fitting of each spectra. A splitting states of 5.7eV between the Ti(2p_{3/2}) at 458.3eV and Ti(2p_{1/2}) at 464.2eV is observed due to the spin-orbit interaction. The FWHM of the Ti2p_{3/2} states for both fitting is 1.3eV, in agreement with NIST XPS database for Ti⁴⁺ states. The strong interaction of the Ti(IV) with the C atoms in the hybrid produces a slight displacement in the Ti2p states of 0.15eV which can indicate that a usual number of Ti-O-Ti bonds have been replaced with Ti-O-C bond. Reduced Ti³⁺ species are often observed at surface states of oxygen vacancies (expected at 457.2eV). However, the absence of Ti³⁺ band in *Figure 4.22* confirms that nor TiO₂ nor hybrid have not been reduced as a consequence of the oxygen vacancies formed during the synthetic process.

Figure 4.23a corresponds to the O1s spectra of the TiO₂ and TiO₂/ox-MWCNTs samples and *Figure 4.23b-c* show their fitting to the O1s states. The main peak centred at 529.5eV corresponds to the Ti-O bond in TiO₂ structure. Additionally, contributions from hydroxyl groups at the surface at 531.3eV and adsorbed water at the TiO₂ surface at ~532.1eV, respectively are also observed. For the hybrid material, an increase of the signal at 531.3eV is observed, meaning a higher contribution of Ti-O-H and/or Ti-O-C bonds, in agreement with literature.[Xing et al. 2014]

Figure 4.23: a) XPS spectra of O1s state and deconvolution of b) TiO₂ and c) TiO₂/ox-MWCNTs spectra using mixed Gaussian/ Lorentzian curves.

The content of carbon and their interaction with TiO₂ were evaluated by XPS spectra of C1s region for raw ox-MWCNTs and TiO₂/ox-MWCNTs (*Figure 4.24a*). For both samples, a main peak was observed at 284.5eV, and correspond to sp² states. The fitted spectra of the ox-MWCNTs in *Figure 4.24b* shows a sharp peak from the sp² carbon

4.4 Evidence of hybridisation in TiO₂/nanocarbon hybrid

states and a certain contribution of sp³ carbon species. The fit peaks at 286.7 and 288.3eV come from C-O and -O-C=O species associated to the functional groups at the nanocarbon surface. π - π^* interactions are also observed at 290.3eV. In contrast to ox-MWCNTs sample, the hybrid sample presents stronger contributions from sp³ carbon peak (*Figure 4.24c*) various C-O species and loose of the π - π^* interactions, which is taken as further evidence of the formation of Ti-O-C bonds.[Xing et al. 2014] Yet, the carbon peak of the XPS spectra is ambiguous because the TiO₂ surface can easily have adsorbed carbon species at their surface that will therefore increase the contribution of sp³ carbon.

Figure 4.24: a) XPS spectra of C1s state and deconvolution of b) Ox-MWCNTs and c) TiO₂/ox-MWCNTs spectra using mixed Gaussian/ Lorentzian curves.

In addition, the XPS spectra at the very low energy region gives information of the valence band electrons. The spectra of the pure inorganic and hybrid samples (*Figure 4.25a*) show a wide band, in the region 3-10eV, which is mainly composed of O2p states. Two peaks at 5.8 and 7.8eV are observed and they are associated to O2p- π and O2p- σ bonding states, respectively.[Sanjinés et al. 1994] The low energy region in *Figure 4.25b* shows the valence band maxima (VBM) position with respect to Fermi energy level. The onset of the valence band presents a small displacement of 0.14eV for the hybrid with respect to the pure TiO₂. Interestingly, additional electronic states between 0.42-2.92eV are observed in the hybrid XPS spectra. They may arise from interfacial states associated with the Ti-O-C bonds. These extra charges in the hybrid are delocalised instead of confined at Ti³⁺ states, usually observed as a small peak at ~1eV for non-stoichiometric metal oxides.[Connelly and Idriss 2012]

Figure 4.25: a) XPS spectra of valence band region of TiO₂ and TiO₂/ox-MWCNTs samples and b) zoom of the onset in the low energy region.

A summary of the evidences gained from the XPS spectra are presented in *Table 4.5*. The multiple evidences of Ti-O-C bonds have been exploited for the hybrid with functionalised MWCNTs of this work. Clearly, the *in-situ* hybridisation with functional groups successfully connects the two components by Ti-O-C bonds rather than Ti-C bonds. The strong interaction between both components is observed in the shift of their modes, and also in the intensity of the X-O-Ti species as well as sp³ hybridisation of the carbon atoms.

Table 4.5: Summary of Ti-O-C evidences obtained from XPS data.

XPS region	Evidence
Ti 2p	Hybrid presents a shift of 0.15eV to lower binding energy.
O 1s	Hybrid presents an increase of the intensity for the peak at 531.3eV, which implies a higher contribution of Ti-O-X bonds and importantly, also related to the Ti-O-C bond.
C 1s	Hybrid presents a significant contribution of sp ² and sp ³ carbon. The increase of the sp ³ peak and C-O species compared with functional CNTs suggests that hybridisation occurs through Ti-O-C interactions at the interface.
VB	Hybrid presents a valence band shift of 0.14eV to lower binding energies. Importantly, density of states below the VBM are presented, which evidences that nanocarbons provides interfacial states through Ti-O-C bonds.

4.4 Evidence of hybridisation in TiO₂/nanocarbon hybrid

Ultraviolet Photoelectron Spectroscopy with UV radiation was employed to probe surface energy states with a source of lower energy and thus, higher resolution near the valence band. To generate UV light, He atoms are ionized with the electric field generating He I line of 21.2eV. The kinetic energy range of analysis and the spectral line are significantly reduced with respect to XPS. Thus, UPS gives accurate information about the valence band surface states (electrons with low binding energies). From the onset of UPS spectra, the VBM position can be accurately obtained, which is crucial to determine the possible interfacial states in the hybrid material. Another important feature obtained from UPS spectra is the secondary electrons cut-off energy, which provides absolute values of the material work function.[Gutmann et al. 2010]

UPS measurements under identical conditions were carried out on different hybrids, pure TiO₂ fibres and raw ox-MWCNTs. The full UPS spectra of different electro-spun materials, pure inorganic and hybrids are illustrated in *Figure 4.26a*. The UPS spectrum of the ox-MWCNTs is shown in *Figure 4.26b*. Whereas the nanocarbons present density of states in the whole range below their Fermi level; the TiO₂ and TiO₂/nanocarbon hybrids presents an energy gap without electronic states, closely related to the bulk bandgap energy. The density of states of the TiO₂/ox-MWCNTs and TiO₂/isof-GR hybrid materials are higher than those of TiO₂ or TiO₂/p-MWCNTs hybrid, which suggests the success in the hybridisation process obtained with nanocarbon functionalisation strategy. Importantly, there is a shift in the edge of the VBM to lower binding energies when the TiO₂ is hybridised with functional nanocarbons.

Figure 4.26: Full UPS spectra of a) TiO₂ and TiO₂/nanocarbon hybrids samples and b) Ox-MWCNTs samples.

Figure 4.27 presents the secondary electron edge at high binding energy. It enables the determination of the work function (Φ) by subtracting the spectrum width (energy difference between the Fermi level and the high binding energy cut-off) from the photon energy. The work function value for TiO₂ fibres results in 4.32eV in good agreement with literature values for anatase nanostructure.[Farsinezhad et al. 2015a] A slightly higher work function (4.37eV) is obtained for the three TiO₂/nanocarbon hybrid studied, which represent a minor variation with respect to TiO₂. The Figure 4.27b shows the secondary edge of the raw oxidised nanocarbons. They have work function of 4.72eV, consistent with literature values for CNTs ranging from 4.3 to 5.6 eV.[Ago et al. 1999:103; Gao et al. 2001]

Figure 4.27: UPS spectra of a) TiO₂ and TiO₂/nanocarbon hybrids and b) Ox-MWCNTs represented at the high binding energy, where secondary electron cut-off energy provides the work function values of each material.

From the low binding energy region (Figure 4.28), the VBM positions are derived as the intercepts between the tangents of the spectra and the baseline. TiO₂ fibres present the valence band at 3.14eV below the Fermi level, confirming XPS observations and corresponding to the bandgap energy of bulk TiO₂. The ionization energy is 7.46eV, in agreement with reported values.[Chi et al. 2011:98] The determination of the VBM for the hybrid material results better defined using the UPS measurements than the VB-XPS spectra of Figure 4.25.

Noticeable differences are observed in the edge of the valence band states of the hybrid materials. For the hybrids using oxidised MWCNTs, TiO₂/ox-MWCNTs sample, a continuous distribution of valence band states are measured up to ~1.72eV with

4.4 Evidence of hybridisation in TiO₂/nanocarbon hybrid

respect to Fermi level. A similar effect is observed for the hybrid using functionalised graphene, TiO₂/isof-GR, with valence band states ~ 1.8 eV. This suggests the presence of states within the band gap of the TiO₂. These states are presumably formed at the TiO₂/nanocarbon interfaces and will give rise to hole transport as dominant mode of charge transfer across the interface.[Kumar et al. 2014] In contrast, the hybrid with pristine MWCNTs, presents the onset of the valence band at 4.28 eV with respect to Fermi level, which indicates that the electron density is significantly reduced. The results, therefore, suggest electron transfer as dominant effect at the interface between TiO₂ and pristine CNTs.

Figure 4.28: Valence band states observed at low binding energy in the UPS spectra for TiO₂ and TiO₂/nanocarbon hybrids.

4.4.3 Optical properties of TiO₂/nanocarbon hybrid

The absorption properties of the samples were analysed by Diffuse Reflectance Spectroscopy. The determination of the absorption properties by reflection mode avoids contributions from internal reflection/absorption arising from the mesoporosity of the material. As a photocatalyst material, the band gap energy is an important parameter to evaluate the use of the sunlight spectrum. The absorption spectra in the Ultraviolet-Visible range (250-800 nm) is shown in *Figure 4.29*.

An intense absorption band is observed below 400 nm in *Figure 4.29* and corresponds to the excitation of electrons from the valence to the conduction band of the

semiconductor. That is, the absorption of UV photons produces charge transfer process between molecular orbitals: $O^{2-} \rightarrow Ti^{4+}$. The absorption edge of electrospun samples presents a change in the slope due to the contribution of optical transitions in anatase and rutile phases. Using the Tauc method (Equation 3.11) and assuming all the samples to be composed entirely of anatase, the indirect bandgap energy have been calculated.[Viezbicke et al. 2015]

Figure 4.29: UV-Visible diffuse reflectance spectroscopy of TiO₂ and TiO₂/nanocarbon hybrid fibres.

Table 4.6 represents the band gap energy of the different TiO₂/nanocarbons hybrids as well as pure TiO₂ fibres. Band gap energy values for all the samples are in the range of 3.11-3.28eV (398.7 and 378nm, respectively). Minor variations are within experimental error. Also, the assumption of pure anatase phase produces an uncertainty in the bandgap calculation. The addition of nanocarbons does not change dramatically the band gap energy due to it is a feature of the bulk material. Instead, the interfacial states previously observed in UPS spectra are manifested as an increase of absorption in the visible range, especially important for those hybrids with functionalised nanocarbons.

Table 4.6: Band gap energy of TiO₂ fibres and TiO₂/nanocarbon hybrids fibres.

Raman modes	E _{gap} (eV)
TiO ₂ fibres	3.16
TiO ₂ / p-MWCNTs	3.11
TiO ₂ /ox-MWCNTs	3.15
TiO ₂ /p-GR	3.13
TiO ₂ /isoft-GR	3.28

In order to study the recombination process of the photogenerated electron-hole pairs, photoluminescence spectroscopy has been used. An excitation energy of 3.5eV, higher than the bandgap of the samples, was employed with a 370nm cut-off filter to avoid PL signal from the band-to-band recombination process. PL spectra of the TiO₂ fibres and TiO₂/ox-MWCNTs hybrid fibre in *Figure 4.30a* shows a wide emission band in the 400-600nm wavelength range and corresponds to multiple contribution of emission phenomena.

The *Figure 4.30b* illustrates the fitting of the wide PL emission band. At about 2.97eV (417nm), the emission corresponds to radiative transitions of self-trapped excitons localised in TiO₆ octahedra.[Kernazhitsky et al. 2014; Lei et al. 2001] Peaks in the energy range of 2.8-2.4eV (440-500nm) are associated to the recombination of trapped electrons from intra-band gap states with holes from the valence band.[Choudhury et al. 2014; Liqiang et al. 2006] The shallow intra-band gap states are related to the presence of oxygen vacancies that create defect levels 0.3-0.7eV below the conduction band. The presence of these vacancies is consistent with Raman analysis.

At higher wavelength, the TiO₂/ox-MWCNTs hybrid sample presents an extra band centred at 2.1eV. Very importantly, this feature is not observed in the TiO₂ spectra. This contribution is originated from the recombination of electrons from conduction band with trapped holes above the valence band.[Mercado et al. 2012] Most likely this emission peak is associated with uncoordinated Ti⁴⁺ that adsorb molecules (i.e. hydroxyl groups) at the surface. Considering that this peak is more pronounced in the hybrids, the hybridisation can be linked to the formation of new intra-band gap states.

Some of the Ti-O-Ti bonds are substituted to Ti-O-C atoms, providing new interfacial states that can trap holes at about 1.1 eV above the valence band, in agreement with the photoelectron studies.

Figure 4.30: a) Photoluminescence spectra of TiO₂ fibres and TiO₂/ox-MWCNTs hybrid. b) Fitting of PL spectra of both samples.

Finally, the PL intensity of the hybrid material is ~4 times lower than the fibres, suggesting that CNTs facilitate the charge separation across the interface between both components, delaying thus the electron-hole recombination.

4.5 Summary

The *in-situ* hybridisation approach using sol-gel method and electrospinning technique results in one-dimensional homogeneous fibres of few microns length and few hundred nanometers of diameter. The subsequent annealing process involves 1) the removal of the polymer in air, 2) the densification, sintering and crystallisation of the inorganic and 3) prevents the degradation of the nanocarbons. The result is a complex architecture of mesoporous fibres that consists in interconnected TiO₂ nanocrystals, quite different from the material produced by standard sol-gel reaction.

The main structural features of the electrospun hybrid fibres are schematically illustrated in *Figure 4.31* and arises mainly from the following steps of the synthetic process: (a) the addition of a large content of a suitable polymer that agglutinates the inorganic domains and the nanocarbons; (b) the removal of the polymer, by a slow

4.5 Summary

annealing the fibres in air, which generates a continuous porous network of interconnected TiO₂ nanoparticles.

In addition, the interfaces produced between the nanocrystals play a role reducing the activation energy of the nucleation and phase transformation processes. Moreover, the crystallisation is also favoured by the inert atmosphere, which limits the complete oxidation of the inorganic, resulting thus in a non-stoichiometric metal oxides. Raman spectroscopy and photoluminescence have revealed the presence of defects such as oxygen vacancies.

Figure 4.31: Schematic representation of the structural evolution of the electro-spun fibres during the thermal annealing.

The addition of nanocarbons to form a hybrid material preserves the morphology, structure and textural properties of the pure inorganic fibre. However, more defects are observed in the TiO₂ crystal structure. Besides the formation of oxygen vacancies, strong interactions formed between components through a Ti-O-C bonds have been observed in Raman, FT-IR and XPS spectroscopies. The strong coupling between both components at their interface demonstrates a successful hybridisation process, especially important for the functional nanocarbons and the TiO₂ nanocrystals. In this case, the inorganic precursor during the sol-gel process covalently interact. The result is a new hybrid material with strong interaction between TiO₂ and CNTs. A schematic representation of chemically bonded TiO₂-CNT structure is illustrated in *Figure 4.32a*.

More importantly, the formation of Ti-O-C bonds provides additional states in the bandgap that enhance the electronic properties by improving interfacial charge transfer processes. Only with a small loading of nanocarbons (<5vol.%), noticeable changes in the electronic structure of the new hybrid material are produced (illustrated in *Figure 4.32b*). The hybridisation process through creation of new interfacial states, extends the VBM position up to 1.42eV above the VB for pure TiO₂. These interfacial states have been additionally observed by photoluminescence studies. Hence, these states will promote the hole transfer process from TiO₂ valence band to functionalised nanocarbons, favouring the photocarrier separation.

Figure 4.32: a) Schematic representation of CNT bonded to (101) anatase. b) Electronic band structure of the hybrid material.

Recent simulations using corrected density functional theory method were applied to interfaces built around graphene and anatase and they document the benefits of hybridisation, through Ti-O-C bonds, for interfacial charge transfer. Most importantly, photoexcited electrons are preferentially accumulated in TiO₂ whereas holes are predominantly found delocalised in graphene.[Ferrighi et al. 2016] The importance of the functionalisation is here evidenced. The fact that pristine MWCNTs are chemically less reactive than those functionalised, results in a hybrid that, with difficulty, can covalently interact through Ti-O-C bond. This is well related with the absence of interfacial states in its UPS spectra. Instead, they probably form a band

4.5 Summary

bending typical from metal-semiconductor heterojunction shifting the valence band up to 1.14eV below than TiO₂, localising thus electrons in the pristine CNTs.

Yet, predicting the directionality of charge transfer requires precise insights into interfacial chemistry, structure and energy states. An added complexity is that the covalently attached MWCNT is not a metal but rather a high mobility semi-metal or even a semiconductor depending on the effect of functionalisation and subsequent covalent attachment to TiO₂. Also, the morphology of these hybrids that consists of a network of TiO₂ nanocrystals (12nm) and covalently attached CNTs are far from the notion of a planar electronic interface. Ultimately, the structural characterisation presented in this report highlights the fact the TiO₂/oxMWCNT fibres are a hybrid material, distinct from its individual components.

CHAPTER 5

PHOTOELECTROCHEMICAL AND PHOTOCATALYTIC PROPERTIES OF ELECTROSPUN HYBRIDS

Chapter 5 discusses the properties of electrospun samples as photodetectors, photoelectrodes or photocatalysts. First, *Section 5.1* studies the electronic conductivity in the dark and under illumination conditions of individual TiO_2 and $\text{TiO}_2/\text{ox-MWCNTs}$ fibres. The photoconducting mechanism and the photoresponse to light in the UV and visible range are analysed and related to structural features of the electrospun materials. *Section 5.2* presents an electrochemical study comparing TiO_2 fibres annealed in air with TiO_2 fibres and $\text{TiO}_2/\text{ox-MWCNTs}$ fibres annealed in inert atmosphere (Ar). The conducting behaviour of the nanostructured semiconductors as well as the study of the semiconductor/liquid interfaces has been investigated by simple open circuit and transient photocurrent measurements. Furthermore, the kinetics of the photo-generated carriers in the electrodes have been studied by electrochemical impedance spectroscopy. *Section 5.3* deals with the photocatalytic hydrogen production of electrospun samples by means of sacrificial water splitting. The photocatalytic test conditions have been optimised with respect to concentration of sacrificial agent, co-catalyst and catalyst amount. Then, the influence of the catalyst crystal structure in the hydrogen production is presented for samples annealed at different temperatures and with different inert gas flows. Moreover, the fibre photocatalyst is compared with

5.1 Photoconductivity of electrospun samples

standard nanoparticle photocatalyst with the aim to investigate effects related to sample morphology. In addition, a large number of hybrid materials including different nanocarbons and metal oxides have been tested in the photocatalytic reactor. The effects of the various nanocarbons on the hybrid structure-properties are also studied. Finally, *Section 5.4* describes the photocatalytic activity of selected samples for photoreduction of CO₂. Again, the photocatalytic activity of the electrospun fibres is compared with that of nanoparticles.

5.1 Photoconductivity of electrospun samples

The optoelectronic properties of the electrospun TiO₂ and TiO₂/ox-MWCNTs hybrid materials as well as their photoresponse to the light, were investigated with collaborators from IMDEA Nanoscience Institute. Each device consists of an individual fibre deposited on conductive substrate by means of pick-up and drop process.[Molina-Mendoza et al. 2016] Briefly, nanofibres deposited on Si wafer by spray coating were peeled off by a PDMS stamp where the fibres remain adhered. With the aid of an optical microscope, nanofibres with diameters above 400nm and $\sim 70\mu\text{m}$ in length were selected and were deterministically deposited onto two bridging Ti/Au (5/50nm) electrodes pre-patterned on a SiO₂/Si substrate.

Figure 5.1a shows an optical image of the device together with a scheme of the device components. *Figure 5.1b* shows SEM images of an electrospun fibre device. This image enables an accurate determination of the length and diameter of the specific fibre, in this case $d = 537\text{nm}$, which are later used for the calculation of the electronic conductivity.

A representative IV curve in the voltage range of $\pm 10\text{V}$ is presented in *Figure 5.2*. Interestingly, even in dark conditions the material is significantly conductive. At 10V, it has a conductivity of $\sim 6 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$, which is orders of magnitude superior to that of sintered mesoporous TiO₂ materials or ordered mesoporous structures from block-copolymer directed growth, all in the $10^{-8} \text{ S} \cdot \text{m}^{-1}$ range.[Zou et al. 2010; Zheng et al. 2014; Pomoni et al. 2013] This is a consequence of the synthetic method used. On the

one hand, the densification of the sol network and the crystallisation produce a mesoporous fibre formed by a network of nanocrystals with tight interfaces, similar to grain boundaries. This is in contrast with samples produced by sintering of pre-formed TiO_2 nanoparticles, leading to a poorer contact between them.

Figure 5.1: a) Optical image of fibre device together to a schematic cross-section of the device. b) SEM image of an individual fibre deposited between the metallic electrodes (inset shows a high resolution SEM image of this fibre).

On the other hand, the presence of oxygen vacancies due to annealing in an inert atmosphere produces sub-bandgap states (*Chapter 4*), which thus contribute to the conductivity of the material.[Sun et al. 2016] Indeed, the conductivity of electrospun TiO_2 fibres crystallised in air was below the detection limit (10 pA) of the equipment, which implies a lower conductivity by at least an order of magnitude.

Figure 5.2: Current-voltage curve of TiO_2 fibre device in dark conditions.

5.1 Photoconductivity of electrospun samples

The illumination of the sample with a high power LED of 455nm wavelength and using different light power, has enabled the study of the electrospun fibre upon illumination. *Figure 5.3* shows the linear and logarithmic scale of the IV curves in dark and under irradiation at different power in the range 1-256 μ W. The current increases with increasing power, and their dependence provides information about the photoconduction mechanisms.

Figure 5.3: a) Current-voltage curves of TiO₂ fibre device in dark conditions and under illumination of 455nm wavelength using different light power. b) Same curves but in logarithmic scale.

Figure 5.4 represents the plot of the photocurrent, taken as the difference between current upon illumination and dark at 10V, as a function of light power. In an ideal semiconductor, the photoconduction mechanism consists in the generation of electron-hole pairs by photon excitation and their separation only by the applied bias, which results in conductivity increasing linearly with power. In contrast, our data shows a sub-linear ratio between the current and the light power, fitted to a power law $I_{ph} \propto P^{0.74}$, which is characteristic of photogating effects.[Buscema et al. 2015] In this case, the electrons get trapped in localised energy states created by defects (e.g. O vacancies) in the semiconductor. These charges generate an electric field able to electrically dope the material.

The photogating effect can be directly distinguished from the photoconductive effect by their response times, which are much slower in the case of photogating.[Furchi et al. 2014; Buscema et al. 2015]

Figure 5.4: Photocurrent measured at different light power and showing a sub-linear relation, indicative of photogating.

The photocurrent profile over time is shown in *Figure 5.5* for irradiation at 455nm and 15μW power. The response for the rise and fall time is defined as the time difference between 10% and 90% of the maximum photocurrent. The plot shows a rapid rise time of 2.5s and a slower fall time of 10s. The relatively slow response of the device agrees well with the presence of photogating effect. Interestingly, the device also shows a fast response occurring in the first 100ms after the illumination is switched on/off. Therefore, it seems that the most likely scenario is a combination of different photocurrent generation mechanisms where photogating plays a major role.

Figure 5.5: Photocurrent response of TiO₂ device over the time with illumination of 455nm of wavelength. The slow fall confirms that photogating is a major photocurrent mechanism in the material.

5.1 Photoconductivity of electrospun samples

A device composing by a hybrid fibre of TiO_2 and 5vol.% ox-MWCNTs was also produced to compare the photoresponse of this device with that composed by pure TiO_2 fibre device. The photoresponse of the hybrid device is evaluated at different wavelengths using LED sources. In order to facilitate the comparison between different materials, it is common to use the responsivity, defined as $R = I_{\text{ph}}/P_{\text{eff}}$, where P_{eff} is the effective power of light reaching the device and is calculated as $P_{\text{eff}} = P_{\text{laser}} * A_{\text{dev}} / A_{\text{spot}}$, (A_{dev} is the surface exposed to the light).

Thus, *Figure 5.6* shows the responsivity as a function of the LED wavelength. Along the visible part, the response of the device is negligible compared to that in the UV. Yet, the hybrid material presents photocurrent of about 2 orders of magnitude higher in the visible range which matches very well with the absorption data of *Figure 4.29*. For higher energies ($>2.5\text{eV}$), the excitation of electrons from valence band to conduction band states increases the photoresponse of the fibre device. Although in the UV range the responsivity of both materials is very similar, the hybrid material still presents photocurrents of about 3 times higher. This result demonstrates that the presence of CNT in the hybrid material can act as electron pathway, increasing the responsivity of the material. But also, they can act as sensitizer material as suggest the increase of responsivity under visible light illumination.

Figure 5.6: Responsivity as a function of the wavelength to compare the optoelectronic properties between pure TiO_2 fibre and $\text{TiO}_2/\text{ox-MWCNTs}$ hybrid fibre devices.

In summary, photocurrent measurements show that the combination of the mesoporous structure and the large content of O vacancies play a dominant role in the photoconduction mechanism of electrospun TiO₂ fibres. Dark current measurements confirm the very high conductivity which arises from the one-dimensional structure of interconnected nanocrystalline domains. The incorporation of CNTs favours the formation of large interfaces with the inorganic and provides electronic states at energies of the inorganic mid-band gap. This explains the much higher responsivity of the hybrid in the visible range but also in the UV range. Overall, the optoelectronic study confirms the enhanced transport properties of the electrospun fibres.

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

The electrochemical properties of the electrospun TiO₂ fibres (annealed in Ar and air) and 5vol.% TiO₂/ox-MWCNTs hybrid fibres were investigated in the dark and under illumination ($\lambda < 400\text{nm}$). The role of the oxygen vacancies in TiO₂ annealed in Ar has been studied by comparison with TiO₂ fibres produced under the same conditions but annealed completely in air and thus, presumably free of oxygen vacancies. Furthermore, the electrochemical properties of the hybrid sample have been measured in order to provide useful insight in the kinetics of the charge transport and transfer processes.

The (photo)electrochemical measurements were carried out in a standard three electrode cell using a Pt wire as counter electrode, Ag/AgCl reference electrode and the electrospun fibres deposited on conducting glass substrate (FTO) as working electrode. The deposition of the nanofibres on FTO was carried out at 90°C by spray coating from a 10mg/mL solution of the nanofibres dispersed in ethanol, resulting in a total active area of 3cm². The electrochemical measurements have been carried out in aqueous solution of Na₂SO₄ (0.1M) at pH 2, under dark and UV illumination with a 150W Xe lamp. *Figure 5.7* shows an electron micrograph of a typical electrospun fibre electrode, which consists in a 500µm thick film of sintered mesoporous fibres. The high surface area of the mesoporous fibres results in a large semiconductor/liquid

5.2 Photoelectrochemical studies of electrospun TiO_2 and TiO_2 /nanocarbon hybrid photoelectrodes

interfaces. Sintering was carried out at 400°C for 30 minutes in inert (Ar) atmosphere. The process led to mechanically stable samples with negligible modification of their structural properties as a consequence of the thermal treatment.

Figure 5.7: SEM image of TiO_2 fibre sample deposited on FTO substrate.

The conductivity type of a semiconductor can be easily identified from the shift in the open circuit potential upon illumination. The shift of the OCP towards more cathodic potentials after irradiation is typical of n-type semiconductors and towards more anodic potential for p-type semiconductors.[Chen et al. 2013] *Figure 5.8a* shows the change of OCP in the dark and upon illumination of the three electrodes studied in aqueous solution. The negative shift in the OCP under irradiation indicates n-type conductivity of all the samples. *Table 5.1* shows the values of the open circuit potential vs SHE in dark condition, under illumination and its difference, which is considered as photopotential. Upon illumination, electrons are excited to the conduction band and produce an upshift of the Fermi level, which is observed by the change in the OCP values. The higher increase of the photopotential and therefore, higher change in the Fermi level is observed for the hybrid sample.

Table 5.1: OCP values at dark, illumination and the difference between both.

	TiO_2 air	TiO_2 Ar	$\text{TiO}_2/\text{ox-MWCNT}$
OCP_dark (V)	-0.15	-0.16	-0.19
OCP_light (V)	-0.26	-0.27	-0.55
Difference (V)	-0.11	-0.11	-0.36

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

Interestingly, the hybrid sample in *Figure 5.8a* shows a secondary slow increase after the first prompt one, which indicates a further increase of the electron concentration in the conduction band of TiO₂. The first OCP increase is similar to pure TiO₂ and it is related to the direct promotion of electrons from the valence to the conduction band of TiO₂ by the light. The second increase is related to injection of electrons from the nanocarbon to the semiconductor that can be originated from different mechanisms.

Figure 5.8: a) Open-circuit potentials under dark and illumination conditions and b) lifetime of injected electrons.

The switching off the light produces the recombination process between electrons in the TiO₂ conduction band and the holes in the valence band under dark conditions.[Jakob et al. 2003] The lifetime of these electrons can be determined from the derivative of the OCP following the equation: $\tau_n = \frac{K_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1}$. [Zaban et al. 2003] Thus, *Figure 5.8b* shows the variation of the electron lifetime as a function of the potential when the light is switched off. The electron lifetime in the hybrid sample is higher than that for pure TiO₂, especially at potential lower than ~ 0.22 V. Importantly, the decay of the curve for the hybrid sample also evidences two different behaviours (as occurs upon illumination) and with the net result of prolonging the electron lifetime.

Further insight into the dynamics of photogenerated carriers can be obtained by chronoamperometry measurements. The photoresponse of the photoelectrodes were determined under potentiostatic control at zero applied voltage and under intermittent irradiation, 20s in the dark and 60s under irradiation using a manual chopper. The efficiency of the photoinduced processes at a given potential can be studied by

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

the magnitude difference of the current under dark and illumination conditions. If the photocurrent is higher than the current in the dark ($j_{ph} > 0$), the photoelectrode behaves as photoanode and if it is lower ($j_{ph} < 0$), it behaves as photocathode.[Chen et al. 2013]

Figure 5.9 presents photocurrent density results for the TiO₂ air, TiO₂ Ar and TiO₂/ox-MWCNTs hybrid electrodes, which behave as photoanodes and present a rapid photoresponse after switching on the UV light. The photocurrent density is 9.4, 15.7 and 51.8 $\mu\text{A}/\text{cm}^2$ corresponding to the TiO₂ air, TiO₂ Ar and TiO₂/ox-MWCNTs hybrid samples, respectively. It is well known that the increase of photocurrent is due to a better charge separation of electron and holes.[Xie et al. 2015] The photocurrent density of TiO₂ annealed in Ar increases a 40% compared with that of TiO₂ annealed in air.

This is a consequence of the defects (oxygen vacancies) formed during the crystallisation in Ar atmosphere that lead to electronic states below the TiO₂ conduction band. Similarly, the presence of nanocarbons in the hybrid material provides additional electronic states within the TiO₂ band gap, which lead to a higher electron density (*Chapter 4*). As a result, the hybrid material shows a higher photocurrent density, about 4 times higher than pure TiO₂ annealed in Ar and about 8 times higher than TiO₂ annealed in air. Furthermore, these observation are consistent with photoconduction measurements on individual fibres discussed before in *Section 5.1*.

Figure 5.9: Chronoamperometry curves of TiO₂ air, TiO₂ Ar and TiO₂/ox-MWCNTs photoelectrodes, showing a rapid photoresponse for all the materials.

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

The electrochemical properties of the photoelectrodes have also been investigated by electrochemical impedance spectroscopy in order to study the kinetics of the electron transport and transfer processes. Measurements were carried out at open circuit potential, in the dark and under UV illumination, in the frequency range of 10kHz-0.1Hz and 10mV of signal amplitude to avoid highly dispersive data and non-linear effects.

EIS data obtained from the frequency scan are interpreted with the use of electrical elements arranged in an equivalent circuit where resistances and capacitances are associated to physical phenomena. Yet, the interpretation of the elements of the circuit can be ambiguous, and it is common to find in the literature several EC used for the same type of materials.

Table 5.2 presents different equivalent circuits used in the literature to describe EIS data from similar systems to the ones of this study, namely electrodes of highly doped metal oxides. First, the *Model A* correspond to the simplest circuit that describes a semiconductor/electrolyte interface, that is, the Randles circuit. It consists in a capacitance associated to the Helmholtz layer (C_H) and a resistance in parallel corresponding to charge transfer process (R_{ct}). [Randles 1947] However, the simplicity of this circuit does not enable an accurate fit of the spectra and cannot explain the behaviour of the photoelectrodes in this work. Therefore, a more complex equivalent circuit is necessary to describe the phenomena that occur in the electrospun fibre photoelectrodes (either pure TiO₂ or TiO₂/CNTs hybrids).

The second EC in *Table 5.2* has been found to accurately describe thick and highly doped nanostructured semiconductors. The *Model B* includes two capacitances, the space charge capacitances (C_{bulk}) described by Mott-Schottky equation and the chemical capacitance (C_{sc}), also referred as surface state capacitance. [Albery et al. 1996; Fabregat-Santiago et al. 2006] It represents the solid/liquid interface by a charge transfer resistance (R_{ct}) and uses another resistance associated to the electron transport in the semiconductor ($R_{t,bulk}$). The electron transport can be limited by the electron trapping at the surface states as well as by the transport at the bulk semiconductor band structure. However, both resistances cannot be determined separately and thus, it is often assumed that one is negligible. As shown in *Table 5.2*, the EC of

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

Model B assumes that the electron resistance of the surface states is more significant than that of the valence band states, which has been found to be a good approximation.[Klahr et al. 2012]

Table 5.2: Description and features of equivalent circuit models used in the literature for fitting the impedance spectra of inorganic semiconductors.

Equivalent circuit	Description of physical/chemical phenomenon	Features
<p>Model A</p>	<p>Randles circuit consisting in the capacitance of the Helmholtz layer (C_H) with a faradaic resistance in parallel (R_{ct}).</p>	<p>Simplest circuit for flat electrodes</p>
<p>Model B</p>	<p>The circuit consists in a bulk capacitance (C_{bulk}) in parallel to charge transfer resistance (R_{ct}). In addition, the chemical capacitances of the semiconductor (C_{sc}) is presented in parallel to electron transport resistance in the bulk ($R_{t,bulk}$).</p>	<p>Circuit for highly doped semiconductors assuming that charge transfer is dominated by the surface states of the semiconductor.</p>
<p>Model C</p>	<p>The circuit presents the Helmholtz capacitance (C_H) in parallel to charge transfer resistance (R_{ct}) for the semiconductor/electrolyte interface. In series, the capacitance of the space charge region of the semiconductor (C_{sc}) and a bulk electron resistance (R_{bulk}).</p>	<p>Circuit for highly doped semiconductors assuming that charge transfer is dominated by the bulk semiconductor.</p>
<p>Model D</p>	<p>The circuit consists in the capacitance of the substrate/liquid interface (Q_{TCS}) and a transmission line that correspond to the porous semiconductor. The transmission line is defined by a charge transport resistance (R_t), a charge transfer resistance (R_{ct}) at the semiconductor/liquid interface and a capacitance related to charging the porous matrix (C_{sc}).</p>	<p>Circuit for nanocrystalline metal oxide films with porous networks assuming a large density of electron traps and band-edge shift under external applied bias.</p>

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

Alternatively, thin layer of highly doped semiconductors have been described by the *Model C* of *Table 5.2*. It consists in a two R|C circuits in series that describe the semiconductor/electrolyte interface and the bulk semiconductor. The resistance are associated to the charge transfer (R_{ct}) and transport (R_{bulk}) processes and the two capacitances correspond to the Helmholtz (C_H) and semiconductor capacitances (C_{sc}), which are of the same order of magnitude.[Lopes et al. 2014b]

Finally, *Model D* of *Table 5.2* presents the transmission line model developed by Bisquert for nanoporous systems in the content of DSSC.[Bisquert et al. 2000] The model implies regular EIS elements (such as resistances and capacitances of the substrate) and extended elements. The latter are modelled by a transmission line of repetitive elements that describes the electron transport resistance in TiO₂ (R_t), the charge transfer resistance at the semiconductor/electrolyte interface (R_{ct}), and a capacitance related to filling the conduction band and surface states of the porous TiO₂ structure (C_{sc}). The model assumes a large density of electron traps, which can limit the electron mobility while increasing capacitance. Furthermore, this model assumes the existence of large density of electron traps that limit the electron mobility whereas exponentially increase the capacitance and the band-edge shift under an external polarisation.[Fabregat-Santiago et al. 2002]

Figure 5.10 shows the Nyquist and Bode plots for dark and illumination conditions of the three photoelectrodes studied here. The general impedance of the photoelectrodes is presented as an open semicircle with undefined time constant values. Interestingly, the hybrid sample behaves slightly different to the pure inorganic in the dark state with a very low impedance spectra (see the inset of *Figure 5.10*). Under illumination, all the spectra present a clearer semicircle with considerably lower impedance values than the corresponding to the dark conditions. Since the measurements are carried out at open circuit potential, higher carrier concentration is expected at the semiconductor/electrolyte interface under irradiation when compared to dark conditions. Subsequently, the photoelectrodes will present faster kinetics of electron transport and transfer processes.

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

Figure 5.10: Nyquist and Bode plots of the EIS data for TiO₂ annealed in air, TiO₂ annealed in Ar and TiO₂/ox-MWCNTs hybrid under dark and illumination conditions. Inset: magnification of the high frequency range.

The data were analysed by using all the circuits included in *Table 5.2*, fitting the impedance spectra with the *EC-Lab* Software. The best fitting was obtained with the equivalent circuit *Model B* of *Table 5.2* for all the samples. This EC has been widely used in literature to describe photoanodes based on semiconductor metal oxides for photocatalytic water splitting and therefore, it is not unreasonable to describe the systems of this study.[Ranganathan et al. 2016; Morais et al. 2016] The lines in *Figure 5.10* show excellent fitting of the EIS spectra using the chosen model. Interestingly, the transmission line model provided inaccurate fitting of the data. This is attributed to the inhomogeneous resistance of the samples in this study, which combines very high conductivity in individual fibres, with poor contact between neighbouring fibres and thus, a much higher resistance through the electrode thickness.

Figure 5.11 provides a schematic illustration of the electrochemical cell together to the equivalent circuit used for the impedance fitting. Moreover, the *Figure 5.11* highlights the electron processes at the working electrode associated to the electrical

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

components of the EC. The contribution of the hybrid has been modelled by the same EC due to the hybrid spectra is similar to that of TiO₂ except for a much lower general impedance. Thus, the effect of the nanocarbons will be directly observed in the fitted values of the equivalent circuit. Similarly, the differences in the anatase/rutile content between samples are expected to change the electrochemical response of the photoelectrodes but just by changing the values of the circuit elements.

Figure 5.11: Proposed equivalent circuit for the mesoporous electrospun fibres photoelectrodes.

Assuming that, our EC model consists in a series resistance (R_1) that includes the resistance of the substrate, electrolyte and external contacts. The semiconductor/electrolyte interface is modelled by the bulk capacitance (Q_1), formed by the contribution of the Helmholtz layer at the electrolyte side and the space charge layer at the semiconductor side, and the charge transfer resistance (R_2) associated mainly to surface states. Finally, the semiconductor capacitance is represented by C_3 and the electron transport in the TiO₂ by the transport resistant (R_3). For nanostructured semiconductor, the bulk capacitance is represented by a constant phase element (Q_1), which describes non-ideal capacitance associated with a non-uniform distribution of charge in a heterogeneous material. Thus, the impedance of a constant phase element Q is defined as: $Z_Q = 1/C_0(j\omega)^a$, where the exponential a indicates the approximation to a capacitor behaviour (i.e. $a=1$).

The parameters obtained by the EIS fitting with the above described equivalent circuit are shown in *Table 5.3*. The series resistances are determined for all the pho-

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

toelectrodes between 27-76 Ω . Similar capacitance values of the double layer are observed for all the samples and are ranged between 13 and 45 μ F in the dark and between 148-235 μ F under illumination. The charge transfer resistance in the dark decreases two order of magnitude for the TiO₂ annealed in Ar and the hybrid samples in comparison with the TiO₂ annealed in air. However, for illumination conditions, the charge transfer resistance of both TiO₂ is similar but it is one order of magnitude lower for the hybrid material. The decrease of charge transfer resistance is associated to the presence of intra-band gap states, which is more relevant in the hybrid material. The same trend is observed in photocurrent density studies (*Figure 5.9*).

Table 5.3: Parameters obtained by fitting the impedance spectra of the photoelectrodes using the equivalent circuit $R1+Q1/(R2+C3/R3)$.

		R1 (Ω)	Q1 (μF$\cdot$s^{a-1})	a1	R2 (kΩ)	C3 (μF)	R3 (kΩ)	χ^2 (10⁻³)
DARK	TiO₂ air	35	43	0.94	120	7.8	281	3.2
	TiO₂ Ar	27	45	0.93	8.5	14	172	1.9
	TiO₂/ox-MWCNT	76	13	0.49	2.4	237	22	4
LIGHT	TiO₂ air	35	148	0.79	6.6	8.8	1.58	6.5
	TiO₂ Ar	27	235	0.81	9.5	9.9	0.86	4.9
	TiO₂/ox-MWCNT	72	159	0.84	0.71	5501	0.05	50

Additionally, the electron transport resistance in the dark takes values of 281, 172 and 22k Ω and under light of 1.58, 0.86 and 0.05k Ω for the TiO₂ air, TiO₂ Ar and TiO₂/ox-MWCNTs hybrid, respectively. In agreement with conductivity studies carried out in a single fibre, the EIS results evidence the higher conductivity of the TiO₂ when it is annealed in inert atmosphere through the creation of oxygen vacancies. Nevertheless, the lowest value of the transport resistant is observed in the hybrid sample either in dark or illumination conditions, which highlights the effect of the CNTs as electron highways. Finally, the effect of the nanocarbons is also reflected in the higher chemical capacitance values of the hybrid electrode, reaching values of 237 and 5501 μ F in the dark and irradiation conditions, respectively. The very high capacitive behaviour of the hybrid film can be due to a higher charge accumulation as consequence of the higher density of states in the hybrid. Yet, the quantum capacitance

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

of the CNTs is expected to contribute to the total capacitance of the hybrid sample.[Senokos et al. 2016]

Further insight of n-type semiconductor in contact with ionic liquid were obtained through Mott-Schottky analysis, although it is not strictly applicable to nanoporous electrodes. At the semiconductor/liquid interface, a depletion layer is usually formed as well as band bending and a change of the Fermi level position.[Albery et al. 1996] Under these conditions, the dependence of the semiconductor capacitance with the potential follows the Mott-Schottky equation (see *Section 3.11.3*). This relationship enables to determine the flat band potential (E_{fb}), the charge carrier concentration at the surface (N_D) and type of conduction.[Gelderman et al. 2007] *Figure 5.12* shows the Mott-Schottky plots for the TiO₂ fibres annealed in air and Ar and TiO₂/ox-MWCNTs hybrid, measured in dark conditions over a potential range between -0.8V to 1V vs SHE. The choice of a high frequency (10kHz) avoids the contribution of surface states or double-layer capacitances and a small amplitude of 10mV minimises the non-linear effects from larger amplitudes. The positive slope of the Mott-Schottky plots for all the materials confirms the n-type semiconductor behaviour with electrons as majority carriers. Moreover, the lower slope of the TiO₂ Ar and especially, that of the hybrid material indicates higher carrier density.

Figure 5.12: Mott-Schottky plot at a frequency of 10 kHz in the dark.

The flat band potential and the carrier density values obtained from the Mott-Schottky plot are represented in *Table 5.4*. The higher donor density of the hybrid

5.2 Photoelectrochemical studies of electrospun TiO₂ and TiO₂/nanocarbon hybrid photoelectrodes

material agrees well with its band structure, which presents additional surface states within the band gap of the TiO₂ semiconductor. The result is the increase of the donor density. Furthermore, the presence of additional states in the hybrid material produce a reduction in the flat band potential, from -0.38V of TiO₂ annealed in air to -0.29V of the TiO₂ annealed in Ar and -0.25V of the hybrid material. The small difference of 0.04V between the flat band potential of TiO₂ Ar and TiO₂/ox-MWCNTs hybrid agrees well with the differences in Fermi level position of 0.05eV obtained from UPS results (see Section 4.4.2).

Table 5.4: Flat band potential and donor density obtained from Mott-Schottky representation.

	Flat band potential vs SHE (V)	Donor density (cm ⁻³)
TiO ₂ air	-0.38	2.38·10 ²¹
TiO ₂ Ar	-0.27	4.38·10 ²¹
TiO ₂ /ox-MWCNTs	-0.21	1.23·10 ²²

In summary, the fibre morphology consisting in interconnected nanoparticles and forming a mesoporous nanostructure with oxygen vacancies at the interfaces, leads to an increase of donor density at the semiconductor/liquid interface, which improves charge transfer processes. Furthermore, the hybridisation with nanocarbons provides high interfacial contact between both components and additional electronic states within semiconductor band gap that can accumulate electrons, thus prolonging their lifetime. In addition, a much higher photocurrent density than pure TiO₂ has been observed which is ascribed to a better charge separation. Finally, a lower transport resistant of the bulk material and high density of carriers at the semiconductor/liquid interface emphasises the attractive properties of the hybrid photoelectrode.

5.3 Photocatalytic hydrogen production

One of the aim of this PhD thesis was to produce mesoporous hybrid materials for hydrogen production. Collaboration with Prof. D. Eder and its group has enabled to test the photocatalytic activity of these materials in their sacrificial water splitting

systems. Some of the reaction experiments were conducted by the author during a research internship at their laboratory. *Section 3.12.1* provides more detailed information of the reactor. Briefly, it consists of a flow-type cylindrical reactor with top light illumination (200W mercury lamp in the 240-500nm wavelength range). A *X-Stream* gas analyser detects hydrogen and other gases simultaneously using different detection systems such as thermal conductivity in the case of hydrogen. Several control experiments were performed in order to establish the optimised parameters of the photocatalytic reaction such as the content of photocatalyst, co-catalyst or sacrificial agent. In addition, a large number of samples containing different type of nanocarbons were tested.

5.3.1 Photocatalytic reaction

Photocatalytic splitting of water includes three main steps, namely 1) light absorption and generation of electron/hole pairs in the metal oxide; 2) electron and hole separation and diffusion to the surface photoactive sites and 3) interfacial charge transfer to the adsorbed species which leads to the water splitting reaction. However, sacrificial water splitting is often performed to evaluate the activity of a single product (hydrogen or oxygen) by favouring only a half-reaction (reduction or oxidation). Such experiments enable discerning limitations of the kinetics and thermodynamics of the overall process. In this work, photocatalytic hydrogen production tests were conducted using methanol as electron donor, extracting holes from the valence band of the metal oxide. Its oxidation occurs over that of water molecules and consequently, this facilitates the reduction of water to hydrogen molecules.[López et al. 2015]

In addition to sacrificial agent, co-catalyst is also commonly used, typically noble metals such as Pt. These metals present a high work function and thus act as electron sinks that favour electron/hole pair separation.[Tipler 1992] As a result, the co-catalyst promotes an enormous increase of the hydrogen production rate. Except where specified, all photocatalytic reactions in this work contain Pt as co-catalyst.

The photocatalytic hydrogen production tests were performed in a water splitting reactor with top UV illumination. In a typical experiment, 30mg of powder samples

5.3 Photocatalytic hydrogen production

were dispersed in 200mL of water and methanol mixture (50:50) to yield a homogeneous slurry. Pt nanoparticles (0.5wt.%) were *in-situ* photodeposited by adding the corresponding amount of H_2PtCl_6 solution into the reaction media and irradiating with UV light.

Figure 5.13a shows a TEM image of TiO_2 fibre catalyst with 0.5wt.% of Pt recovered by filtration after the photocatalytic test. Pt nanoparticles have been uniformly photodeposited and effectively, they consist in small nanoparticles of about 2-3nm on the TiO_2 surface.

Figure 5.13: a) TEM image of TiO_2 fibre after photocatalytic test showing well dispersed Pt nanoparticles of 2-3nm size. b) Continuous H_2 monitoring during a typical photocatalytic test.

Hydrogen generation was continuously measured over time and a typical curve of the samples studied in this thesis is shown in Figure 5.13b. The data show an instant activity of the catalyst and thus, an incubation time is not required. Its activity stabilises rapidly in the first 40 minutes and remains constant along the experiment, lead-

ing to a *plateau* in the hydrogen flow. As figure of merit, the value of hydrogen production at the *plateau* of H_2 rate, ~ 180 min of UV irradiation, has been chosen for further comparison between the different photocatalyst materials.

5.3.2 Optimisation of photocatalytic reaction conditions

Figure 5.14a shows the H_2 production rate over time using different methanol/water ratio (0-50%). The hydrogen production rate values at the *plateau* of the curves are plotted in Figure 5.14b as a function of the methanol/water ratio. The addition of methanol increases the hydrogen production, since methanol molecules can effectively accept photoexcited holes and increase the rate of water reduction to hydrogen. For reference, the true water splitting reaction in the absence of methanol produces a small amount of hydrogen of $0.7 \mu\text{mol/h}$ under the same conditions. For further experiments a methanol/water ratio of 0.5 was used based on these results.

Figure 5.14: H_2 evolution rate a) curves and b) values, varying the sacrificial agent (methanol) content.

Figure 5.15a presents the hydrogen production profile for different loading of Pt nanoparticles. The figure demonstrates that the presence of Pt is required to catalyse the water reduction reaction. Pure TiO₂ fibres gives just $3.7 \mu\text{mol/h}$ of pure H_2 production. In contrast, addition of small amounts of Pt as low as 0.1 wt.% increases activity to $423.4 \mu\text{mol/h}$. At higher Pt loadings, activity levels off. Doubling of the amount of Pt, from 0.25 to 0.5 wt.%, provides an increase of only 9% in the hydrogen production rate. Further addition of Pt (e.g. at 1 wt. %) is detrimental for the reaction, probably as a consequence of Pt nanoparticle agglomeration, reducing the amount of active sites for the photocatalytic reaction. Hence, for the samples studied in this thesis, 0.5 wt.% of Pt was fixed as co-catalyst amount added to the reaction.

5.3 Photocatalytic hydrogen production

Figure 5.15: H₂ evolution rate a) curves and b) values, varying the loading of co-catalyst (Pt nanoparticles).

Tests were also performed to study the influence of the photocatalyst concentration in solution on the H₂ production rate. Whereas higher amounts of catalyst provide more active sites, factors such as agglomeration of the catalyst or the efficiency for light absorption can limit absolute values of photocatalytic hydrogen generation for a given reactor.

Figure 5.16a shows the photocatalyst mass test performed with electrospun TiO₂ samples. Different amounts of TiO₂ were tested under the same experimental conditions. Small amount of catalyst such as 10mg already present high hydrogen production rates. Further increase of the photocatalyst amount produces higher photocatalytic activity. However, minor differences of the H₂ generation (~2%) is observed using 50 or 70mg of photocatalyst mass.

Figure 5.16b shows the H₂ production for the different catalyst amount. The fit demonstrates that the H₂ evolution rates is not significantly affected for mass loadings larger than 30mg, corresponding to a concentration of only 0.15g/L. Similar mass effects were obtained for the hybrid samples containing nanocarbon and thus, 30mg of catalyst were fixed for the following photocatalytic tests.

Figure 5.16: H₂ evolution rate a) curves and b) values, varying the amount of photocatalyst. Fit of the plot in b) shows that above 30mg a *plateau* in the H₂ production is observed.

In summary, the optimisation of various parameters indicates that the evolution of hydrogen is only possible by means of sacrificial water splitting reaction and with the aid of co-catalyst. 50% methanol and 0.5% of Pt have been fixed for further photocatalytic experiments. The optimum concentration of catalyst in this photocatalytic systems was 0.15g/L, enough to obtain large amounts of hydrogen. For this concentration, the catalyst is dispersed in less than 30s of sonication time.

5.3.3 Structure-photoactivity relation of electrospun fibres

The samples studied in *Section 4.2.1*, produced under different annealing conditions, were subjected to photocatalytic test in order to relate their structure and properties to their photocatalytic activity for H₂ production. *Figure 5.17a* shows the corresponding H₂ evolution curves. As was expected, the crystal structure of electrospun TiO₂ nanofibres is significantly related to their photocatalytic properties. *Figure 5.17b* shows the hydrogen production values related to the crystal structure of the TiO₂ fibres annealed at different temperatures. At 400°C, the TiO₂ fibre is composed by 100% of anatase phase. However, the pure anatase composition does not produce the highest photocatalytic activity between the samples of this batch. The best photocatalytic performance is observed for the sample annealed at 500°C, which contains a ~16% of rutile. The presence of more rutile (~50% presented in samples annealed at 650°C) shows a lower H₂ production rate, possibly because the increase of crystal size has negative effect of reducing the surface area. Finally, the sample annealed at 800°C

5.3 Photocatalytic hydrogen production

formed by pure rutile shows a significant decrease of the photocatalytic activity. It is well established that small fraction of rutile benefits the electron-hole pair separation between the anatase and rutile nanocrystals.[Scanlon et al. 2013] In the case of electrospun fibres, the close interface between nanocrystals is expected to facilitate this mechanism, by improving transport properties and delaying the photocarrier recombination.

Figure 5.17: a) H₂ evolution rate curves of TiO₂ fibres annealed at different temperatures and b) the effect of the crystal phase on the H₂ production.

In view of the effect of the Ar flow used during the crystallisation on the anatase/rutile ratio, these samples were also analysed for H₂ production. The data are presented in Figure 5.18a. Ar flow above 100 L/h reduces the hydrogen production by up to 50%. Figure 5.18b shows the decrease of the hydrogen production in comparison with the anatase/rutile ratio. Again, the drop in activity corresponds to the increase of anatase/rutile ratio. Therefore, the optimised synthesis condition consists in annealing at 500°C in Ar but importantly, without flow.

Figure 5.18: a) H₂ evolution rate curves of TiO₂ fibres annealed at different Ar gas flow and b) the effect of the crystal phase and size on the H₂ production.

5.3.4 Morphological effect in photocatalytic activity

The morphology of the electrospun fibres has influence on the photocatalytic activity. The one-dimensional morphology with a characteristic mesoporosity could benefit adsorption/desorption processes of the water/hydrogen molecules. In view of these assumptions and in order to understand the origin of such behaviour, nanoparticle control samples were synthesised and tested for H_2 activity. Furthermore, the morphological effects of the one-dimensional fibres have been investigated for other metal oxides (see *Appendix A*). They were produced by sol-gel process using identical conditions than that used for the fibres except to the addition of the polymer and the use of the electrospinning technique. The annealing conditions were also the same in order to reproduce the crystal structure of the hybrid.

Figure 5.19 shows the hydrogen evolution curves of TiO_2 fibres in comparison with bare nanoparticles. The electrospun fibres enhance substantially the photocatalytic hydrogen production, more than 10 times higher hydrogen production rate than standard TiO_2 nanoparticles. The values of activity obtained ($29.37\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) for electrospun TiO_2 fibres are in fact very high, nearly an order of magnitude higher than most literature data obtained under similar reaction conditions (discussed later).

Figure 5.19: H_2 evolution rate curves of TiO_2 nanoparticles (black curve) and TiO_2 fibres (red curve), tested under identical conditions.

5.3 Photocatalytic hydrogen production

The results demonstrate that electrospun TiO_2 fibres exhibit a remarkable enhancement of H_2 production rate with respect to TiO_2 nanoparticles. Amongst key differences between the two materials discussed in *Section 4.2.2*, the mesoporous fibre structure is originated through the polymer removal, leading to large pores that facilitate the accessibility of the molecules to more active sites. However, the porosity originated between agglomerations of nanoparticles leads to a total surface area of $95.5\text{m}^2/\text{g}$, which are about the double than that of TiO_2 fibres ($41.4\text{m}^2/\text{g}$). Even when the surface area is a very important parameter of the material for its photocatalytic performance, other morphological effects can predominate in the H_2 activity obtained by these two photocatalyst. For instance, the polymer used as vehicle for electrospinning keeps the sol units in close contact, resulting in a much faster crystallisation caused by a lower activation energy for the nucleation at the interface between particles. This explains the presence of a certain amount of rutile in the TiO_2 fibres in contrast to the TiO_2 nanoparticles, which are formed by purely anatase phase. Furthermore, the fibres can favour the electron transport along the interfaces between nanoparticles.

Therefore, TiO_2 fibres have a continuous and highly porous nanostructure and can be visualised as a network of nanocrystals forming large $\text{TiO}_2/\text{TiO}_2$ interfaces that facilitates charge transfer processes. In contrast, TiO_2 nanoparticles probably lack the contact between nanocrystals and thus, the possibility of internal charge transfers. Importantly, the TiO_2 fibres contain a certain amount of rutile that facilitates the photocarrier separation and ultimately, a higher hydrogen production rate.

5.3.5 Photocatalytic activity of TiO_2 -nanocarbon hybrids

The hybridisation with nanocarbon has demonstrated the creation of new hybrid material. The incorporation of small amount of functionalised nanocarbons produces a huge interfacial area between components. The key point is that the electronic structure of the hybrid material has changed in comparison with pure inorganic. The use of functionalised nanocarbons create new interfacial states within the band gap of the inorganic that can benefit charge transfer processes. The high photoconductivity and

lower charge transfer resistance from electrolytes point out that the hybrid material is a promising candidate as photocatalyst.

Figure 5.20 illustrates representative hydrogen curves for hybrids with 1vol.% of pristine and ox-MWCNTs and bare TiO_2 fibres. All the samples present similar hydrogen profile, however the hydrogen production value significantly changes. The TiO_2 /ox-MWCNTs hybrid presents an enhancement in the hydrogen activity of about 20% with respect to pure TiO_2 fibres. The explanation for the higher hydrogen performance is the additional interfaces created between the inorganic and the nanocarbons during the *in-situ* hybridisation process. In contrast, the TiO_2 /p-MWCNTs hybrid decreases dramatically the production of hydrogen. Whereas the covalent functionalisation has produced a strong coupling through Ti-O-C bond and provides new interfacial states, the hybridisation with pristine nanocarbons has resulted in a decrease of the electron density in the edge of the valence band states. In addition, the use of pristine CNTs leads to less uniform fibre due to CNT agglomeration and a possible reduction of surface area and interfacial contact between both components. This is in good agreement with the electronic structure of both hybrid materials, previously described in Section 4.4.2.

Figure 5.20: Hydrogen production curves over time. The maximum hydrogen production rate at the *plateau* is detailed in the graph.

5.3 Photocatalytic hydrogen production

The synthesis method used produces a noticeable variation in anatase/rutile ratio for different batches. This is attributed mainly to two factors, namely differences in the actual temperature of the whole material due to the air flow and the difficulty in achieving a uniform temperature profile in the large electrospun fibre membranes (which are very good thermal insulators). These variations in phase composition have been very instructive to identify the predominant factors affecting photocatalytic activity. Such variations are more pronounced by the presence of the nanocarbons because they affect the crystal phases of the TiO_2 fibres and therefore, to the available surface area. As a result, it is more appropriated to compare hybrid and TiO_2 considering the anatase/rutile ratio of each sample.

Thus, *Figure 5.21* represents the hydrogen production of various electrospun materials, which have a fraction of rutile lower than 20%. The linear fits show the increase of hydrogen production with the amount of rutile. In particular, an increase in hydrogen production of 10% is observed in pure inorganic fibres with anatase/rutile ratios between 0.98 and 0.82. For the hybrid samples, the H_2 production increases with the increment of the CNT volume fraction and also the amount of rutile rate. An increase of $\sim 30\%$ in the H_2 production is observed, however this enhancement is mostly associated to the effects of the nanocarbons in the hybrid structure. Therefore, the result of the very high $\text{TiO}_2/\text{ox-MWCNTs}$ photoactivities highlights the importance of the design of new hybrid materials.

Figure 5.21: Hydrogen production of pure TiO_2 and $\text{TiO}_2/\text{ox-MWCNTs}$ hybrid fibres with different anatase/rutile ratio.

For a more accurate comparison of the hybrid materials, it has been done between samples prepared and tested in the same batch. The hydrogen production is presented normalised by the catalyst mass. *Figure 5.22* illustrates the effect of the type of nanocarbon and the amount of them in the final hybrid material. The point with 0% of nanocarbons corresponds to a pure TiO_2 fibre produced in the same batch than each type of hybrids. Due to the hybrids with pristine and functionalised MWCNTs belong to the same batch, only one TiO_2 has been plotted.

In general, the strategy of using functionalised nanocarbons improves the photocatalytic H_2 production in comparison to the pure TiO_2 . This has been observed for hybrid with functionalised MWCNTs and graphene and is a direct consequence of the successful *in-situ* hybridisation approach. In fact, these results agrees well with those of their corresponding electronic structure described by UPS in *Section 4.4.2*. Furthermore, the photocatalytic hydrogen production increases with the amount of nanocarbons which arises from the increase of interfaces that improve charge transfer processes. In contrast, the pristine nanocarbons, either CNTs or graphene, decrease the H_2 evolution rate, probably because the agglomeration of nanocarbon reduces considerably the interfacial area between the nanocarbon and the metal oxide, resulting in a worst charge separation. Thus, the increase of volume fraction for the pristine nanocarbons results in lower photocatalytic activities, which highlight their effect in the deterioration of the hybrid properties.

Figure 5.22: Hydrogen production rate of the four different type of nanocarbons as a function of their volume fraction.

5.3 Photocatalytic hydrogen production

Effectively, the consequence of the huge interfaces in the hybrids is the increase of charge transfer processes. The electron-hole separation is facilitated, increasing the photocarrier lifetime and consequently, improving the photocatalytic process. The most active material has been achieved for TiO₂ hybridised with functionalised MWCNTs. Overall, the results highlight the relevance of the chemistry of the functional groups with the inorganic precursor during the *in-situ* hybridisation process.

5.3.6 Comparison of TiO₂-based photocatalyst

In order to put in perspective the activity values of the catalyst produced in this thesis, we have gathered literature data for TiO₂-based photocatalysts from experiments under comparable conditions: using Pt co-catalyst, sacrificial agent and under UV irradiation. *Table 5.5* shows the details of the photocatalytic reaction conditions and the hydrogen production rate normalised by catalyst mass.

The data from *Table 5.5* are represented in the histogram of *Figure 5.23*. In addition, it also includes collected data of hydrogen generation from tests performed along this thesis. They are separated in mesoporous TiO₂ fibres, hybrids fibres containing pristine nanocarbons (CNT + Gr) and hybrids with functionalised nanocarbons (CNT + Gr). The hydrogen activity of TiO₂ nanoparticles produced in this work is marked in the histogram of TiO₂. The standard sol-gel process that we have used as reference in this thesis, produce a photocatalyst with activities in the same range than those in literature. Interestingly, the electrospun materials, either pure inorganic or inorganic/nanocarbon hybrid, outperform the reported literature values. Despite scattering in the data, related to synthesis-structure-property effects or light power effects, even the lowest activities of these materials are at the higher end of literature data.

Table 5.5: Literature data of photocatalyst for hydrogen production.

H ₂ evolution rate (mmol·h ⁻¹ ·g ⁻¹)	Lamp sources	Catalyst amount (g/L)	References
0.07	500W Xe	0.25	[Zhang et al. 2012]
0.04	400W Xe	1.25	[Ni et al. 2007]
0.25			
0.07	200W Xe	1	[Fan et al. 2011:2]
0.17	450W Hg	0.75	[Luo et al. 2004]
3.55	300W Xe	1.67	[Cheng et al. 2012]
0.26	400W Hg	0.5	[Lee et al. 2012b]
0.59			
0.05	> 320nm	0.5	[Kim et al. 2014]
0.25			
1.2	300-400nm	0.5	[Kandiel et al. 2011]
4.67			
6			
0.05	300W Xe	0.5	[Choi et al. 2012]
0.04			
1.87			
7.11			
1.23	500W Hg	0.2	[Ahmmad et al. 2008]
7.85			
9.75	>295nm	0.2	[Choi et al. 2010]
2.53			
7.45	350W Xe	0.25	[Yu et al. 2010]
0.12			
0.33			
1.49	500W Hg	0.3	
0.03	450W Hg	1	
1.89	400W Hg	0.3	
0.35	250W Hg	0.3	
3.3	300W Xe	0.2	
6.7	300W Xe	0.2	[Chen et al. 2010]
4	450W Hg	0.025	
6.92	300W Hg	0.2	
0.05	450W Hg	1	
0.28	450W Hg	1	
0.12	450W Hg	1	
6.6		1	[Melián et al. 2013]

5.3 Photocatalytic hydrogen production

The *Figure 5.23* also confirms the enhancement of the hydrogen production when the hybridisation has been performed using functionalised nanocarbons. The interaction between TiO_2 and functionalised nanocarbons is more favourable through the chemistry of the functional groups. In contrast, pristine nanocarbons tend to agglomerate in the hybrid material, reducing the interaction with the TiO_2 .

Figure 5.23: Photocatalytic H_2 production rate of electrospun TiO_2 and hybrids with pristine and functionalised nanocarbons compared against data from literature (see *Table 5.5*).

Yet, comparison between catalysts is difficult because the overall process is not standardised. The comparison of H_2 activity is presented normalised by catalyst amount. In principle, this can take into account differences in catalyst amount used in

the different laboratories, which for the literature data usually ranges from 0.03 to 1g. This comparison should be taken with caution since activity saturates at a sufficiently high concentration, from which point increasing the amount of catalyst will not increase activity. In addition to the effects related to the catalyst, the reactor design and the reaction conditions difficult the comparison between photocatalysts.

5.4 Photocatalytic CO₂ reduction

Collaborations with Dr. de la Peña and their group at IMDEA Energy Institute has enabled the evaluation of photocatalytic activity for gas-phase CO₂ photoreduction using water as electron donor of one-dimensional electrospun TiO₂ fibres, further compared with those of simple TiO₂ nanoparticles prepared by sol-gel method.

Artificial photosynthesis using CO₂ and water vapour as reactor feed leads to the formation, of hydrogen, hydrocarbons and other minor products under illumination. Photocatalyst based on metal oxide such as TiO₂ have been widely used for artificial photosynthesis.[Fresno et al. 2014] However, very low activities are still reported for the photoreduction of CO₂, especially when water is used as the only electron donor without any sacrificial reagent.[Protti et al. 2014] In contrast to water reduction, the photoreduction of the CO₂ is a multi-electron process that can lead to the formation of CO and H₂ by 2e⁻ reaction and/or small hydrocarbons by 4-8e⁻ reactions. This results in multiple reaction products and thus, the efficiency of the photocatalyst needs to be expressed in terms of the activity but also selectivity of the reaction products.

The effect of morphological properties of hierarchical nanofibres on the enhancement of CO₂ photoreduction using water as electron donor was investigated under UV light. Their activity and selectivity values are compared with bare nanoparticles. CO₂ photoreduction experiments were conducted in an in-house reaction system in continuous-flow mode. Details of the gas-phase photoreactor and the catalyst test conditions are provided in *Section 3.12.2*. As control of the reaction, photocatalytic activities of the material under different atmospheres (Ar, Ar-H₂O and CO₂) were investigated. With these tests, the influence of the adsorbed species at the catalyst surface is separated to the effect of the CO₂-H₂O reaction atmosphere. Finally, blank catalyst under

5.4 Photocatalytic CO₂ reduction

dark and illumination were performed to discard any CO₂ or H₂O conversion due to thermal or photochemical reaction. *Figure 5.24* shows the kinetic profiles of the main products (H₂, CO, CH₄ and CH₃OH) obtained in the CO₂ photoreduction reaction over 20 h under UV irradiation. A rapid activation of the catalyst is observed after switching on the UV light and forming mainly hydrogen (H₂), carbon monoxide (CO) and methanol (CH₃OH). After 5 hour of reaction, the maximum production rates of the predominant products (H₂ and CO) are reached and after, their evolution decays. However, the production of methane (CH₄) and CH₃OH starts to increase up to reach the maximum at ~11h of reaction time.

Figure 5.24: Temporal evolution rates of the photoreduction products: a) H₂ b) CO, c) CH₄ and d) CH₃OH under UV/Vis illumination.

Table 5.6 shows the cumulative productions after 20 h reaction. The comparison between catalysts shows a better performance of the TiO₂ fibres, which present an increase of nearly 5 times in the C-containing products and approximately 4 times in H-obtained products. Compared to commercial TiO₂ photocatalysts, the TiO₂ fibre sample shows a higher overall Apparent Quantum Yield (AQY=0.036%) than the usual benchmark P25 from Evonik (0.030%) tested in the same conditions, and higher than G5 from Millenium and PC500 from CrystalACTIV.[Collado et al. 2013; Collado et al.]

This further supports the interest of the samples studied in this work as CO₂ reduction photocatalysts. Clearly, the use of 1-D nanostructures lead to an increase of the CO₂ photoreduction in comparison with reference nanoparticles.

Table 5.6: Comparison of cumulative production ($\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}$) in the CO₂ photo-reduction reaction over the catalysts after 20h of UV illumination.

Sample	H ₂	CO	CH ₄	CH ₃ OH	C ₂₊	Converted C	Converted H
TiO ₂ fibres	398.8	203.9	26.9	5.0	6.9	253.4	977.7
TiO ₂ nano-particles	105	37.4	3.3	2.2	3.3	52.0	257.4

Finally, the selectivity of both catalysts is compared in *Figure 5.25*. Similar selectivity values lead to the formation of syngas (CO and H₂) for both catalysts. The high amounts of H₂ comes from the water reduction process. Both catalysts preferentially promote the photocatalytic reaction involving only 2 electrons instead of the formation of hydrocarbons, which requires a high demand of electrons.

Figure 5.25: Selectivity (%) of the main reaction products obtained with TiO₂ nanoparticles and TiO₂ fibres materials under UV irradiation and CO₂/H₂O atmosphere.

The higher efficiencies of the photocatalytic reaction of the TiO₂ fibres compared with nanoparticles can be mainly ascribed to the hierarchical nanostructure obtained

5.4 Photocatalytic CO₂ reduction

by electrospinning technique. The fibres consist in packed grains that has close interfaces between nanocrystals with characteristic mesoporosity. The improved connections of TiO₂ crystals in the fibre structure favour a fast charge transport processes across the interfaces between crystals. Moreover, the mixture of anatase and rutile phases presented in the TiO₂ fibres leads to a better charge separation. The overall effect is the enhancement of the photocatalytic CO₂ reduction because of favoured electron transfer and transport processes. This highly agrees with the results obtained for these photocatalysts in the sacrificial water splitting process.

Finally, a hybrid sample containing ox-MWCNTs in a volume fraction of 10% were tested under the same procedure. The kinetic of the four main photocatalytic products was very similar to that of pure inorganic, however, the cumulative production values was slightly lower, about 25% lower but yet, 2.5 times higher than the nanoparticle sample. Possibly, the amount of ox-MWCNTs of this hybrid sample or maybe, the content of carbon species are not appropriated and thus, its effect on the CO₂ photoreduction was rather detrimental. In order to find the benefit of the TiO₂/CNT hybrid materials, a hybrid with considerably lower CNT volume fraction should be used.

5.5 Summary

The results indicate the very high conductivity of the nanofibers even in dark conditions, which is reminiscent of the synthetic process. The one-dimensional confinement of the TiO₂ fibres consisting in a mesoporous network of interconnected crystalline domains favours the transport properties of the TiO₂. The oxygen vacancies originated by the Ar annealing act as trap states, increasing the photoconductivity of the electrospun samples but also increasing the photoresponse of the material. Furthermore, the hybrid material produces an increase of the photoresponse either under UV or noticeable, under visible light.

Electrochemical studies on TiO₂ and TiO₂/nanocarbon photoelectrodes have been carried out. The continuous and large pores of the fibre structure together to the high surface area facilitate the accessibility and diffusion of the liquid molecules such electrolytes or photocatalytic reactants. Electrospun fibre materials behave as n-type

semiconductors with electrons as majority carriers. The electrochemical impedance study of the materials as photoelectrodes has enabled the determination of important parameters of the material such as transport and transfer resistances or surface state capacitance, which are enhanced in the hybrid material due to the presence of additional states formed during the *in-situ* hybridisation process. The net result is the increase of the photocarrier lifetimes, especially in the hybrid material, which shows a higher photocurrent density ($51.8\mu\text{A}/\text{cm}^2$), with an increase of 230% in comparison with the pure inorganic ($15.7\mu\text{A}/\text{cm}^2$). These parameters are further related to phenomena relevant for energy applications such as generation, separation and accumulation of carriers.

The photocatalytic results, either sacrificial water splitting or CO_2 photoreduction, have effectively demonstrated that the electrospun fibres are highly efficient photocatalysts. We could identify three particular contributions to an enhanced activity: a) the specific morphology of the electrospun fibres, which consist of a network of nanosized TiO_2 particles, which share tight interfaces and facilitates charge transfer between the particles; b) the presence of anatase and rutile phases that also facilitate charge separation and c) the high open porosity with large mesopores, which enable diffusion and adsorption/desorption processes.

The role of the interfaces between TiO_2 nanocrystals is highly evidenced by a more efficient generation and separation of photoexcited carriers. Interfacial charge transfer and transport processes facilitates the enhancement of hydrogen production. Higher photocatalytic performance is presented for the hybrid materials, which present additional TiO_2 /nanocarbon interfaces. However, only the hybrids with functionalised nanocarbons can reach higher hydrogen rates than pure TiO_2 fibres. In fact, small amounts of functionalised nanocarbons considerably enhance the hydrogen activity. The chemical functionalisation of MWCNTs and graphene creates strong interaction between the two components during the *in-situ* hybridisation. The result is the creation of new interfacial states that facilitate the separation of photocarriers, enhancing the photocatalyst efficiency.

5.5 Summary

The highest hydrogen evolution rate measured was 1218.5 $\mu\text{mol/h}$ and, normalised by catalyst mass of up to 40.6 mmol/h/g , obtained from $\text{TiO}_2/\text{ox-MWCNTs}$ hybrid. Their photocatalytic performance is higher than literature values from tests using TiO_2 under similar reaction conditions: sacrificial agent, co-catalyst and UV illumination. Importantly, the chemical reaction at particle surface is instantaneous upon irradiation and it remains constant over the whole of duration of the tests (>24h).

CHAPTER 6

NEW TiO₂/CNTf HYBRID MATERIAL

Chapter 6 contains details of the synthesis and characterisation of a different type of inorganic/nanocarbon hybrid material based on macroscopic fibres of CNTs. The main goal is to create a new hybrid material with a large and well-defined interface between the CNT and inorganic phases. Consequently, the interfacial effects will be more evident over bulk properties. First, *Section 6.1* provides results of the morphology and crystal structure of the new hybrid material, formed by *in-situ* growth of TiO₂ on CNT fibre film. A controlled deposition of the metal oxide on the nanocarbon surface is achieved using atomic layer deposition. Insights into the TiO₂ nucleation and growth on the CNT fibre is gained by varying the inorganic thickness. *Section 6.2* presents results of the crystal and electronic structure of the hybrids, which are found to be considerably different to the individual components. Finally, *Section 6.3* presents the electrochemical properties of the TiO₂/CNTf hybrids. The conducting behaviour of the hybrid electrodes and the kinetics of the semiconductor/electrolyte interface have been investigated under dark and illumination conditions

6.1 Morphology and crystal structure of new TiO₂/CNTf hybrid

Immobilised inorganic/nanocarbon hybrid materials are promising materials for photocatalysis because they can be easily recovered and also, reused in further tests. In addition, they can be used in photoelectrocatalysis where nanocarbons can act as current collectors. In this case, nanocarbons can be conveniently used as planar porous electrodes for the deposition of the inorganic. For instance, the assembly of CNTs into carbon paper or other porous membranes, known as *bucky-paper*, and subsequent combination with metal oxide by ALD has led to well controlled interfaces.[Kemnade et al. 2015] The network of nanocarbons (i.e. CNTs) is thus presented as an interesting support material, mechanically stable and highly conductive.[Stano et al. 2008] Furthermore, the hybridisation with the inorganic and specifically, the type of deposition technique is crucial not only to control the crystallinity of the inorganic, but also to cover the nanocarbons. In the case that the nanocarbon surface is not completely covered, short-circuits and high recombination rates at the nanocarbon/electrolyte interface can occur, resulting in a decrease of the material performance.[Chen et al. 2012]

In this Chapter, CNT fibre is used as a tough scaffold material that provides high surface area (256m²/g) for the inorganic deposition and high electrical conductivity (3.5·10⁵S/m) for the separation of the photogenerated electrons in the inorganic.[Senokos et al. 2016] The CNTs in the fibre have been produced by chemical vapour deposition using the direct spinning process under synthesis conditions that produce predominantly MWCNTs with 3±2 layer and a diameter around 4nm. Thus, a few layer MWCNTs are obtained with a small diameter and very large length.[Reguero et al. 2014] *Figure 6.1* shows optical and electron microscope images of the CNT fibre material exhibiting its hierarchical structure. The CNT fibre consists in a continuous macroscopic fibre easily transferable to any substrate to form planar electrodes as it can be seen in *Figure 6.1a*. The SEM image of *Figure 6.1b* shows that the CNT fibre is formed by bundles of CNTs, which are entangled as TEM image of *Figure 6.1c* shows.

Figure 6.1: a) Optical image of a CNT fibre electrode, b) SEM image showing the CNT bundles forming the CNT fibre and c) TEM image illustrating the entanglement of the CNTs in the bundles.

Atomic layer deposition has been used for the deposition of TiO₂ on CNT fibre electrodes. ALD is a gas-phase technique that enables the control in the deposition of the inorganic precursor at atomic level. The use of this technique over high surface area materials such as nanocarbons enables the formation of homogeneous and conformal inorganic coating.[Jin et al. 2012] Importantly, they present a large inorganic/nanocarbon interface of high interest for the increase in energy performance of the hybrid material. Recent studies of inorganic/nanocarbon photoanodes have demonstrated that the increase of interfacial area facilitates charge (electron) transfer processes towards the current collector.[Lee et al. 2007]

ALD technique has been used for the growth of TiO₂ on CNT fibre surface. The process has been optimised until the obtaining of conformal coating of the CNT bundles. ALD process using two oxidising agents (water and oxygen plasma) have been used (see more details in *Section 3.2.3*). Characterisation of samples obtained by both ALD treatments have led to similar crystal structures, confirmed by XRD and Raman measurements. *Figure 6.2* shows a schematic picture of a typical TiO₂/CNTf sample. It evidences that the CNT fibre film consists in entangled bundles of CNTs forming a unique macroscopic fibre. As collected fibre is in the form of a film of ~10 μm, only the exposed surface of the electrode is covered by the ALD precursors.

Figure 6.2: Schematic picture of a TiO₂/CNTf sample.

6.1 Morphology and crystal structure of new TiO₂/CNTf hybrid

Due to the mesoporosity of the CNTf, the interfacial area with the inorganic is large but still lower than the total area of the CNT fibre in the electrode. The picture represents a bicontinuous structure with an intimate contact between the TiO₂ and the CNT bundles. Importantly, the coated CNT bundles are still connected along the fibre structure, which act as electron pathways. Therefore, the CNT fibre acts as support for the nucleation and growth of TiO₂, and also as current collector electrode.

Figure 6.3: SEM images of a) as-grown CNT fibre, b-f) CNT fibre with ALD deposition of 10, 20, 40, 60 and 80nm of TiO₂.

Figure 6.3a shows the morphology of CNTf before ALD treatment and Figure 6.3b-f shows the TiO₂/CNTf samples containing different ALD deposition cycles. Figure 6.3a presents the CNT fibre consisting in CNTs bundles of ~40nm of diameter that are entangled forming a unique fibre structure with open porosity. The ALD precursors

have penetrated through the CNTf pores and nucleate on the surface of the CNTf bundles. In general, a successful coating of the CNTf is achieved for all the samples. Effectively, the increase of the ALD cycles produces thicker TiO₂ coating of the CNT bundles (*Figure 6.3b-f*). Although the TiO₂ layers are quite uniform and form a conformal growth on the CNT fibres, particle nucleation on TiO₂ layer is also observed at the surface, especially for the highest ALD cycles.

Table 6.1 shows the TiO₂ thickness theoretically obtained from the growth rate (0.54Å/cycle) and number of ALD cycles in comparison with experimental observations of TiO₂ thickness on SEM images. Note that the *Table 6.1* includes the bundle diameter measured from the SEM images of *Figure 6.3*, from which the thickness of the TiO₂ is estimated considering 45nm of CNT bundle diameter. The correlation between expected and measured thickness confirms the control on the metal oxide deposition and thickness. Yet the measured values correspond to the average of several SEM images with different resolution and therefore, they accumulate an error of about 5-10nm.

Table 6.1: Measurements of TiO₂ thickness by SEM images of *Figure 6.3*.

Theoretical thickness* (nm)	Measured bundle diameter (nm)	Measured TiO ₂ thickness (nm)
10	63	9
20	87	21
40	129	42
60	158	57
80	199	77

*Calculated from the growth rate and assuming homogeneous TiO₂ coverage.

The conditions employed in the ALD process for TiO₂/CNTf hybrid have resulted in an amorphous coating of titanium oxide as it is confirmed by the XRD pattern of the hybrid samples (*Figure 6.4*). Only diffraction from the CNT fibre is observed with a large background that comes from the amorphous TiO₂ layer. Thus, a heat treatment at 400°C for 1h was carried out to crystallise the metal oxide into anatase phase. Inert atmosphere (Ar) was used to prevent the degradation of the CNT fibre.

Figure 6.4: XRD pattern of TiO₂/CNTf sample after ALD process, showing the peaks of the graphite structure and the wide background of the amorphous TiO₂.

The conformability of the TiO₂ layer on the CNT surface is further confirmed by TEM observations (*Figure 6.5a*). The annealing treatment in Ar atmosphere has not changed the conformal coating of the TiO₂ and furthermore, the CNT structure has been preserved. A uniform nucleation of TiO₂ layer on the CNT fibre surface is observed in *Figure 6.5b* with a good adhesion between a hybrid with 20nm of TiO₂ layer and a CNT bundle. *Figure 6.5b* also presents two inset with FFT and HRTEM images associated to anatase TiO₂, more specifically, to the (101) anatase plane that corresponds to a interplanar distance of 0.352nm.

Finally, *Figure 6.5c* corresponds to a STEM image obtained from high angle annular dark field (HAADF) detector that has been further analysed by energy-dispersion spectroscopy. The spectrum in *Figure 6.5d* shows signals from Ti, O, C and S, corresponding to both components. The mapping of Ti and O atoms shows the successful inorganic coating of the CNT bundles.

Figure 6.5: a) TEM image and b) HRTEM image of 20nm-TiO₂/CNTf sample showing the conformal coating of the CNT bundles. The FFT and HRTEM images of the inset demonstrate that the coating consists in anataseTiO₂. c) HAADF-STEM image of 80nm-TiO₂/CNTf sample and d) corresponding EDS spectrum and Ti, O mapping images.

The crystal structure of the samples annealed at 400°C for 1 hour has been analysed by XRD. *Figure 6.6a* shows the XRD patterns of the hybrid samples with different TiO₂ thickness, presenting all of them pure anatase phase in agreement with TEM observations. Effectively, the annealing at 400°C for 1h was enough to crystallise the thin layer of metal oxide into pure anatase phase, whose diffraction peaks are more pronounced in the samples with the higher coatings. *Figure 6.6b* presents the XRD patterns in the range of $2\theta=23-29^\circ$ and shows the deconvolution of this peak by fitting two Lorentzian curves. The most intense peak of the anatase phase, the (101) plane at 25.3° , is broadened by the contribution of the graphitic structure of the CNT fibre at about 26.5° , (002) plane. The change in position and width of the two peaks can be

6.1 Morphology and crystal structure of new TiO₂/CNTf hybrid

attributed to crystal size effects and/or microstrain induced by the inorganic growth on the CNT fibre surface.

Figure 6.6: a) XRD patterns of the hybrid samples annealed at 400°C in Ar atmosphere and corresponding to anatase phase. b) Magnification in the range of 23-29° showing the deconvolution of the anatase and carbon peaks.

Possibly, the growth of the inorganic on the CNTf surface has important influences on the crystal structure of both, TiO₂ and CNT fibre. The parameters of the fitted peaks were used to calculate the crystal size and also the microstrain of these batch of samples by using *HighScore Plus* software. *Table 6.2* shows the crystallite size of the anatase TiO₂ and the microstrain originated in the graphitic structure of the CNT fibre as consequences of the *in-situ* hybridisation process. As was observed in TEM images, the inorganic consists in a continuous and conformal coating the CNTf. Thus, the crystallite size calculated is ascribed to crystal domains more than to particle sizes. Yet, the crystallite size increases with the highest TiO₂ content, especially up to 40nm and then only small increases are presented. The *in-situ* growth of the inorganic on the CNT surface has produced an important interaction between them, leading to microstrain effects, more relevant for the thinnest anatase coating (*Table 6.2*). The microstrain, which is associated to a strain induced in the crystal lattice, can increase by small particles but also can be induced by the presence of defects. Furthermore, microstrain has been determined in the graphene sheet when it is interfacing with (101) anatase surface. The interaction between both components, for example through a chemical bond, cause disorder in the crystal lattice of the individual components. For example L. Ferrigui et al. have calculated a microstrain of 2-3% in graphene layer hybridised with anatase.[Ferrighi et al. 2016] The effects of the

TiO₂/CNTf interface can be extended a certain tens of nanometers towards the bulk TiO₂ structure. Yet, these interfacial effects on the strain induced in the crystal lattice has been better observed for the thinnest anatase coating since the interfacial area over the total analysed area is much higher for samples with lower TiO₂ thickness.

Table 6.2: Crystallite size and microstrain calculated from XRD patterns of *Figure 6.6b*, in particular, from the (001) anatase plane and (002) carbon plane.

Sample	Crystallite size (nm)	Microstrain
10nm_TiO ₂ /CNTf	8.20	$1.91 \cdot 10^{-2}$
20nm_TiO ₂ /CNTf	14.72	$1.07 \cdot 10^{-2}$
40nm_TiO ₂ /CNTf	17.22	$9.12 \cdot 10^{-3}$
60nm_TiO ₂ /CNTf	18.62	$8.43 \cdot 10^{-3}$
80nm_TiO ₂ /CNTf	18.79	$8.31 \cdot 10^{-3}$

Overall, the characterisation of these samples has confirmed the optimum strategy to produce hybrid with controlled deposition of the inorganic on the CNTf surface. The choice of ALD has enabled the control on the morphology, resulting in a conformal growth of amorphous TiO₂ layer on the CNT bundles. The annealing at 400°C for 1h under Ar atmosphere produces anatase TiO₂ and preserves the conformal coating obtained by ALD. Furthermore, a close contact between both components has been observed in TEM images. Importantly, XRD analysis point out to a residual strain in the hybrid, which itself provides evidence of the strong interaction between the two phases.

6.2 Understanding the electronic structure of TiO₂/CNTf hybrid

Raman spectroscopy is widely used to characterise sp² graphitic materials and evaluate their structure. In the content of this work, it can help to determine the effects of metal oxide deposition and subsequent annealing on the graphitic structure of the fibre.[Pimenta et al. 2007] All the measurements have been performed using identical experimental conditions to avoid laser-induced effects in the TiO₂/CNTf structure. Thus, the comparison of the Raman modes can be correctly compared.

6.2 Understanding the electronic structure of TiO₂/CNTf hybrid

The structure of the TiO₂/CNTf produced by ALD has been evaluated before and after annealing, as illustrated in *Figure 6.7*. The main bands of MWCNT Raman spectra are identified as G-band presented around 1580 cm⁻¹, the D band at about 1345cm⁻¹, the D' at about 1620cm⁻¹, and the 2D (also known as G' mode) at about 2685cm⁻¹. More specifically, the G and 2D modes correspond to vibration of the hexagonal lattice of sp² carbon atom. The D and D' modes indicate the presence of structural defects/disorders in the graphitic carbon structure. Both modes are used as indication of the sp³ contribution of C atoms.[Dresselhaus et al. 2005]

Figure 6.7: Raman spectra of as-grown CNTf and TiO₂/CNTf hybrids a) before and b) after annealing at 400°C for 1h in Ar atmosphere.

Minor differences are observed for the spectra obtained before and after annealing (*Figure 6.7*). The as-grown CNT fibre, also annealed at 400°C, presents minor shifts of its Raman bands ($\sim 1\text{cm}^{-1}$) and their intensity is similar, confirming that the annealing does not significantly affect to the CNT structure. However, the comparison between the CNT structure of as-grown fibre with that of the hybrids reveals a huge increase of the D band, increasing the D/G intensity ration from 0.18 to about 1.2. Similarly, D' band is more pronounced for the hybrid samples. On the one hand, the increase of the D and D' modes can arise from the O₂ plasma used as oxidising agent during the ALD process, which can damage the CNTs. On the other hand, the defects observed in the Raman spectra can be associated to the interaction formed during the hybridisation process (ALD deposition of molecular precursors on the CNTf surface). It is noteworthy that the metal oxide can catalyse the oxidation of the CNT fibre, however, this effect has been determined for higher temperatures (565°C) in oxidising (air) atmosphere[Aksel and Eder 2010] and thus, it can be discarded.

In order to investigate if the CNT fibre structure has been changed due to the interaction with the titanium precursor or however, due to the oxidation pulse (300W oxygen plasma) of the ALD process, a sample of CNT fibre was subjected to the ALD process in the absence of precursors. Raman spectra of this sample is compared to pristine CNT fibre and a hybrid sample (*Figure 6.8*), including the D/G ratio for each spectrum. Clearly, the hybridisation from C sp² to C sp³ is observed in the sample just exposed to the oxygen plasma during ALD process, as confirms the abrupt increase in D/G ratio from 0.18 to 0.91. Hence, the plasma treatment of the ALD process oxides the CNT fibres but it is expected to occur only during the first ALD cycles, where the CNT fibre surface is still exposed.

The oxidation of the CNT fibre surface produces a more chemically reactive surface of the CNT fibre, necessary to anchor the metal oxide. But very importantly, this work has shown (*Section 4*) that an appropriate surface functionalisation of the nanocarbons leads to a stronger interaction between phases of the hybrid. In addition to the increase of D/G ratio for the hybrid sample, the hybridisation with metal oxide produces a shift of the hybrid spectrum. The shift of its Raman modes to higher wave-number is a consequence of the interaction created between both components since this effect has not been observed in fibres exposed only to the O₂ plasma. Thus, this shift indicates a distortion of the graphitic structure that occurs at the inorganic/nanocarbon interface.

Figure 6.8: Raman of pristine CNTf (black line) and CNTf treated by ALD without (red line) and with (blue line) pulses of inorganic precursor.

6.2 Understanding the electronic structure of TiO₂/CNTf hybrid

The Raman spectra of the pure CNT fibre and TiO₂/CNTf hybrids with different thickness of anatase TiO₂ (Figure 6.7b) were fitted using mixed Gaussian/Lorentz peak functions. The fitting values of peak positions and intensity ratios between Raman modes are presented in the Table 6.3.

Table 6.3: Raman peak position, I_D/I_G and I_{D'}/I_G ratios for hybrid with several TiO₂ thickness and annealed at 400°C.

TiO ₂ layer (nm)	Position (cm ⁻¹)				I _D /I _G	I _{D'} /I _G
	D-band	G-band	D'-band	2D-band		
0	1344.4	1578.8	1619.6	2679.5	0.18	0.06
10	1351.2	1583.1	1619.8	2692.5	1.24	0.28
20	1352.4	1584.4	1620.9	2695.2	1.17	0.28
40	1352.7	1585.0	1621.6	2695.4	1.17	0.27
60	1352.93	1585.24	1621.95	2695.73	1.15	0.28
80	1352.48	1585.13	1622.16	2695.47	1.20	0.27

The graphitic structure of the pristine CNT fibre (0nm thickness) is clearly influenced during the hybridisation process with TiO₂, producing an important shift in all the Raman bands. The increase of the TiO₂ thickness produces a more disordered structure as evidences the higher displacements in the Raman modes of the hybrid compared with pure CNTf (Figure 6.9). The dash lines of the Figure 6.9 correspond to the position of the Raman modes for the CNT fibres only exposed to the plasma, showing minor displacements and highlighting the effect of the interaction between the metal oxide and the CNTf.

Shifts in the D peak of 6.8-8.6cm⁻¹ can arise from stress induced by the nucleation and growth of TiO₂ on CNTf surface, which agrees with the microstrain determined from XRD measurements. The distortion induced in the CNT structure due to the TiO₂ formation can be also observed in its overtone, the 2D band, which presents a displacement of 13-16cm⁻¹. Interestingly, the G peak is shifted 4.3-6.5cm⁻¹, which expresses changes in the C-C bonds of the graphitic structure. Finally, the higher intensity and also, shift of the D' mode can arise from external induced defects such as bending of the inner/outer cylinders or by physical/chemical functionalization treatments.[Wang et al. 2012b; Ali et al. 2013; Curran et al. 2005] Therefore, the interaction between both components, TiO₂ and CNT fibre with a close interface, modifies

the carbon lattice for example through the C-O-Ti bonds, thus displacing the Raman modes.[Min et al. 2012; Yu et al. 2005; Ahn et al. 2006]

Figure 6.9: Shift of the CNT Raman modes as a function of the TiO₂ thickness in TiO₂/CNTf hybrids. Dash-dot lines represents the peak position for the CNTf exposed only to O₂ plasma.

The D/G and also D'/G intensity ratios of Table 6.3 are illustrated in Figure 6.10 for the pristine CNTf and 10-80nm TiO₂/CNTf hybrid samples. Also, the CNT fibre treated with O₂ plasma is represented with dash lines. The small D/G ratio (0.17) of the as grown CNT fibre confirms the low defect density of the raw material. Either plasma or inorganic deposition produces an increase of the D mode intensity. Commonly, the D/G intensity ratio is used as indication of the quality of CNTs in terms of defects in the graphitic structure. This ratio is preserved in the CNT fibre treated at 400°C in Ar for 1h, which confirms that annealing has not influence on the CNT structure. However, it significantly increases in the fibres treated with plasma (up to 0.91) and even more in the final hybrid, up to ~1.2. Similarly, the intensity of the D' peak is increased for the fibre treated by ALD, especially after the interaction with the inorganic. The increase of this band is attributed to changes in the density of states (DOS) induced by the formation of defects or interaction by physical and/or chemical functionalisations.[Curran et al. 2005] Thus, this peak evidences that a more chemically reactive surface of the CNTs enables an important interaction with the TiO₂ during the *in-situ* growing from molecular precursors.

Figure 6.10: Intensity ratio of D and D' mode with respect to G mode as a function of the TiO₂ thickness in TiO₂/CNTf hybrids. Dash-dot lines represents the peak position for the CNTf exposed only to O₂ plasma.

In addition to the study of the CNT structure, Raman spectroscopy also enables to determine the structure of TiO₂ separately to that of the CNT fibre. Similarly, structural disorders in the TiO₂ originated during their growth on the CNT surface can be determined. The Raman spectra of the TiO₂ was only observed for those samples annealed at 400°C, which present a crystalline anatase TiO₂ structure. *Figure 6.11* shows the low wavenumber region of CNT fibre and the annealed TiO₂/CNTf hybrid samples. The Raman spectra presents the modes of TiO₂ anatase, which are clearer observed for the highest thickness of TiO₂. Raman bands at about 147 (E_g), 199 (E_g), 395 (B_{1g}), 514 (A_{1g}) and 636 cm⁻¹ (E_g), all correspond to anatase TiO₂ phase.[Ohsaka et al. 1978] The most intense anatase peak is centred at about 147 cm⁻¹ and shifted up to 150 cm⁻¹ for the samples with the smallest TiO₂ thickness. Yet, the Raman modes for all the hybrids are shifted to higher frequencies in comparison with bulk anatase Raman modes (in the range of 6-9 cm⁻¹). As was commented above, the interfacial effects become more important for very thin layer of TiO₂ and thus, the effects of a possible formation of Ti-O-C bonds can be better studied for the thinnest coating.

Figure 6.11: Raman spectra of anatase active modes for the pure CNTf and TiO₂/CNTf hybrids. The inset shows a magnification of the most intense peak, where a shift to lower wavenumber is observed when the TiO₂ layer increases.

Further information of the chemical composition and environment of the atoms in the TiO₂/CNTf hybrid material has been investigated by photoelectron spectroscopy for a TiO₂ thickness of 20nm produced by ALD and using water as oxidising agent. The layer of TiO₂ is presumably thin enough to study the effects of the interface between both components in the hybrid since they are expected to affect various tens of nanometers to the bulk. The XPS spectra of the C1s in the TiO₂/CNTf hybrid is presented in *Figure 6.12* in comparison with that of the pristine CNT fibre and TiO₂. For a better understanding of the hybrid material, the three spectra have been fitted with mixed Lorentzian/Gaussian curves (*Figure 6.12a-c*). In order to minimise the contribution of carbon species adsorbed at the surface, a 24 hours degasification of the sample was done prior the experiment, yet a contribution of adsorbed species might be presented. In this regard, the C1s spectra for pure TiO₂ produced by ALD is shown in *Figure 6.12c* and it can be very useful for its comparison with the hybrid spectra. Pure TiO₂ may only contain carbon from titanium precursor and/or adsorbed species at the TiO₂ surface. Hence, the pure TiO₂ presents two main peaks, the C-C signal presented at 284.8eV and corresponding to C sp³ hybridisation and a considerable contribution of C-O species at 287.6nm, possibly arising from carbonates species.

6.2 Understanding the electronic structure of TiO₂/CNTf hybrid

The XPS spectra of the pristine CNT fibre (*Figure 6.12b*) presents a large contribution of C-C sp² hybridisation. In addition, it shows a small peak from the C-C sp³ hybridisation as well as a small C-O signal. Finally, the CNTf spectra shows a wide band between 288-292eV that is assigned to O-C=O species and importantly, π - π^* interactions between the CNT bundles.[Reguero et al. 2014]

Figure 6.12: C1s region of XPS spectra for a) 20nm_TiO₂/CNTf hybrid, b) pristine CNTf and c) pure TiO₂ sample.

The fitting of the C1s region of the hybrid (*Figure 6.12a*) presents the contribution of the graphitic structure of the CNT fibre with an increased contribution of the C sp³ hybridisation and C-O species, in agreement with Raman observations. The similarity of the hybrid spectra with the pristine CNT fibre (more than with the pure TiO₂) suggests that the changes in the C region can be mainly ascribed to the hybridisation process, which modifies the graphitic CNTf structure. Yet, the spectra is not free of adsorbed species at the TiO₂ surface, which contribute to the spectra and limit the spectra quantification.

Additionally, *Table 6.4* shows the FWHM for all the contributions fitted in the C1s region of the three spectra. The *Table 6.4* shows an increase of the peak width of the hybrid in comparison with the CNTf, especially for the C sp² hybridisation whom width increases about the double in comparison with the pristine material. Finally, the width of O-C=O contribution in the hybrid spectra, which is the half than that for the pure CNT fibre, is due to the loose of π - π^* interactions between CNT bundles. This confirms the modification of the CNTf structure by the inorganic coating of the CNT bundles and importantly, suggests that the formation of C-O-Ti bonds at the hybrid interface is totally plausible.

Table 6.4: FWHM of C1s contributions for the TiO₂/CNTf and CNTf spectra.

	TiO ₂ /CNTf	CNTf
C-C sp²	1.69	0.88
C-C sp³	2.68	1.2
C-O	1.64	1.8
O-C=O	2.06	4.43

The XPS of the Ti2p region is presented in *Figure 6.13a*. Ti 2p_{3/2} at 458.4eV and Ti 2p_{1/2} at 464.2eV peaks are assigned to spin-orbit interaction of the Ti⁴⁺ states with a splitting of 5.8eV, which is in agreement with TiO₂ structure.[Umrao et al. 2014] No evidences of Ti³⁺ are observed, which confirms that the metal oxide has not been reduced as consequence of annealing in inert atmosphere during synthesis.

Figure 6.13b also presents the XPS spectra of O1s region for the hybrid sample. The deconvolution of the spectra (*Figure 6.13b*) correspond to the contribution of Ti-O-Ti (529.5eV), Ti-O-X (532eV) and C-O (533.3eV) bonds.[Umrao et al. 2014] The peak at 532eV is associated to an oxygen bonded with Ti and a heteroatom, such as an interfacial Ti-O-C bonds or as Ti-O-H species, the latter commonly presented at the TiO₂ surface. The content of C-O species in the hybrid together with the high presence of Ti-O-X bond confirms the interaction between both components. During the hybridisation process, the oxidation of the plasma treatment is expected to increase the O bonded with C atoms, which later are able to interact with the TiO₂. In the case of a chemical bonding between both compounds, through Ti-O-C, the oxygen atom is the one that can reveal more information about the electronic change in its coordination environment.

6.2 Understanding the electronic structure of TiO₂/CNTf hybrid

Figure 6.13: a) Ti2p and b) O1s region of XPS spectra for 20nm_TiO₂/CNTf.

Combination of XPS with UPS enables to study the electronic structure of the new hybrid material at surface levels. UPS provides information of the valence band electrons due to the lower energy excitation of the UPS (21.2eV) compared with XPS (1253.6eV) technique. The low penetration depth of the UPS technique (~ 2 nm) will only enable to study the surface electronic effects. *Figure 6.14a* illustrates the full UPS spectra of the pure CNT fibre, TiO₂ and a hybrid TiO₂/CNTf with 20nm of ALD coating. The TiO₂/CNTf hybrid presents a UPS spectrum similar to that of TiO₂, although it is wider, especially at the low binding energy, suggesting a higher density of states.

In the UPS spectra analysis, the onset at the lowest and highest binding energies reveal the effects of the interface in the electronic structure of the hybrid material. *Figure 6.14b* shows the secondary electron cut-off energy, which enables determination of the work function by subtracting the onset from the photon energy (21.2eV). The pure CNT fibre has a work function of 4.41eV, which perfectly agrees with literature values for MWCNTs as well as high ordered pyrolytic graphitic materials (HOPG).[Ago et al. 1999] The work function of the TiO₂ is 4.23eV, also in the range of TiO₂ literature values.[Farsinezhad et al. 2015b] Finally, the work function of the hybrid sample is 4.27eV, an intermediate value between both materials but closer to that of the TiO₂ work function.

Figure 6.14: a) Full UPS spectra and b) secondary electron cut-off of CNT fibre (black line), TiO₂ (red line) and TiO₂/CNTf hybrid (blue line).

The low binding energy region displays the clearest evidence of different electronic structure of the hybrid material in comparison with pure components. *Figure 6.15* shows the position of the valence band maxima, which can be determined from the intercept between the tangents of the spectra and the baseline. The CNT fibre presents (*Figure 6.15a*) a continuous density of states up to the Fermi level, which agrees with the metallic behaviour of the MWCNTs. For the TiO₂ produced by ALD (*Figure 6.15b*), the valence band maxima is determined at 2.59 eV with respect to the Fermi level, which is lower than the bulk band gap energy of anatase TiO₂ (~3.2 eV) but in the range of reported values for oxygen-deficient TiO₂. [Sarkar et al. 2016]

Finally, the hybrid sample (*Figure 6.15c*) presents the maxima valence band at 1.05 eV below the Fermi level, which is significantly smaller than that from TiO₂. The presence of Ti³⁺ species usually appear as a small band at this energy. [Connelly and Idriss 2012] However, the presence of reduced titania was not detected by XPS analysis and the hybrid spectrum presents a continuous density of states from ~1 eV instead of a small band. Overall, UPS data show a very high density of states of the hybrid in comparison with that of the TiO₂. A clear implication is that the presence of the CNT causes changes in the electronic structure of pure TiO₂ over large distances.

6.2 Understanding the electronic structure of TiO₂/CNTf hybrid

Figure 6.15: UPS spectra showing the valence band region of a) CNTf, b) TiO₂ and c) TiO₂/CNTf hybrid.

In summary, the electronic structure of TiO₂ and CNTf have been considerably affected by the *in-situ* hybridisation process of metal oxide nanocrystals nuclei and growth on CNT surface. This induces defects in the carbon network through the huge interfacial interaction between both components. The hybridisation process could induce defects from mechanical strain, electrical doping or more probably, chemical functionalisation. All of them produces changes in the electron-phonon coupling, which explain the displacements of the Raman modes. Similarly, the anatase Raman modes have been affected during the ALD process. At the nanoscale, the thickness, morphology, structure and porosity of the metal oxide have huge influences in the charge transfer processes between both materials. Therefore, Raman analysis has provided useful insights into interfaces that consequently, will facilitate electron transfer process and finally will improve the performance of the hybrid material. Additionally, photoelectron spectroscopy has enabled to determine the electronic structure of the hybrid material, which shows that overall, the hybridisation of the nanocarbons with the inorganic molecular precursors plays an important role in the interface formation, leading to the metal oxide growth on their surface and importantly, remaining them chemically bonded. Finally, this leads to the formation of additional states within the TiO₂ band gap facilitating charge transfer and transport processes. These observations agree well with theoretical studies that predict the onset in binding energy at 1.74 eV for TiO₂/graphene hybrid, indicating a very strong interaction between both components. Furthermore, this simulation reveals that the electronic behaviour of a hybrid material cannot be explained with classical junction models.[Ferrighi et al. 2016]

6.3 Electrochemical properties of new TiO₂/CNT fibre hybrid

The photoelectrochemical properties of TiO₂/CNTf hybrid electrodes were analysed for thickness of TiO₂ ranged between 10 and 80nm. *Figure 6.16* shows an electron micrograph of a TiO₂/CNTf electrode. It consists in a CNTf film with TiO₂ layer of 20 nm coating the CNT bundles of the surface whereas the inner CNT bundles are not coated with the inorganic. Moreover, all the CNT bundles are connected between them, forming the fibre structure and acting as pathway for the photogenerated electrons in the TiO₂. Furthermore, the morphology of the new hybrid with the inorganic covering a very high surface area of the CNT fibre, provides large semiconductor/liquid interfaces.

Figure 6.16: Scanning electron micrograph of TiO₂/CNTf hybrid electrode with 40nm of inorganic deposition.

The electrochemical measurements were carried out in a standard three electrode cell with 0.1M Na₂SO₄ electrolyte at pH 2 and using a Pt wire as counter electrode and Ag/AgCl reference electrode. The TiO₂/CNTf electrodes annealed at 400°C for 1h in Ar atmosphere were used as working electrodes with an active area of 5cm². In order to study the electronic behaviour of the hybrid, the change of the open circuit potential and the photocurrent density have been studied for the TiO₂/CNTf electrodes with different TiO₂ thickness. The electrochemical measurements were recorded using a *SP-200 BioLogic* potentiostat under dark and illumination conditions (150W Xe lamp,

6.3 Electrochemical properties of new TiO₂/CNT fibre hybrid

$\lambda < 400\text{nm}$). The power density of the UV light that reached the surface of the TiO₂ is $530\text{mW}/\text{cm}^2$.

Conventional open circuit potential was measured with and without illumination to study the photo-excited voltage generated by the UV illumination. *Figure 6.17* shows the changes in the OCP upon irradiation for the hybrid electrodes. The switching on the UV light produces a negative shift in the OCP, which indicates n-type semi-conducting behaviour with electrons as majority carriers. The photogenerated electrons in the conduction band of the TiO₂ change the surface potential of the hybrid.

Figure 6.17: Open circuit potential measurements of TiO₂/CNTf hybrid photoelectrodes.

To verify the effects of charge separation and/or accumulation upon illumination, the photocurrent transient have been measured by chronoamperometry measurements at zero bias potential. *Figure 6.18* presents the photocurrent density for all the TiO₂/CNTf hybrids. The irradiation with UV light produces a positive increase of the photocurrent density values, which is characteristic of photoanodes. All the samples present a quick response to the on/off of the incident light and also show that the photocurrent density is highly dependent on the TiO₂ layer. The photocurrent density reaches 2, 8, 16, 23 and $22\mu\text{A}/\text{cm}^2$ for the TiO₂/CNTf samples with 10, 20, 40, 60 and 80nm, respectively. The photocurrent density increases with the thickness, reaching the maximum for 60nm TiO₂ layer and further increase of the inorganic coating decrease the photocurrent density. For example, the sample with 80nm of TiO₂ present a slightly lower photocurrent than that of the 60nm TiO₂.

Figure 6.18: Chronoamperometry curves at OCP of TiO₂/CNTf hybrid photoelectrodes.

The kinetic of the charge transfer at the hybrid electrodes annealed at 400°C has been studied by electrochemical impedance spectroscopy in the dark and illumination conditions. The hybrid sample with 40nm TiO₂ layer has been chosen for the electrochemistry impedance study. This sample presents a CNTf surface completely covered by the inorganic, avoiding contributions from the CNTf/liquid interface. The impedance measurements were carried out at zero applied voltage, in the frequency range of 10kHz-10mHz and using 10mV of signal amplitude. *Figure 6.19* shows the Nyquist and Bode plots of the TiO₂/CNTf sample studied before and after UV irradiation. The impedance spectra consist in an open semicircle with smaller arc diameter for the sample measured under UV irradiation than that measured in dark conditions. The smaller arc diameter in a Nyquist plot is related to a higher efficiency of the charge separation.

The EIS data have been analysed by fitting the impedance spectra with the equivalent circuit model of *Figure 6.20*. The lines of the Nyquist and Bode plots (*Figure 6.19*) correspond to the fit spectra using this equivalent circuit. The chosen equivalent circuit model, explained in *Section 5.2*, has been commonly used in literature for metal oxide thin films, although one of its limitations is that it cannot separate the effects from the surface than that from the bulk semiconductor material.[Lopes et al. 2014b] Briefly, the circuit consists in a series resistance (R1) that contains all the external resistance contributions such as the resistance of the electrolyte or the wires. The

6.3 Electrochemical properties of new TiO₂/CNT fibre hybrid

semiconductor/liquid interface is modelled by two double RC circuits in series. The first corresponds to the Helmholtz layer (Q2) at the electrolyte side and the charge transfer resistance at the TiO₂/electrolyte interface. The second RC element describes the space charge layer (Q3) at the hybrid side, and its resistance (R3). Both capacitances are represented by constant phase elements due to the non-ideal behaviour of the nanostructured semiconductors.

Figure 6.19: a) Nyquist and b) Bode plots of the EIS raw data (scatter) and fit data (lines) of TiO₂/CNTf hybrids with 40nm of TiO₂ coating after annealing in Ar at 400°C for 1h.

The impedance spectra of the hybrid have been also fitted with a three RC circuit in series in order to separate the effect of the TiO₂ from that of the CNT fibre. However, the fitting gives negative values for the third RC elements, which suggests that the charge transfer resistance of the TiO₂/CNTf interface is negligible. This circuit reinforces the view that the CNT fibre provides direct electric contact to the semiconductor. Although a prior Q3 could contain features of the CNT/TiO₂ interface.

The parameters of the chosen equivalent circuit were obtained by the fitting of the impedance spectra and are shown in *Table 6.5*. At low frequencies, the electrochemical processes are ascribed to the semiconductor/electrolyte interface whereas at higher frequencies, the electrochemical processes are attributed to the semiconductor material. This is due to charge transfer processes at the semiconductor/liquid interface as well as ion diffusion are slower processes than the charge transfer and transport processes within the semiconductor material, either surface or bulk. Hence, the resulting parameters are significantly different before and after illumination except to the series resistance, which is 28 Ω for both conditions. For the low frequency

6.3 Electrochemical properties of new TiO₂/CNT fibre hybrid

processes at 0V, the Helmholtz capacitance takes values of 47.7 and 52.4mF whereas the charge transfer resistance takes values of 562.5 and 180.3 Ω for dark and light conditions, respectively. Effectively, the photogeneration of electrons in the conduction band of the semiconductor increases the photocarrier density at the semiconductor/electrolyte interface and leads to more favourable charge separation and transfer processes.

Figure 6.20: Proposed equivalent circuit model for the TiO₂/CNTf hybrid photoelectrodes.

At the high frequency range, the capacitance of the semiconductor material takes values of 187.3 and 254.8mF for dark and illumination conditions, respectively. This semiconductor capacitance is one order of magnitude higher than the Helmholtz capacitance, which is in contrast to the expected behaviour. Usually, the majority carriers generated upon illumination are extended into the bulk semiconductor, forming the space charge layer in the semiconductor side of the semiconductor/electrolyte interface. This layer is usually wider than the Helmholtz layer, formed at the electrolyte side by accumulation of water ions of opposite charge. The result would be a semiconductor capacitance lower than the Helmholtz capacitance. In this context, the high capacitance of the hybrid is attributed to its high density of states in the bandgap arising from the hybridisation process. In addition to the new states in the hybrid, the quantum capacitance of the CNT fibre itself should be considered.[Senokos et al. 2016] This material might present a different dielectric constant to that of the metal oxide, which can perturb the capacitance of the hybrid material. In fact, the very low

6.3 Electrochemical properties of new TiO₂/CNT fibre hybrid

exponent of the semiconductor capacitance can be ascribed to the influence of the CNTf capacitance. Finally, the semiconductor resistance takes values of 443.9 and 11.82 Ω for dark and light conditions, respectively. The very low resistance of the semiconductor under UV irradiation evidences that the photocarriers can be easily separated through the interaction between the metal oxide and the nanocarbons.

Table 6.5: Parameters obtained by fitting the EIS spectra of the hybrid photoelectrodes using the equivalent circuit R1+R2/Q2+R3/Q3.

	R1 (Ω)	Q2 (F·s ^{a-1})	a2	R2 (Ω)	Q3 (F·s ^{a-1})	a3	R3 (Ω)	χ^2 (10 ⁻³)
TiO ₂ /CNTf_dark	28	0.0477	0.99	562.5	0.1873	0.42	443.9	1.64
TiO ₂ /CNTf_light	28	0.0524	0.94	180.3	0.2548	0.33	11.82	1.33

In summary, the electrochemical measurements have revealed the attractive properties of the new TiO₂/CNTf hybrids for their use as photoelectrodes. The most probable scenario is that after electrons are excited from the valence band to the conduction band of TiO₂, they are trapped rapidly in surface states within the TiO₂ bandgap and become localised. Furthermore, a more efficient separation of photoinduced electrons and holes could be obtained through the electronic interaction between the TiO₂ and the CNT fibre. Thus, the hybrid samples facilitate the charge transport and enhance interfacial charge transfer processes, finally leading to higher photocatalytic performance.

6.4 Summary

The *in-situ* synthesis of TiO₂ by ALD on the CNT fibre surface has resulted successful since a conformal inorganic coating has been achieved on the CNTf surface. The subsequent annealing in inert atmosphere of the hybrid material has enabled the crystallisation of the metal oxide whereas the morphology has been preserved. Furthermore, the CNT fibre structure has not been highly degraded nor during hybridisation by ALD nor during annealing. As a result, the CNT fibre can be considered a very attractive material for their use as planar electrode due to the very high electron conductivity and high surface area that enables the formation of huge inorganic/nanocarbon interface. Consequently, interfacial effects on the hybrid structure

has been confirmed by XRD and Raman spectroscopy. The CNT fibre structure has been modified by the inorganic growth on their surface. The formation of Ti-O-C is completely plausible during the ALD treatment since the oxidising agent can originate a more chemically reactive CNTf surface and can easily interact with the inorganic molecular precursors. The result is the formation of huge interfaces between the two components chemically bonded. Importantly, the interfacial effects have also affected to the electronic structure of the hybrid material. The formation of Ti-O-C bonds, confirmed by XPS, provides a higher density of states within the TiO₂ bandgap. Finally, the improvements due to the electronic structure of the hybrid material are confirmed by its electrochemical properties. The new hybrid presents n-type semiconducting behaviour with electrons as majority carriers and a very efficient charge separation, especially under illumination conditions. This leads to large photocurrent density values and confirms its use as photoanode material for energy applications.

CHAPTER 7

CONCLUSIONS AND FUTURE WORKS

7.1 Conclusions

The main purpose of this work is the development of new materials for clean energy, for the post-fossil era. A photocatalyst material that uses the sunlight as energy source and produces a powerful and clean fuel such as hydrogen has been investigated using a bottom-up approach for the fabrication of inorganic/nanocarbon hybrid materials. The following conclusions can be drawn from the analysis that outcomes this thesis.

Hybrid materials formed by molecular engineering of nanocarbons and nanoscale semiconductors has enabled the formation of TiO₂/nanocarbon hybrids. The *in-situ* hybridisation of the inorganic from molecular precursors with the nanocarbons using sol-gel method and electrospinning technique has resulted in one-dimensional mesoporous hybrid fibres. The use of the polymer as requirement for electrospinning agglutinates the inorganic domains and embeds the nanocarbons within the inorganic fibre structure. This leads to interconnected TiO₂ nanocrystals along the fibre structure and rises to large interparticle contacts similar to multiple grain boundaries. In contrast, nanoparticles produced by standard sol-gel process lead to randomly agglomerations of nanoparticles with poor contact between them.

7.1 Conclusions

The crystallisation of the inorganic requires a relatively high temperature (500°C) and due to the thermal stability of the nanocarbons, the heat treatment was carried out in Ar. This affected to the structure and composition of the inorganic and finally to the properties related to the structure of the hybrid material. In particular, the absence of oxygen in Ar atmosphere leads to the formation of oxygen-deficient TiO₂ that among other effects, favours the rearrangement of Ti-O octahedral from anatase to rutile phase, which has important consequence in its properties.

It should be emphasised the importance of the interfaces created between the TiO₂ and the nanocarbons as a key parameter for the emerging properties of the hybrid material. The strategy of functionalisation leads to a more chemically reactive surface of the nanocarbons, enabling an improved dispersion during the molecular assembly of the inorganic precursor and consequently, forming large interfaces between TiO₂ and nanocarbons. During the synthesis, the functional groups of the nanocarbons react with the inorganic precursors and form Ti-O-C bonds that keep strongly coupled the two components of the hybrid material. This interaction produces distortions in the structure of both components as is confirmed by Raman spectroscopy. But very importantly, photoelectron spectroscopy has demonstrated the emergency of a new electronic band structure as results of the Ti-O-C bonds at the hybrid interface. Interfacial states up to ~1.2eV above the valence band of the TiO₂ has been observed in the UPS spectra of the hybrids with chemically functionalised nanocarbons, either CNTs or graphene. However, pristine nanocarbons result detrimental for the electronic band structure of the corresponding hybrids. This emphasises the relevance of the interface for a successful hybridisation since the new intra-band gap are crucial for photoinduced process.

Overall, the original contribution of this study is that covalently attached nanocarbons to TiO₂ are far from the idea of metal/semiconductor compounds junctions since the interface is not planar and the functionalised nanocarbons are not really metals but rather high mobility semi-metals or even semiconductors.

The hybrids and pure semiconductors have been tested as photocatalyst for sacrificial water splitting using a co-catalyst. They present remarkable photocatalytic hydrogen production with a very rapid activation. Several aspects has been considered

to understand the structure-properties relation with the improvement in photocatalytic activities. The fixed conditions for the *in-situ* hybridisation have been designed according to the effects of the resulted morphology and structure on its photocatalytic performance. In this sense, TiO₂ nanoparticles produced by standard sol-gel process and annealed under identical conditions have been very instructive for the understanding of the fibre morphology and structure by comparison with the formers.

The enhancement in the hydrogen production of the electrospun fibres is ascribed to the TiO₂/TiO₂ interfaces, which facilitate internal charge transfer along the nanoparticles network in the fibre. In contrast, randomly aggregated nanoparticles might be loose the contact between nanocrystals, resulting in very low efficiencies in the hydrogen production even when they present about the double of surface area. This has been also demonstrated by CO₂ photoreduction experiments. The increase of carbon and hydrogen containing products produced by TiO₂ fibres in comparison with nanoparticles has led to an increase of 4 and 5 times higher, respectively. In fact, the CO₂ photoreduction has been improved for the hierarchical fibre structure, reaching higher efficiencies than commercial P25. However, in this particular case, the hybrid fibres have not improved the photocatalytic activity of pure fibres, but have overcome those of the nanoparticles. Other important feature of the electrospun fibres is its phase composition with anatase-to-rutile ratio ranged principally between 0.8-0.98, which has resulted very favourable for its photocatalytic performance.

Therefore, the improvements in the morphology and structure of the inorganic have resulted beneficial for photocatalysis since the agglomerations of nanoparticles in the fibre improve the charge separation through interparticle contacts. Importantly, the alignment of the band structure of anatase and rutile phases supports the enhanced charge separation, delaying thus the electron-hole recombination as is further confirmed by photoluminescence and finally, leading to higher photocatalytic efficiencies.

The effect of the TiO₂/TiO₂ and TiO₂/nanocarbon interfaces on the electron transport properties has been studied by the preparation of a single fibre device, further very useful as photodetector. The conductivity of the nanofibres even in dark condition are significantly high, showing about two order of magnitude higher than

7.1 Conclusions

typical mesoporous films of TiO_2 . The high electrical conductivity is a direct consequence of its morphology and structure, consisting in oxygen deficient nanoparticles interconnected along the electrospun fibre structure. Photogating effect in UV range has been determined as majority conducting mechanism through the oxygen vacancies presented in the fibre. The additional presence of CNTs in the hybrid fibres increases the UV photoresponse but especially the photoresponse in the visible range, reaching up to 2 order of magnitude higher than bare TiO_2 fibre.

The electrochemical properties of the fibres has been analysed by the preparation of electrodes by spray coating from a fibre dispersion either pure TiO_2 or TiO_2/CNT hybrids. In addition, a sample of TiO_2 fibres annealed in air atmosphere has been analysed to separately study the effects of the oxygen vacancies from those of the CNTs presence. The electrochemical processes have been evaluated in dark and illumination conditions, which has enabled the study of its behaviour for further use as photo(electro)catalyst material. The high electron transport of the TiO_2 fibre annealed in Ar due to the presence of oxygen vacancies below the conduction band and the high donor density improve the charge transfer processes at the solid/liquid interface. In addition, the electrochemical properties of the solid/liquid interface in the hybrid material have been improved by increasing the donor density and reducing the flat band potential. Also, lower resistance to the charge transport was determined since they can act as electron pathways. Overall, the additional electronic states within the band gap provides higher donor density and enables a very efficient charge separation, finally prolonging the photocarrier lifetime.

The agreement of the electronic band structure and the electrochemical properties of the hybrid material has been effectively probed in higher photocatalytic efficiencies. The enhancement of about 20% on the hydrogen production with only 1vol.% of CNTs with respect to pure TiO_2 fibre is attributed to the strategy of using functionalised nanocarbons. In contrast, pristine nanocarbons decrease the hydrogen evolution rate, possibly because the agglomerations of nanocarbon during the synthesis reduce considerably the interfacial contacts with the metal oxide, resulting in a worst charge separation. This is good agreement with the electronic structure of both hybrid materials. Overall, the key parameter of the hybrids with functionalised MWCNTs and graphene is the successful hybridisation achieved by in-situ approach,

which favours the charge separation through covalent interaction at the TiO₂/nanocarbon interface.

The interest emerging from the interface between TiO₂ and nanocarbons has been further exploited in TiO₂/CNT fibre hybrids with large interfacial contact. The controlled deposition of TiO₂ on the surface of the CNT fibre has resulted in a film of TiO₂ coating the CNT fibre bundles. The fact that the macroscopic fibre remains interconnected the bundles of CNTs makes this new hybrid a very attractive material with potential applications in photo(electro)catalysis since they can favour the charge separation and act as current collectors. In this case, the formation of a covalent bond is plausible by the oxidation of the bundles during the oxidation and posterior hybridisation with molecular precursor of the ALD process. Similar to the electrospun hybrid fibres, strong interactions have been observed in this new hybrid material and a high density of states has been confirmed by photoelectron spectroscopy. Furthermore, electrochemical studies show an improvement in the charge separation upon irradiation, which is related to a higher efficiency in energy applications.

7.2 Future work

As crucial point in the molecular engineering of the nanocarbons with inorganic nanoparticles to create large interfacial contacts, the development of functionalisation strategies, for example for the macroscopic CNT fibre could be very useful for its hybridisation with inorganic by chemical methods and exploits new types of hybrids based on a macroscopic material with the properties of the CNTs.

The knowledge gained for the electrospun TiO₂/nanocarbon hybrids can be applied to other inorganic semiconductors with suitable band structure for the photocatalytic applications. The possibility of electrospun aligned fibres or core-shell structures makes more interesting the exploitation of this technique for the fabrication of as photo(electro)catalyst. The use of other semiconductor photocatalyst could lead to a free co-catalyst and/or sacrificial agent during the water splitting treatment. Furthermore, the lower efficiency of the hybrid compared with pure TiO₂ fibres in the

7.2 Future work

photoreduction of CO₂ could be further investigated. Possibly, the use of the new hybrid based on CNT fibre could be more appropriate for this photocatalytic reaction. Also, other semiconductors could be tested in order to increase the selectivity of the CO₂ photoreduction reaction.

In general, the study of the electronic band structure of the hybrid is essential to confirm that the hybridisation between both components has been achieved. In this context, the study of the band structure at different distances from the interface, deterministically selected by the use of a focused beam, could be determined to know how far the interfacial effects are extended to the bulk material.

As analytical tool, electrochemistry can be considered as a fundamental study of the hybrid material, which further enables the direct relation of the structural properties with its photo(electro)catalytic performance. Additionally, photocurrent spectroscopy could be exploited to study the properties of the hybrids at different wavelengths, which could demonstrate the potential use of hybrid materials for a certain reaction in the visible range.

Finally, study of the direction of electron and holes upon illumination could be studied by more sophisticated techniques such as transient absorption spectroscopy, transient photocurrent spectroscopy.

APPENDIX A

ELECTROSPUN NIOBIUM/TANTALUM OXIDE FIBRES FOR PHOTOCATALYSIS

Nowadays, TiO_2 is the main material for photocatalysis, but in the recent years more and more researchers are focusing their efforts in tantalum and niobium oxides, promising materials in the field of photocatalysis. The interest in Nb_2O_5 and Ta_2O_5 is growing in the scientific community due to their high photoactivities, and their application in water splitting to obtain hydrogen, a clean and suitable energy, among other fields.[Cherevan et al. 2014; Cherevan et al. 2016; Zhao et al. 2012] Furthermore, one dimensional nanostructured materials, such as nanotubes and nanofibers have been widely used in the field of catalysis.[Moya et al. 2015] Catalysts in form of fibres present several advantages in relation to catalysts supported on alumina or nanoparticles, such as a high surface area, more intimate contact between reactants and the active sites or the absence of closed pores, while obviating the necessity of using a support reduces diffusion problems, specially reactions in liquid media.[Macías et al. 2005; Dharmaraj et al. 2006] In this regard, electrospinning has been demonstrated to be a simple, versatile and useful technique for fabrication of fibres with diameters in the range of hundreds of nanometers.

In this work, we have synthesised nanofibers of Ta_2O_5 and Nb_2O_5 by the combination of sol-gel process and electrospinning technique, which enable the production of

A.1 Synthesis of Nb₂O₅ and Ta₂O₅ by sol-gel and electrospinning

mesoporous ceramic nanofibers. For comparison, nanoparticles of niobium and tantalum oxides have been produced by sol-gel method in order to confirm the enhanced properties obtained because the choice of sol-gel and electrospinning or in other words, by the one-dimensional fibre morphology. In addition, structural and morphological characterisation of the obtained fibres has been carried out to study their evolution into mesoporous fibres. Finally, this work exploits the photocatalytic performance of the niobium/tantalum oxide fibres in the hydrogen production compared to corresponding nanoparticles.

A.1 Synthesis of Nb₂O₅ and Ta₂O₅ by sol-gel and electrospinning

The knowledge gain with the TiO₂ fibres production was used to exploit the production of other metal oxide fibres. Sol-gel process with transition metal precursors and processing of electrospinning technique is presented in this *Section*.

In a typical synthesis, a 10wt.% of PVP solution in ethanol is prepared as binder solution for the electrospinning technique. Under Ar atmosphere, 1:0.01 mol ratio of acetic acid:inorganic precursor, either for Nb(OC₂H₅)₅ or for Ta(OC₂H₅)₅, were added to the binder solution. The viscous precursor was transferred to a syringe and fed by a pump to the stainless needle. The electrospinning parameters were optimised for an applied voltage of 30kV, a feed rate of 2 mL/h and a distance between the needle and the collector of 10 cm.

Scanning electron micrographs of *Figure A.1* show the as-spun polymeric fibres of niobium and tantalum. The fibres are uniform in diameter with smooth surface, indicating that the parameters fixed in the electrospinning process were appropriated.

Figure A.1: Scanning electron micrographs of a) PVP/Nb system and b) PVP/Ta system.

In order to crystallise the metal oxide and remove the polymer, an annealing treatment was carried out in Ar atmosphere, which further was expected to improve the surface of the metal oxide, similarly to the results obtained for the TiO₂ fibres. Additionally, this fibre crystallised in inert atmosphere could be better compared with a future sample that will consist in the hybridisation of these metal oxides with nanocarbons. Similarly to the annealing treatment of the TiO₂ fibres, the samples of PVP/Nb and PVP/Ta were heated in air flow of 400L/h up to 400°C (heat rate of 5°C/min) and kept during 3 hours to remove the polymer. Then, the atmosphere was changed to Ar and the temperature was increased to crystallise the oxide. The crystallisation temperature was fixed in 575°C/1h and 700°C/10h for niobium and tantalum oxide, respectively. The fibres of Nb₂O₅ and Ta₂O₅ after annealing process are presented in the *Figure A.2*, concluding that the morphology is preserved after the heat treatment.

Figure A.2: Scanning electron images of a) Nb₂O₅ crystallised at 575°C/1h and b) Ta₂O₅ at 700°C/10h.

A.1 Synthesis of Nb₂O₅ and Ta₂O₅ by sol-gel and electrospinning

A decrease of the fibre diameter was observed as consequence of the polymer removal but still, they remain uniform with smooth surface. The annealing process leads to a reduction of 30-40% in the fibre diameter, which is in agreement with the PVP content over the electrospun solution. The average fibre diameter are 433 and 495nm for the niobium and tantalum oxides, respectively. In addition, the loss of the polymer has produced shorter fibres due to the brittleness of the metal oxide fibres.

A.2 Highly crystalline mesoporous structure

The influence of the fibre morphology on the crystal structure of the metal oxides has been studied by XRD, TEM/ED and Raman spectroscopy in comparison with reference samples that consists in metal oxides nanoparticles synthesised under identical conditions, that is, by sol-gel method but without use of the electrospinning technique.

Figure A.3a shows the X-ray diffraction patterns of nanoparticles and nanofibres of Nb₂O₅ annealed at 575°C for 1 hour and *Figure A.3b* shows those patterns of Ta₂O₅ annealed at 700°C for 10 hours. For both metal oxides, the fibre morphology presents the same crystal structure than the corresponding nanoparticles. Thus, the patterns of Nb₂O₅ have been indexed for the hexagonal phase and those of Ta₂O₅ for the orthorhombic phase, corresponding to JCPDs card numbered as 01-071-0336 and 00-021-1198, respectively.

Figure A.3: X-ray diffraction patterns of a) Nb₂O₅ and b) Ta₂O₅ fibres.

Due to these metal oxides have many different polymorphs, literature usually refers to low temperature (LT) and high temperature (HT) phases. In the case of Nb_2O_5 , the low temperature phases consist in the hexagonal phase obtained at $\sim 550^\circ\text{C}$. Orthorhombic phase is usually obtained at 700°C , however it is sometimes presented as temperatures as low as 600°C . Both phases result to be highly active in photocatalytic water splitting.[Qi et al. 2013] Yet, hexagonal phase is expected to produce more hydrogen because its lower crystallisation temperature leads to a larger surface area. For the case of Ta_2O_5 , at least 700°C needs to be reached to obtain orthorhombic phase. Furthermore, longer times are also necessary for its crystallization due to Ta_2O_5 presents a slow kinetic of the crystallisation process.[Zhu et al. 2005b] In particular, 10 hours at 700°C were fixed to complete the transformation of amorphous Ta_2O_5 into crystalline structure. Longer times would induce crystal growth, which would reduce the surface area and therefore, the photocatalytic activity of the material. Finally, the average crystal size was calculated using *HighScore* software, resulting in 16 and 13nm for Nb_2O_5 and 14 and 15nm for Ta_2O_5 nanoparticles and nanofibres, respectively. Thus, minor differences in the crystal size of these samples have been determined by the XRD patterns.

Further analysis of the crystal structure of Nb and Ta fibres were carried out by TEM. *Figure A.4* shows HRTEM images of niobium and tantalum oxides. Both oxides consist in nanocrystals interconnected along the fibre morphology. Interestingly, the most of the particles exist as single crystals due to an anisotropic growth along the fibre direction has been favoured during the annealing treatment. Importantly, the fibres either of niobium or of tantalum oxides present a large number of mesopores ($\sim 10\text{nm}$), probably caused by the escaping of polymer. This confirms the success in the creation of highly mesoporous inorganic fibres by means of using electrospinning technique. Yet, the niobium oxide fibre sample seems to present higher mesoporosity than the tantalum oxide fibre sample, which can be related to a higher densification of the mesoporous tantalum structure since it has been annealed at higher temperatures and for longer times.

Figure A.4: HRTEM images of a-b) Nb_2O_5 and c-d) Ta_2O_5 fibres.

Further structural features were studied by Raman spectroscopy (*Figure A.5*). As described before, many polymorphs exist for the Nb and Ta oxides and generally, different M-O polyhedral can form the metal structure.[Lopes et al. 2014a] In fact, the broadening of the Raman modes for these oxides suggest a disorder of the polyhedra. *Figure A.5a* presents the Raman spectra in the range of $100\text{-}1000\text{cm}^{-1}$ for the Nb_2O_5 nanoparticles and nanofibres annealed at $575^\circ\text{C}/1\text{h}$. The main peak between 650 and 710cm^{-1} is the most characteristic vibrational mode of niobium oxide and it is assigned to the symmetric stretching mode of Nb-O polyhedral.[Ma et al. 2015] A narrower and shifted peak of 14cm^{-1} to higher wavenumbers is observed for the fibre sample in comparison with the nanoparticles. This suggests a better crystallinity of the sample for the fibre morphology. The Raman modes at about 234 and 316cm^{-1} are assigned to the Nb-O-Nb bonds of the hexagonal Nb_2O_5 phase.[Soares et al. 2011] Moreover, the band at 125cm^{-1} corresponds to optical vibrations of the hexagonal phase and indicates a highly ordered crystal structure.[Aquino et al. 2014] In addition, *Figure A.5b* shows the Raman spectra of Ta_2O_5 nanoparticles and nanofibres annealed at $700^\circ\text{C}/10\text{h}$ and in the same frequency range than the niobium oxide spectra. The

Raman bands at about 110, 178, 255, 482, 668 and 844 cm^{-1} correspond to the orthorhombic phase.[Joseph et al. 2012] Minor difference between the Raman spectra of Ta_2O_5 nanoparticles and nanofibres are observed.

Figure A.5: Raman spectra of a) Nb_2O_5 and b) Ta_2O_5 fibres and nanoparticles for comparison of their Raman modes.

Finally, the absorption properties of the Nb_2O_5 and Ta_2O_5 fibres were determined by UV-Vis diffuse reflectance spectroscopy in order to determine the ability of light absorption of these materials for their use as photocatalyst. The absorbance spectra of all the samples (*Figure A.6*) are typical of semiconductor materials with a strong absorption band in the UV range, although they also exhibit a visible absorption background with the exception of the Nb_2O_5 nanoparticles sample. The bandgap values were calculated applying the Tauc model and considering both metal oxides as indirect semiconductors.[Viezbicke et al. 2015] Thus, the calculated band gap energies are 3, 3.2, 3.7 and 4eV for Nb_2O_5 nanoparticles, Nb_2O_5 fibres, Ta_2O_5 nanoparticles and Ta_2O_5 fibres, respectively. Interestingly, the band gap of the nanoparticles have resulted slightly lower than that of the fibres, which will benefit the amount of light absorption and consequently the photocatalytic activity. Yet, the band gap values obtained are in the range of that for the bulk, which are 3.4 and 3.9eV for Nb_2O_5 and Ta_2O_5 , respectively.[Qi et al. 2013; Nashed et al. 2013] The differences in the gap energy values can be due to the assumption of indirect transitions and/or quantum confinements.

Figure A.6: UV-Vis DRS spectra of Nb₂O₅ and Ta₂O₅ nanoparticles and fibres.

A.3 Photocatalytic hydrogen production tests

The metal oxide based on niobium and tantalum oxides have been tested as photocatalyst for hydrogen production in the group of Prof. D. Eder. The reactor system used for these metal oxides is an extended version of the reactor system used for the titanium dioxide photocatalysts. It consists in 850mL quartz gas flow reactor system, illuminated with a high power Hg lamp (700W Hg TQ 718 lamp) that is placed in the middle of the reaction in order to improve the photon absorption by the photocatalyst dispersed in the reaction solution. In a typical experiment, a 50mg of the photocatalyst, either nanoparticles or fibres, are dispersed into a water/methanol solution of ratio 9/1. The sacrificial water splitting experiments were carried out without and with use of 0.5wt.% of Pt, which was *in-situ* photodeposited into the reaction media from H₂PtCl₆. The same detection system than for TiO₂ catalysts was used (*X-Stream* gas analyser).

The hydrogen production rates for all the samples presented in this *Appendix A* are summarised in the histogram of *Figure A.7*. The most active material is the sample of Nb₂O₅ fibres (945µmol/h) followed by the Ta₂O₅ fibres (847µmol/h). The photoac-

tivities of those fibres have increased about 25 and 48% in comparison with the randomly agglomerated nanoparticles of niobium and tantalum oxide, respectively. Regarding to the experiments without Pt, *Figure A.7* confirms the possibility of the use of Ta₂O₅ without co-catalyst, presenting only the half of H₂ production rate. This suggests that the tantalum oxide surface, either nanoparticles or fibres, is highly photo-active and can lead to the H⁺ reduction reaction.

Figure A.7: Hydrogen production rates of Nb₂O₅ and Ta₂O₅ photocatalysts tested with and without the use of Pt as co-catalyst.

In general, the comparison of photocatalytic activity shows that the mesoporous interconnected structure leads to much higher activity for all the metals oxides tested. Due to the crystal structure of the nanoparticles and the fibres is similar and furthermore, the absorption properties of the nanoparticles are better than those of the corresponding fibres, a considerable improvement on the photocatalytic activity has been concluded by the use of fibre morphology instead of randomly agglomerated nanoparticles. Importantly, the relevance of this enhancement in activity is not just purely because of the obvious benefits of a higher H₂ production rate, but because such catalyst architecture could be used either as supported catalyst (membrane) or in dispersion.

A.4 Summary

In conclusion, the synthesis of different metal oxides by the combination of sol-gel process and electrospinning technique results in a very interesting approach to improve the performance of the semiconductor in energy application such as photocatalysis. The feasibility of this synthesis strategy to be applied for the synthesis of similar compounds has been confirmed. It enables the formation of a mesoporous fibre structure that presents higher performance compared to conventional sol-gel derived metal oxides. Several benefits are obtained from the one-dimensional structure, from structural aspects to textural properties. The growth of the inorganic along the fibre structure and in the presence of a polymer favours a high degree of crystallinity and a characteristic mesoporosity, both responsible of a better electron transport and an enhanced surface chemistry for the adsorption of reactant molecules. Finally, an improvement of the H₂ production rates highlight the potential application of the fibres as photocatalyst material either niobium or tantalum oxides, being the latter highly interesting for water splitting process free of co-catalyst.

BIBLIOGRAPHY

- AGO, H., KUGLER, T., CACIALLI, F., ET AL. 1999. Work Functions and Surface Functional Groups of Multiwall Carbon Nanotubes. *The Journal of Physical Chemistry B* 103, 38, 8116–8121.
- AHMAD, B., KUSUMOTO, Y., SOMEKAWA, S., AND IKEDA, M. 2008. Carbon nanotubes synergistically enhance photocatalytic activity of TiO₂. *Catalysis Communications* 9, 6, 1410–1413.
- AHN, Y.R., LEE, Y.S., OGALE, A.A., YUN, C.H., AND PARK, C.R. 2006. Compressional behavior of carbon nanotube reinforced mesophase pitch-based carbon fibers. *Fibers and Polymers* 7, 1, 85–87.
- AKHAVAN, O., AZIMIRAD, R., AND SAFA, S. 2011. Functionalized carbon nanotubes in ZnO thin films for photoinactivation of bacteria. *Materials Chemistry and Physics* 130, 1–2, 598–602.
- AKSEL, S. AND EDER, D. 2010. Catalytic effect of metal oxides on the oxidation resistance in carbon nanotube-inorganic hybrids. *J. Mater. Chem.* 20, 41, 9149–9154.
- ALBERY, W.J., O'SHEA, G.J., AND SMITH, A.L. 1996. Interpretation and use of Mott-Schottky plots at the semiconductor/electrolyte interface. *J. Chem. Soc., Faraday Trans.* 92, 20, 4083–4085.
- AL-HOMOUDI, I.A., ZHANG, L., MCCULLEN, E.F., ET AL. 2004. Fabrication of Anatase TiO₂ Thin Film Using Pulsed DC Magnetron Sputtering. *MRS Proceedings* 848.
- ALI, M.A., SRIVASTAVA, S., SOLANKI, P.R., ET AL. 2013. Highly Efficient Bionzyme Functionalized Nanocomposite-Based Microfluidics Biosensor Platform for Biomedical Application. *Scientific Reports* 3, 2661.
- ANTONY, R.P., DASGUPTA, A., MAHANA, S., TOPWAL, D., MATHEWS, T., AND DHARA, S. 2015. Resonance Raman spectroscopic study for radial vibrational modes in ultra-thin walled TiO₂ nanotubes. *Journal of Raman Spectroscopy* 46, 2, 231–235.
- AQUINO, F.T., PEREIRA, R.R., FERRARI, J.L., ET AL. 2014. Unusual broadening of the NIR luminescence of Er³⁺-doped Nb₂O₅ nanocrystals embedded in silica host: Preparation and their structural and spectroscopic study for photonics applications. *Materials Chemistry and Physics* 147, 3, 751–760.
- ARUNA, S.T., TIROSH, S., AND ZABAN, A. 2000. Nanosize rutile titania particle synthesis a hydrothermal method without mineralizers. *J. Mater. Chem.* 10, 10, 2388–2391.
- B. Q. WEI, R. VAJTAI, AND P. M. AJAYAN. 2001. Reliability and current carrying capacity of carbon nanotubes. *Applied Physics Letters* 79, 8, 1172–1174.

BIBLIOGRAPHY

- BAK, T., NOWOTNY, J., REKAS, M., AND SORRELL, C.C. 2003. Defect chemistry and semiconducting properties of titanium dioxide: II. Defect diagrams☆. *Journal of Physics and Chemistry of Solids* 64, 7, 1057–1067.
- BALANDIN, A.A. 2011. Thermal properties of graphene and nanostructured carbon materials. *Nat Mater* 10, 8, 569–581.
- BANERJEE, S. AND WONG, S.S. 2002. Synthesis and Characterization of Carbon Nanotube–Nanocrystal Heterostructures. *Nano Letters* 2, 3, 195–200.
- BARD, A.J. 1979. Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors. *Journal of Photochemistry* 10, 1, 59–75.
- BARNARD, A.S., ZAPOL, P., AND CURTISS, L.A. 2005. Modeling the Morphology and Phase Stability of TiO₂ Nanocrystals in Water. *Journal of Chemical Theory and Computation* 1, 1, 107–116.
- BARRETT, E.P., JOYNER, L.G., AND HALENDA, P.P. 1951. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society* 73, 1, 373–380.
- BHARDWAJ, N. AND KUNDU, S.C. 2010. Electrospinning: A fascinating fiber fabrication technique. *Biotechnology Advances* 28, 3, 325–347.
- BISQUERT, J., GARCIA-BELMONTE, G., FABREGAT-SANTIAGO, F., FERRIOLS, N.S., BOGDANOFF, P., AND PEREIRA, E.C. 2000. Doubling Exponent Models for the Analysis of Porous Film Electrodes by Impedance. Relaxation of TiO₂ Nanoporous in Aqueous Solution. *The Journal of Physical Chemistry B* 104, 10, 2287–2298.
- BOSTWICK, A., OHTA, T., MCCHESENEY, J.L., ET AL. 2007. Symmetry breaking in few layer graphene films. *New Journal of Physics* 9, 10, 385.
- BRUNAUER, S., EMMETT, P.H., AND TELLER, E. 1938. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society* 60, 2, 309–319.
- BUSCEMA, M., ISLAND, J.O., GROENENDIJK, D.J., ET AL. 2015. Photocurrent generation with two-dimensional van der Waals semiconductors. *Chem. Soc. Rev.* 44, 11, 3691–3718.
- CABANA, L., BALLESTEROS, B., BATISTA, E., ET AL. 2014. Synthesis of PbI₂ Single-Layered Inorganic Nanotubes Encapsulated Within Carbon Nanotubes. *Advanced Materials* 26, 13, 2016–2021.
- CARP, O., HUISMAN, C.L., AND RELLER, A. 2004. Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry* 32, 1–2, 33–177.
- CASTELLANOS-GOMEZ, A., BUSCEMA, M., MOLENAAR, R., ET AL. 2014. Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. *2D Materials* 1, 1, 011002.

- CHEN, J., LI, B., ZHENG, J., ZHAO, J., AND ZHU, Z. 2012. Role of Carbon Nanotubes in Dye-Sensitized TiO₂-Based Solar Cells. *The Journal of Physical Chemistry C* 116, 28, 14848–14856.
- CHEN, L.-C., HO, Y.-C., GUO, W.-S., HUANG, C.-M., AND PAN, T.-C. 2009. Enhanced visible light-induced photoelectrocatalytic degradation of phenol by carbon nanotube-doped TiO₂ electrodes. *Electrochimica Acta* 54, 15, 3884–3891.
- CHEN, W., WANG, H., MAO, L., CHEN, X., AND SHANGGUAN, W. 2014. Influence of loading Pt, RhO₂ co-catalysts on photocatalytic overall water splitting over H_{1.9}K_{0.3}La_{0.5}Bi_{0.1}Ta₂O₇. *Catalysis Communications* 57, 115–118.
- CHEN, X., LIU, L., YU, P.Y., AND MAO, S.S. 2011. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* 331, 6018, 746–750.
- CHEN, X., SHEN, S., GUO, L., AND MAO, S.S. 2010. Semiconductor-based Photocatalytic Hydrogen Generation. *Chemical Reviews* 110, 11, 6503–6570.
- CHEN, Z., HUYEN, D., AND MILLER, ERIC. 2013. *Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols*. .
- CHENG, P., YANG, Z., WANG, H., ET AL. 2012. TiO₂-graphene nanocomposites for photocatalytic hydrogen production from splitting water. *2010 AIChE Annual Meeting Topical Conference on Hydrogen Production and Storage Special Issue* 37, 3, 2224–2230.
- CHEREVAN, A.S., GEBHARDT, P., SHEARER, C.J., MATSUKAWA, M., DOMEN, K., AND EDER, D. 2014. Interface engineering in nanocarbon-Ta₂O₅ hybrid photocatalysts. *Energy Environ. Sci.* 7, 2, 791–796.
- CHEREVAN, A.S., ROBBINS, S., DIETERLE, D., GEBHARDT, P., WIESNER, U., AND EDER, D. 2016. Ordered gyroidal tantalum oxide photocatalysts: eliminating diffusion limitations and tuning surface barriers. *Nanoscale* 8, 37, 16694–16701.
- CHI, C.-F., CHO, H.-W., TENG, H., ET AL. 2011. Energy level alignment, electron injection, and charge recombination characteristics in CdS/CdSe cosensitized TiO₂ photoelectrode. *Applied Physics Letters* 98, 1.
- CHOI, S.K., KIM, S., LIM, S.K., AND PARK, H. 2010. Photocatalytic Comparison of TiO₂ Nanoparticles and Electrospun TiO₂ Nanofibers: Effects of Mesoporosity and Interparticle Charge Transfer. *The Journal of Physical Chemistry C* 114, 39, 16475–16480.
- CHOI, S.K., KIM, S., RYU, J., LIM, S.K., AND PARK, H. 2012. Titania nanofibers as a photo-antenna for dye-sensitized solar hydrogen. *Photochem. Photobiol. Sci.* 11, 9, 1437–1444.
- CHOUDHURY, B., DEY, M., AND CHOUDHURY, A. 2014. Shallow and deep trap emission and luminescence quenching of TiO₂ nanoparticles on Cu doping. *Applied Nanoscience* 4, 4, 499–506.

BIBLIOGRAPHY

- COLLADO, L., JANA, P., SIERRA, B., ET AL. 2013. Enhancement of hydrocarbon production via artificial photosynthesis due to synergetic effect of Ag supported on TiO₂ and ZnO semiconductors. *7th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA7)* 224, 128–135.
- COLLADO, L., REYNAL, A., CORONADO, J.M., SERRANO, D.P., DURRANT, J.R., AND DE LA PEÑA O'SHEA, V.A. Effect of Au surface plasmon nanoparticles on the selective CO₂ photoreduction to CH₄. *Applied Catalysis B: Environmental* 0.
- CONNELLY, K.A. AND IDRIS, H. 2012. The photoreaction of TiO₂ and Au/TiO₂ single crystal and powder surfaces with organic adsorbates. Emphasis on hydrogen production from renewables. *Green Chem.* 14, 2, 260–280.
- COOKE, D.J., EDER, D., AND ELLIOTT, J.A. 2010. Role of Benzyl Alcohol in Controlling the Growth of TiO₂ on Carbon Nanotubes. *The Journal of Physical Chemistry C* 114, 6, 2462–2470.
- CRADIO, A., MELCHIONNA, M., MARCHESAN, S., AND PRATO, M. 2015. The Covalent Functionalization of Graphene on Substrates. *Angewandte Chemie International Edition* 54, 37, 10734–10750.
- CURRAN, S.A., TALLA, J.A., ZHANG, D., AND CARROLL, D.L. 2005. Defect-induced vibrational response of multi-walled carbon nanotubes using resonance Raman spectroscopy. *Journal of Materials Research* 20, 12, 3368–3373.
- DAM, D.T., WANG, X., AND LEE, J.-M. 2014. Graphene/NiO Nanowires: Controllable One-Pot Synthesis and Enhanced Pseudocapacitive Behavior. *ACS Applied Materials & Interfaces* 6, 11, 8246–8256.
- DAS, A., HALL, E., AND WAI, C.M. 2014. Noncovalent Attachment of PbS Quantum Dots to Single- and Multiwalled Carbon Nanotubes. *Journal of Nanotechnology* 2014, 7.
- DATSYUK, V., KALYVA, M., PAPAGELIS, K., ET AL. 2008. Chemical oxidation of multiwalled carbon nanotubes. *Carbon* 46, 6, 833–840.
- DAY, T.M., UNWIN, P.R., WILSON, N.R., AND MACPHERSON, J.V. 2005. Electrochemical Templating of Metal Nanoparticles and Nanowires on Single-Walled Carbon Nanotube Networks. *Journal of the American Chemical Society* 127, 30, 10639–10647.
- DEANE K. SMITH AND FRANK H. CHUNG. 1999. Industrial Applications of X-Ray Diffraction. 798.
- DEMBELE, K.T., SELOPAL, G.S., SOLDANO, C., ET AL. 2013. Hybrid Carbon Nanotubes–TiO₂ Photoanodes for High Efficiency Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C* 117, 28, 14510–14517.
- DHARMARAJ, N., PARK, H.C., KIM, C.H., VISWANATHAMURTHI, P., AND KIM, H.Y. 2006. Nanometer sized tantalum pentoxide fibers prepared by electrospinning. *Materials Research Bulletin* 41, 3, 612–619.

- DI VALENTIN, C., PACCHIONI, G., AND SELLONI, A. 2005. Theory of Carbon Doping of Titanium Dioxide. *Chemistry of Materials* 17, 26, 6656–6665.
- DONG, X., ZHANG, H.-B., LIN, G.-D., YUAN, Y.-Z., AND TSAI, K.R. 2003. Highly Active CNT-Promoted Cu–ZnO–Al₂O₃ Catalyst for Methanol Synthesis from H₂/CO/CO₂. *Catalysis Letters* 85, 3, 237–246.
- DRESSELHAUS, M.S., DRESSELHAUS, G., SAITO, R., AND JORIO, A. 2005. Raman spectroscopy of carbon nanotubes. *Physics Reports* 409, 2, 47–99.
- DU, A., SANVITO, S., LI, Z., ET AL. 2012. Hybrid Graphene and Graphitic Carbon Nitride Nanocomposite: Gap Opening, Electron–Hole Puddle, Interfacial Charge Transfer, and Enhanced Visible Light Response. *Journal of the American Chemical Society* 134, 9, 4393–4397.
- DÜRKOP, T., GETTY, S.A., COBAS, E., AND FUHRER, M.S. 2004. Extraordinary Mobility in Semiconducting Carbon Nanotubes. *Nano Letters* 4, 1, 35–39.
- EDER, D. 2010. Carbon Nanotube–Inorganic Hybrids. *Chemical Reviews* 110, 3, 1348–1385.
- EDER, D., MOTTA, M.S., AND WINDLE, A.H. 2010. Nanoengineering with residual catalyst from CNT templates. *Acta Materialia* 58, 13, 4406–4413.
- EDER, D. AND WINDLE, A.H. 2008. Morphology control of CNT–TiO₂ hybrid materials and rutile nanotubes. *J. Mater. Chem.* 18, 17, 2036–2043.
- ELISEEV, A.A., KHARLAMOVA, M.V., CHERNYSHEVA, M.V., ET AL. 2009. Preparation and properties of single-walled nanotubes filled with inorganic compounds. *Russian Chemical Reviews* 78, 9, 833.
- FABREGAT-SANTIAGO, F., GARCIA-BELMONTE, G., BISQUERT, J., ZABAN, A., AND SALVADOR, P. 2002. Decoupling of Transport, Charge Storage, and Interfacial Charge Transfer in the Nanocrystalline TiO₂/Electrolyte System by Impedance Methods. *The Journal of Physical Chemistry B* 106, 2, 334–339.
- FABREGAT-SANTIAGO, F., RANDRIAMAHAZAKA, H., ZABAN, A., GARCIA-CANADAS, J., GARCIA-BELMONTE, G., AND BISQUERT, J. 2006. Chemical capacitance of nanoporous-nanocrystalline TiO₂ in a room temperature ionic liquid. *Phys. Chem. Chem. Phys.* 8, 15, 1827–1833.
- FAN, W., LAI, Q., ZHANG, Q., AND WANG, Y. 2011. Nanocomposites of TiO₂ and Reduced Graphene Oxide as Efficient Photocatalysts for Hydrogen Evolution. *The Journal of Physical Chemistry C* 115, 21, 10694–10701.
- FARSINEZHAD, S., SHARMA, H., AND SHANKAR, K. 2015a. Interfacial band alignment for photocatalytic charge separation in TiO₂ nanotube arrays coated with CuPt nanoparticles. *Phys. Chem. Chem. Phys.* 17, 44, 29723–29733.

BIBLIOGRAPHY

- FARSINEZHAD, S., SHARMA, H., AND SHANKAR, K. 2015b. Interfacial band alignment for photocatalytic charge separation in TiO₂ nanotube arrays coated with CuPt nanoparticles. *Phys. Chem. Chem. Phys.* 17, 44, 29723–29733.
- FERRIGHI, L., FAZIO, G., AND VALENTIN, C.D. 2016. Charge Carriers Separation at the Graphene/(101) Anatase TiO₂ Interface. *Advanced Materials Interfaces* 3, 6, 1500624–n/a.
- FINNIE, K.S., LUCA, V., MORAN, P.D., BARTLETT, J.R., AND WOOLFREY, J.L. 2000. Vibrational spectroscopy and EXAFS study of Ti(OC₂H₅)₄ and alcohol exchange in Ti(iso-OC₃H₇)₄. *J. Mater. Chem.* 10, 2, 409–418.
- FRANK, O., ZUKALOVA, M., LASKOVA, B., KURTI, J., KOLTAL, J., AND KAVAN, L. 2012. Raman spectra of titanium dioxide (anatase, rutile) with identified oxygen isotopes (16, 17, 18). *Phys. Chem. Chem. Phys.* 14, 42, 14567–14572.
- FRESNO, F., PORTELA, R., SUAREZ, S., AND CORONADO, J.M. 2014. Photocatalytic materials: recent achievements and near future trends. *J. Mater. Chem. A* 2, 9, 2863–2884.
- FUJISHIMA, A. AND HONDA, K. 1972. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 238, 5358, 37–38.
- FUJISHIMA, A., RAO, T.N., AND TRYK, D.A. 2000. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 1, 1, 1–21.
- FURCHI, M.M., POLYUSHKIN, D.K., POSPISCHIL, A., AND MUELLER, T. 2014. Mechanisms of Photoconductivity in Atomically Thin MoS₂. *Nano Letters* 14, 11, 6165–6170.
- GAMBOA, J.A. AND PASQUEVICH, D.M. 1992. Effect of Chlorine Atmosphere on the Anatase–Rutile Transformation. *Journal of the American Ceramic Society* 75, 11, 2934–2938.
- GAO, R., PAN, Z., AND WANG, Z.L. 2001. Work function at the tips of multiwalled carbon nanotubes. *Applied Physics Letters* 78, 12, 1757–1759.
- GAUDREAU, L., TIELROOIJ, K.J., PRAWIROATMODJO, G.E.D.K., OSMOND, J., DE ABAJO, F.J.G., AND KOPPENS, F.H.L. 2013. Universal Distance-Scaling of Nonradiative Energy Transfer to Graphene. *Nano Letters* 13, 5, 2030–2035.
- GAUTAM, U.K., COSTA, P.M.F.J., BANDO, Y., ET AL. 2010. Recent developments in inorganically filled carbon nanotubes: successes and challenges. *Science and Technology of Advanced Materials* 11, 5, 054501.
- GEGENHUBER, T., GRÖSCHEL, A.H., LÖBLING, T.I., ET AL. 2015. Noncovalent Grafting of Carbon Nanotubes with Triblock Terpolymers: Toward Patchy 1D Hybrids. *Macromolecules* 48, 6, 1767–1776.
- GELDERMAN, K., LEE, L., AND DONNE, S.W. 2007. Flat-Band Potential of a Semiconductor: Using the Mott–Schottky Equation. *Journal of Chemical Education* 84, 4, 685.

- GENNARI, F.C. AND PASQUEVICH, D.M. 1998. Kinetics of the anatase–rutile transformation in TiO₂ in the presence of Fe₂O₃. *Journal of Materials Science* 33, 6, 1571–1578.
- GUTMANN, S., WOLAK, M.A., CONRAD, M., BEERBOM, M.M., AND SCHLAF, R. 2010. Effect of ultraviolet and x-ray radiation on the work function of TiO₂ surfaces. *Journal of Applied Physics* 107, 10.
- HANAOR, D.A.H. AND SORRELL, C.C. 2011. Review of the anatase to rutile phase transformation. *Journal of Materials Science* 46, 4, 855–874.
- HIRANO, M., NAKAHARA, C., OTA, K., TANAIKE, O., AND INAGAKI, M. 2003. Photoactivity and phase stability of ZrO₂-doped anatase-type TiO₂ directly formed as nanometer-sized particles by hydrolysis under hydrothermal conditions. *Journal of Solid State Chemistry* 170, 1, 39–47.
- HITOKI, G., ISHIKAWA, A., TAKATA, T., KONDO, J.N., HARA, M., AND DOMEN, K. 2002a. Ta₃N₅ as a Novel Visible Light-Driven Photocatalyst ($\lambda < 600$ nm). *Chemistry Letters* 31, 7, 736–737.
- HITOKI, G., TAKATA, T., KONDO, J.N., HARA, M., KOBAYASHI, H., AND DOMEN, K. 2002b. An oxynitride, TaON, as an efficient water oxidation photocatalyst under visible light irradiation ($[\lambda] \leq 500$ nm). *Chem. Commun.* 16, 1698–1699.
- HOU, H., SHANG, M., WANG, L., LI, W., TANG, B., AND YANG, W. 2015. Efficient Photocatalytic Activities of TiO₂ Hollow Fibers with Mixed Phases and Mesoporous Walls. *Scientific Reports* 5, 15228.
- HUANG, S. AND DAI, L. 2002. Plasma Etching for Purification and Controlled Opening of Aligned Carbon Nanotubes. *The Journal of Physical Chemistry B* 106, 14, 3543–3545.
- HUANG, S.-H., WANG, C.-C., LIAO, S.-Y., GAN, J.-Y., AND PERNG, T.-P. 2016. CNT/TiO₂ core-shell structures prepared by atomic layer deposition and characterization of their photocatalytic properties. *Thin Solid Films* 616, 151–159.
- HUNGRÍA, A.B., EDER, D., WINDLE, A.H., AND MIDGLEY, P.A. 2009. Visualization of the three-dimensional microstructure of TiO₂ nanotubes by electron tomography. *Catalysis for Sustainability - Professor Javier Soria Festschrift* 143, 3–4, 225–229.
- HURUM, D.C., AGRIOS, A.G., GRAY, K.A., RAJH, T., AND THURNAUER, M.C. 2003. Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO₂ Using EPR. *The Journal of Physical Chemistry B* 107, 19, 4545–4549.
- IJIMA, S. 1991. Helical microtubules of graphitic carbon. *Nature* 354, 6348, 56–58.
- INAGAKI, M., KONNO, H., AND TANAIKE, O. 2010. Carbon materials for electrochemical capacitors. *Journal of Power Sources* 195, 24, 7880–7903.
- ISHII, T., KATO, H., AND KUDO, A. 2004. H₂ evolution from an aqueous methanol solution on SrTiO₃ photocatalysts codoped with chromium and tantalum ions under

BIBLIOGRAPHY

- visible light irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* 163, 1–2, 181–186.
- ISHIKAWA, A., TAKATA, T., KONDO, J.N., HARA, M., KOBAYASHI, H., AND DOMEN, K. 2002. Oxysulfide $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$ as a Stable Photocatalyst for Water Oxidation and Reduction under Visible Light Irradiation ($\lambda \leq 650$ nm). *Journal of the American Chemical Society* 124, 45, 13547–13553.
- ISHIKAWA, A., TAKATA, T., MATSUMURA, T., ET AL. 2004. Oxysulfides $\text{Ln}_2\text{Ti}_2\text{S}_2\text{O}_5$ as Stable Photocatalysts for Water Oxidation and Reduction under Visible-Light Irradiation. *The Journal of Physical Chemistry B* 108, 8, 2637–2642.
- IT NIST DIGITAL LIBRARY OF MATHEMATICAL FUNCTIONS. .
- JAKOB, M., LEVANON, H., AND KAMAT, P.V. 2003. Charge Distribution between UV-Irradiated TiO_2 and Gold Nanoparticles: Determination of Shift in the Fermi Level. *Nano Letters* 3, 3, 353–358.
- JIANG, G., LIN, Z., ZHU, L., DING, Y., AND TANG, H. 2010. Preparation and photoelectrocatalytic properties of titania/carbon nanotube composite films. *Carbon* 48, 12, 3369–3375.
- JIN, S.H., JUN, G.H., HONG, S.H., AND JEON, S. 2012. Conformal coating of titanium suboxide on carbon nanotube networks by atomic layer deposition for inverted organic photovoltaic cells. *Carbon* 50, 12, 4483–4488.
- JOHNSON, R.W., HULTQVIST, A., AND BENT, S.F. 2014. A brief review of atomic layer deposition: from fundamentals to applications. *Materials Today* 17, 5, 236–246.
- JOSEPH, C., BOURSON, P., AND FONTANA, M.D. 2012. Amorphous to crystalline transformation in Ta_2O_5 studied by Raman spectroscopy. *Journal of Raman Spectroscopy* 43, 8, 1146–1150.
- JUNG, K., HONG, J.S., VITTAL, R., AND KIM, K.-J. 2002. Enhanced Photocurrent of Dye-Sensitized Solar Cells by Modification of TiO_2 with Carbon Nanotubes. *Chemistry Letters* 31, 8, 864–865.
- KANDIEL, T.A., DILLERT, R., ROBBEN, L., AND BAHNEMANN, D.W. 2011. Photonic efficiency and mechanism of photocatalytic molecular hydrogen production over platinumized titanium dioxide from aqueous methanol solutions. *Selected contributions of the 6th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA 6), 13th to 16th June 2010*. 161, 1, 196–201.
- KEMNADE, N., SHEARER, C.J., DIETERLE, D.J., ET AL. 2015. Non-destructive functionalisation for atomic layer deposition of metal oxides on carbon nanotubes: effect of linking agents and defects. *Nanoscale* 7, 7, 3028–3034.
- KERNAZHITSKY, L., SHYMANOVSKA, V., GAVRILKO, T., ET AL. 2014. Room temperature photoluminescence of anatase and rutile TiO_2 powders. *Journal of Luminescence* 146, 199–204.

- KHANNA, K.N. 1980. Work Function in Alkali and Noble Metals. *physica status solidi (b)* 100, 1, 315–319.
- KILIC, B., TURKDOGAN, S., ASTAM, A., ET AL. 2016. Preparation of Carbon Nanotube/TiO₂ Mesoporous Hybrid Photoanode with Iron Pyrite (FeS₂) Thin Films Counter Electrodes for Dye-Sensitized Solar Cell. *Scientific Reports* 6, 27052.
- KIM, H., KIM, S., KANG, J.-K., AND CHOI, W. 2014. Graphene oxide embedded into TiO₂ nanofiber: Effective hybrid photocatalyst for solar conversion. *Journal of Catalysis* 309, 49–57.
- KIM, J.-Y., KIM, K.-H., PARK, S.-H., AND KIM, K.-B. 2010. Microwave-polyol synthesis of nanocrystalline ruthenium oxide nanoparticles on carbon nanotubes for electrochemical capacitors. *EMERGING TRENDS AND CHALLENGES IN ELECTRO-CHEMISTRY* Selection of papers from the 60th Annual Meeting of the International Society of Electrochemistry 16–21 August 2009, Beijing, China 55, 27, 8056–8061.
- KLAHR, B., GIMENEZ, S., FABREGAT-SANTIAGO, F., HAMANN, T., AND BISQUERT, J. 2012. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. *Journal of the American Chemical Society* 134, 9, 4294–4302.
- KONGKANAND, A. AND KAMAT, P.V. 2007. Electron Storage in Single Wall Carbon Nanotubes. Fermi Level Equilibration in Semiconductor–SWCNT Suspensions. *ACS Nano* 1, 1, 13–21.
- KOZIOL, K., VILATELA, J., MOISALA, A., ET AL. 2007. High-Performance Carbon Nanotube Fiber. *Science* 318, 5858, 1892–1895.
- KRISSANASAERANEE, M., WONGKASEMJIT, S., CHEETHAM, A.K., AND EDER, D. 2010. Complex carbon nanotube-inorganic hybrid materials as next-generation photocatalysts. *Chemical Physics Letters* 496, 1–3, 133–138.
- KUDO, A. AND MISEKI, Y. 2009. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* 38, 1, 253–278.
- KUILA, B.K., PARK, K., AND DAI, L. 2010. Soluble P3HT-Grafted Carbon Nanotubes: Synthesis and Photovoltaic Application. *Macromolecules* 43, 16, 6699–6705.
- KUMAR, S., MUKHERJEE, C., AND PHASE, D.M. 2014. Valence Band Onset and Valence Plasmons of SnO₂ and In_{2-x}Sn_xO₃ Thin Films. *ArXiv e-prints*.
- LAKSHMINARASIMHAN, N., KIM, W., AND CHOI, W. 2008. Effect of the Agglomerated State on the Photocatalytic Hydrogen Production with in Situ Agglomeration of Colloidal TiO₂ Nanoparticles. *The Journal of Physical Chemistry C* 112, 51, 20451–20457.
- LARRUDE, D.G., MAIA DA COSTA, M.E.H., AND FREIRE, F.L. 2014. Synthesis and Characterization of Silver Nanoparticle-Multiwalled Carbon Nanotube Composites. *Journal of Nanomaterials* 2014, 7.

BIBLIOGRAPHY

- LEARY, R. AND WESTWOOD, A. 2011. Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis. *Carbon* 49, 3, 741–772.
- LEE, J.E., AHN, G., SHIM, J., LEE, Y.S., AND RYU, S. 2012a. Optical separation of mechanical strain from charge doping in graphene. *Nature Communications* 3, 1024.
- LEE, S.S., BAI, H., LIU, Z., AND SUN, D.D. 2012b. Electrospun TiO₂/SnO₂ nanofibers with innovative structure and chemical properties for highly efficient photocatalytic H₂ generation. *International Journal of Hydrogen Energy* 37, 14, 10575–10584.
- LEE, T.Y., ALEGAONKAR, P.S., AND YOO, J.-B. 2007. Fabrication of dye sensitized solar cell using TiO₂ coated carbon nanotubes. *The Third International Symposium on Dry Process (DPS 2005)* 515, 12, 5131–5135.
- LEI, Y., ZHANG, L.D., MENG, G.W., ET AL. 2001. Preparation and photoluminescence of highly ordered TiO₂ nanowire arrays. *Applied Physics Letters* 78, 8, 1125–1127.
- LI, N., ZHENG, M., LU, H., ET AL. 2012. High-rate lithium-sulfur batteries promoted by reduced graphene oxide coating. *Chem. Commun.* 48, 34, 4106–4108.
- LI, Q., GUO, B., YU, J., ET AL. 2011. Highly Efficient Visible-Light-Driven Photocatalytic Hydrogen Production of CdS-Cluster-Decorated Graphene Nanosheets. *Journal of the American Chemical Society* 133, 28, 10878–10884.
- LI, Y.-L., KINLOCH, I.A., AND WINDLE, A.H. 2004. Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis. *Science* 304, 5668, 276.
- LIANG, Y., LI, Y., WANG, H., AND DAI, H. 2013. Strongly Coupled Inorganic/Nanocarbon Hybrid Materials for Advanced Electrocatalysis. *Journal of the American Chemical Society* 135, 6, 2013–2036.
- LIN, Y., ZHANG, K., CHEN, W., ET AL. 2010. Dramatically Enhanced Photoresponse of Reduced Graphene Oxide with Linker-Free Anchored CdSe Nanoparticles. *ACS Nano* 4, 6, 3033–3038.
- LINSEBIGLER, A.L., LU, G., AND YATES, J.T. 1995. Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Reviews* 95, 3, 735–758.
- LIQIANG, J., YICHUN, Q., BAIQI, W., ET AL. 2006. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Solar Energy Materials and Solar Cells* 90, 12, 1773–1787.
- LIU, G., YANG, H.G., WANG, X., ET AL. 2009. Enhanced Photoactivity of Oxygen-Deficient Anatase TiO₂ Sheets with Dominant {001} Facets. *The Journal of Physical Chemistry C* 113, 52, 21784–21788.
- LIU, J., LIU, Z., ZHANG, T., ZHAI, J., AND JIANG, L. 2013. Low-temperature crystallization of anodized TiO₂ nanotubes at the solid-gas interface and their photoelectrochemical properties. *Nanoscale* 5, 13, 6139–6144.

- LIU, L., ZHANG, J., ZHAO, J., AND LIU, F. 2012. Mechanical properties of graphene oxides. *Nanoscale* 4, 19, 5910–5916.
- LOPES, O.F., PARIS, E.C., AND RIBEIRO, C. 2014a. Synthesis of Nb₂O₅ nanoparticles through the oxidant peroxide method applied to organic pollutant photodegradation: A mechanistic study. *Applied Catalysis B: Environmental* 144, 800–808.
- LOPES, T., ANDRADE, L., LE FORMAL, F., GRATZEL, M., SIVULA, K., AND MENDES, A. 2014b. Hematite photoelectrodes for water splitting: evaluation of the role of film thickness by impedance spectroscopy. *Phys. Chem. Chem. Phys.* 16, 31, 16515–16523.
- LÓPEZ, C.R., MELIÁN, E.P., ORTEGA MÉNDEZ, J.A., SANTIAGO, D.E., DOÑA RODRÍGUEZ, J.M., AND GONZÁLEZ DÍAZ, O. 2015. Comparative study of alcohols as sacrificial agents in H₂ production by heterogeneous photocatalysis using Pt/TiO₂ catalysts. *Journal of Photochemistry and Photobiology A: Chemistry* 312, 45–54.
- LUO, H., TAKATA, T., LEE, Y., ZHAO, J., DOMEN, K., AND YAN. 2004. Photocatalytic Activity Enhancing for Titanium Dioxide by Co-doping with Bromine and Chlorine. *Chemistry of Materials* 16, 5, 846–849.
- M. HATHERLY, HUMPHREYS, F., G. S. ROHRER, AND A. ROLLETT. 2004. *Recrystallization and Related Annealing Phenomena*. Pergamon.
- MA, X., CHEN, Y., LI, H., CUI, X., AND LIN, Y. 2015. Annealing-free synthesis of carbonaceous Nb₂O₅ microspheres by flame thermal method and enhanced photocatalytic activity for hydrogen evolution. *Materials Research Bulletin* 66, 51–58.
- MACÍAS, M., CHACKO, A., FERRARIS, J.P., AND BALKUS JR., K.J. 2005. Electrospun mesoporous metal oxide fibers. *Microporous and Mesoporous Materials* 86, 1–3, 1–13.
- MAEDA, K. AND DOMEN, K. 2010. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *The Journal of Physical Chemistry Letters* 1, 18, 2655–2661.
- MAO, S., CUI, S., YU, K., WEN, Z., LU, G., AND CHEN, J. 2012. Ultrafast hydrogen sensing through hybrids of semiconducting single-walled carbon nanotubes and tin oxide nanocrystals. *Nanoscale* 4, 4, 1275–1279.
- MARTINEZ, U. AND HAMMER, B. 2011. Adsorption properties versus oxidation states of rutile TiO₂(110). *The Journal of Chemical Physics* 134, 19, 194703.
- MELIÁN, E.P., LÓPEZ, C.R., MÉNDEZ, A.O., ET AL. 2013. Hydrogen production using Pt-loaded TiO₂ photocatalysts. *International Journal of Hydrogen Energy* 38, 27, 11737–11748.
- MERCADO, C.C., KNORR, F.J., MCHALE, J.L., USMANI, S.M., ICHIMURA, A.S., AND SARAF, L.V. 2012. Location of Hole and Electron Traps on Nanocrystalline Anatase TiO₂. *The Journal of Physical Chemistry C* 116, 19, 10796–10804.
- MICHAL, R., SFAELOU, S., AND LIANOS, P. 2014. Photocatalysis for Renewable Energy Production Using PhotoFuelCells. *Molecules* 19, 12, 19732–19750.

BIBLIOGRAPHY

- MIN, Y., ZHANG, K., ZHAO, W., ZHENG, F., CHEN, Y., AND ZHANG, Y. 2012. Enhanced chemical interaction between TiO₂ and graphene oxide for photocatalytic decolorization of methylene blue. *Chemical Engineering Journal* 193–194, 203–210.
- MIRANDA, S.M., ROMANOS, G.E., LIKODIMOS, V., ET AL. 2014. Pore structure, interface properties and photocatalytic efficiency of hydration/dehydration derived TiO₂/CNT composites. *Applied Catalysis B: Environmental* 147, 65–81.
- MOLINA-MENDOZA, A., MOYA, A., FRISENDA, R., ET AL. 2016. Highly responsive UV-photodetectors based on single electrospun TiO₂ nanofibres. *J. Mater. Chem. C*.
- MORAIS, A., LONGO, C., ARAUJO, J.R., BARROSO, M., DURRANT, J.R., AND NOGUEIRA, A.F. 2016. Nanocrystalline anatase TiO₂/reduced graphene oxide composite films as photoanodes for photoelectrochemical water splitting studies: the role of reduced graphene oxide. *Phys. Chem. Chem. Phys.* 18, 4, 2608–2616.
- MOSER, J., A. BARREIRO, AND A. BACHTOLD. 2007. Current-induced cleaning of graphene. *Applied Physics Letters* 91, 16, 163513.
- MOYA, A., CHEREVAN, A., MARCHESAN, S., ET AL. 2015. Oxygen vacancies and interfaces enhancing photocatalytic hydrogen production in mesoporous CNT/TiO₂ hybrids. *Applied Catalysis B: Environmental* 179, 574–582.
- MUDULI, S., LEE, W., DHAS, V., ET AL. 2009. Enhanced Conversion Efficiency in Dye-Sensitized Solar Cells Based on Hydrothermally Synthesized TiO₂–MWCNT Nanocomposites. *ACS Applied Materials & Interfaces* 1, 9, 2030–2035.
- NAGAVENI, K., HEGDE, M.S., RAVISHANKAR, N., SUBBANNA, G.N., AND MADRAS, G. 2004. Synthesis and Structure of Nanocrystalline TiO₂ with Lower Band Gap Showing High Photocatalytic Activity. *Langmuir* 20, 7, 2900–2907.
- NAKADE, S., MATSUDA, M., KAMBE, S., ET AL. 2002. Dependence of TiO₂ Nanoparticle Preparation Methods and Annealing Temperature on the Efficiency of Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry B* 106, 39, 10004–10010.
- NASHED, R., HASSAN, W.M.I., ISMAIL, Y., AND ALLAM, N.K. 2013. Unravelling the interplay of crystal structure and electronic band structure of tantalum oxide (Ta₂O₅). *Phys. Chem. Chem. Phys.* 15, 5, 1352–1357.
- NG, Y.H., IWASE, A., KUDO, A., AND AMAL, R. 2010. Reducing Graphene Oxide on a Visible-Light BiVO₄ Photocatalyst for an Enhanced Photoelectrochemical Water Splitting. *The Journal of Physical Chemistry Letters* 1, 17, 2607–2612.
- NI, M., LEUNG, M.K.H., LEUNG, D.Y.C., AND SUMATHY, K. 2007. A review and recent developments in photocatalytic water-splitting using for hydrogen production. *Renewable and Sustainable Energy Reviews* 11, 3, 401–425.
- NIE, Z., PETUKHOVA, A., AND KUMACHEVA, E. 2010. Properties and emerging applications of self-assembled structures made from inorganic nanoparticles. *Nat Nano* 5, 1, 15–25.

- NIISHIRO, R., KATO, H., AND KUDO, A. 2005. Nickel and either tantalum or niobium-codoped TiO₂ and SrTiO₃ photocatalysts with visible-light response for H₂ or O₂ evolution from aqueous solutions. *Phys. Chem. Chem. Phys.* 7, 10, 2241–2245.
- OHSAKA, T., IZUMI, F., AND FUJIKI, Y. 1978. Raman spectrum of anatase, TiO₂. *Journal of Raman Spectroscopy* 7, 6, 321–324.
- OHTANI, B., PRIETO-MAHANEY, O.O., LI, D., AND ABE, R. 2010. What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. *3rd International Conference on Semiconductor Photochemistry, SP-3, April, 2010, Glasgow UK* 216, 2–3, 179–182.
- OSTERLOH, F.E. 2013. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. *Chem. Soc. Rev.* 42, 6, 2294–2320.
- PAN, C., GUO, W., DONG, L., ZHU, G., AND WANG, Z.L. 2012. Optical Fiber-Based Core–Shell Coaxially Structured Hybrid Cells for Self-Powered Nanosystems. *Advanced Materials* 24, 25, 3356–3361.
- PARK, Y., KIM, W., MONLLOR-SATOCA, D., TACHIKAWA, T., MAJIMA, T., AND CHOI, W. 2013. Role of Interparticle Charge Transfers in Agglomerated Photocatalyst Nanoparticles: Demonstration in Aqueous Suspension of Dye-Sensitized TiO₂. *The Journal of Physical Chemistry Letters* 4, 1, 189–194.
- PATTERSON, A.L. 1939. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.* 56, 10, 978–982.
- PEI, Z., DING, L., LIN, H., ET AL. 2013. Facile synthesis of defect-mediated TiO₂-x with enhanced visible light photocatalytic activity. *J. Mater. Chem. A* 1, 35, 10099–10102.
- PENG, B., LOCASCIO, M., ZAPOL, P., ET AL. 2008. Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements. *Nat Nano* 3, 10, 626–631.
- PFAFF, G. AND REYNDERS, P. 1999. Angle-Dependent Optical Effects Deriving from Sub-micron Structures of Films and Pigments. *Chemical Reviews* 99, 7, 1963–1982.
- PIMENTA, M.A., DRESSELHAUS, G., DRESSELHAUS, M.S., CANCADO, L.G., JORIO, A., AND SAITO, R. 2007. Studying disorder in graphite-based systems by Raman spectroscopy. *Phys. Chem. Chem. Phys.* 9, 11, 1276–1290.
- POMONI, K., GEORGAKOPOULOS, T., SOFIANOU, M.V., AND TRAPALIS, C. 2013. Thermal treatment and environment effect on transient photoconductivity behavior of anatase TiO₂ with dominant {0 0 1} facets. *Journal of Alloys and Compounds* 558, 1–5.
- PROTTI, S., ALBINI, A., AND SERPONE, N. 2014. Photocatalytic generation of solar fuels from the reduction of H₂O and CO₂: a look at the patent literature. *Phys. Chem. Chem. Phys.* 16, 37, 19790–19827.

BIBLIOGRAPHY

- PYRGIOTAKIS, G., LEE, S.-H., AND SIGMUND, W. 2005. Advanced Photocatalysis with Anatase Nano-coated Multi-walled Carbon Nanotubes. *MRS Proceedings* 876.
- QI, S., ZUO, R., LIU, Y., AND WANG, Y. 2013. Synthesis and photocatalytic activity of electrospun niobium oxide nanofibers. *Materials Research Bulletin* 48, 3, 1213–1217.
- RAMAKRISHNA, S., FUJIHARA, K., TEO, W.-E., YONG, T., MA, Z., AND RAMASESHAN, R. 2006. Electrospun nanofibers: solving global issues. *Materials Today* 9, 3, 40–50.
- RANDLES, J.E.B. 1947. Kinetics of rapid electrode reactions. *Discuss. Faraday Soc.* 1, 0, 11–19.
- RANGANATHAN, K., MORAIS, A., NONGWE, I., LONGO, C., NOGUEIRA, A.F., AND COVILLE, N.J. 2016. Study of photoelectrochemical water splitting using composite films based on TiO₂ nanoparticles and nitrogen or boron doped hollow carbon spheres as photoanodes. *Contributions of Homogeneous and Heterogeneous Catalysis in Biorefining: Special Issue in Honor of Prof. Ulf Schuchardt* 422, 165–174.
- RANJIT, K.T., COHEN, H., WILLNER, I., BOSSMANN, S., AND BRAUN, A.M. 1999. Lanthanide oxide-doped titanium dioxide: Effective photocatalysts for the degradation of organic pollutants. *Journal of Materials Science* 34, 21, 5273–5280.
- RAWALEKAR, S. AND MOKARI, T. 2013. Rational Design of Hybrid Nanostructures for Advanced Photocatalysis. *Advanced Energy Materials* 3, 1, 12–27.
- REGONINI, D., TELOEKEN, A.C., ALVES, A.K., ET AL. 2013. Electrospun TiO₂ Fiber Composite Photoelectrodes for Water Splitting. *ACS Applied Materials & Interfaces* 5, 22, 11747–11755.
- REGUERO, V., ALEMÁN, B., MAS, B., AND VILATELA, J.J. 2014. Controlling Carbon Nanotube Type in Macroscopic Fibers Synthesized by the Direct Spinning Process. *Chemistry of Materials* 26, 11, 3550–3557.
- REIDY, D.J., HOLMES, J.D., AND MORRIS, M.A. 2006. The critical size mechanism for the anatase to rutile transformation in TiO₂ and doped-TiO₂. *Journal of the European Ceramic Society* 26, 9, 1527–1534.
- REZA GHOLIPOUR, M., DINH, C.-T., BELAND, F., AND DO, T.-O. 2015. Nanocomposite heterojunctions as sunlight-driven photocatalysts for hydrogen production from water splitting. *Nanoscale* 7, 18, 8187–8208.
- ROUQUEROL, F., ROUQUEROL, J., AND SING, K. 1999. CHAPTER 3 - Methodology of Adsorption at the Gas–Solid Interface. In: *Adsorption by Powders and Porous Solids*. Academic Press, London, 51–92.
- S. NEOCLEUS, S. W. PATTISON, A. M. MOISALA MOTTA, A. H. WINDLE, AND D. EDER. 2011. HIERARCHICAL CARBON NANOTUBE-INORGANIC HYBRID STRUCTURES INVOLVING CNT ARRAYS AND CNT FIBERS. *Functional Materials Letters* 04, 01, 83–89.

- SANJINÉS, R., TANG, H., BERGER, H., GOZZO, F., MARGARITONDO, G., AND LÉVY, F. 1994. Electronic structure of anatase TiO₂ oxide. *Journal of Applied Physics* 75, 6, 2945–2951.
- SARKAR, D., ISHCHUK, S., TAFFA, D.H., ET AL. 2016. Oxygen-Deficient Titania with Adjustable Band Positions and Defects; Molecular Layer Deposition of Hybrid Organic–Inorganic Thin Films as Precursors for Enhanced Photocatalysis. *The Journal of Physical Chemistry C* 120, 7, 3853–3862.
- SCANLON, D.O., DUNNILL, C.W., BUCKERIDGE, J., ET AL. 2013. Band alignment of rutile and anatase TiO₂. *Nat Mater* 12, 9, 798–801.
- SCHNEIDER, J. AND BAHNEMANN, D.W. 2013. Undesired Role of Sacrificial Reagents in Photocatalysis. *The Journal of Physical Chemistry Letters* 4, 20, 3479–3483.
- SCHNEIDER, J., MATSUOKA, M., TAKEUCHI, M., ET AL. 2014. Understanding TiO₂ Photocatalysis: Mechanisms and Materials. *Chemical Reviews* 114, 19, 9919–9986.
- SCLAFANI, A. AND HERRMANN, J.M. 1996. Comparison of the Photoelectronic and Photocatalytic Activities of Various Anatase and Rutile Forms of Titania in Pure Liquid Organic Phases and in Aqueous Solutions. *The Journal of Physical Chemistry* 100, 32, 13655–13661.
- SELF, E.C., WYCISK, R., AND PINTAURO, P.N. 2015. Electrospun titania-based fibers for high areal capacity Li-ion battery anodes. *Journal of Power Sources* 282, 187–193.
- SEKOKOS, E., REGUERO, V., PALMA, J., VILATELA, J.J., AND MARCILLA, R. 2016. Macroscopic fibres of CNTs as electrodes for multifunctional electric double layer capacitors: from quantum capacitance to device performance. *Nanoscale* 8, 6, 3620–3628.
- SERP, P., CORRIAS, M., AND KALCK, P. 2003. Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis A: General* 253, 2, 337–358.
- SERPONE, N. 2006. Is the Band Gap of Pristine TiO₂ Narrowed by Anion- and Cation-Doping of Titanium Dioxide in Second-Generation Photocatalysts? *The Journal of Physical Chemistry B* 110, 48, 24287–24293.
- SHEARER, C.J., CHEREVAN, A., AND EDER, D. 2014. Application and Future Challenges of Functional Nanocarbon Hybrids. *Advanced Materials* 26, 15, 2295–2318.
- SHENG, W., WOO LEE, S., CRUMLIN, E.J., CHEN, S., AND SHAO-HORN, Y. 2011. Synthesis, Activity and Durability of Pt Nanoparticles Supported on Multi-walled Carbon Nanotubes for Oxygen Reduction. *Journal of The Electrochemical Society* 158, 11, B1398–B1404.
- SIMON, P. AND GOGOTSI, Y. 2008. Materials for electrochemical capacitors. *Nat Mater* 7, 11, 845–854.
- SING K. S. W. 2009. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure and Applied Chemistry* 57, 4, 603.

BIBLIOGRAPHY

- SOARES, M.R.N., LEITE, S., NICO, C., ET AL. 2011. Effect of processing method on physical properties of Nb₂O₅. *Journal of the European Ceramic Society* 31, 4, 501–506.
- SPURR, R.A. AND MYERS, H. 1957. Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer. *Analytical Chemistry* 29, 5, 760–762.
- STANO, K.L., KOZIOL, K., PICK, M., ET AL. 2008. Direct spinning of carbon nanotube fibres from liquid feedstock. *International Journal of Material Forming* 1, 2, 59–62.
- SUMITA, T., YAMAKI, T., YAMAMOTO, S., AND MIYASHITA, A. 2002. Photo-induced surface charge separation of highly oriented TiO₂ anatase and rutile thin films. *Applied Surface Science* 200, 1–4, 21–26.
- SUN, B., SHI, T., TAN, X., LIU, Z., WU, Y., AND LIAO, G. 2016. Titanium Dioxide Nanorods with Hydrogenated Oxygen Vacancies for Enhanced Solar Water Splitting. *Journal of Nanoscience and Nanotechnology* 16, 6, 6148–6154.
- SUN, Y., WANG, W., ZHANG, L., AND ZHANG, Z. 2012. Design and controllable synthesis of α -/ γ -Bi₂O₃ homojunction with synergetic effect on photocatalytic activity. *Chemical Engineering Journal* 211–212, 161–167.
- T. TSUNEDA, J.-W. SONG, S. SUZUKI, AND K. HIRAO. 2010. On Koopmans' theorem in density functional theory. *The Journal of Chemical Physics* 133, 17, 174101.
- TAN, Z., ABE, H., NAITO, M., AND OHARA, S. 2010. Arrangement of palladium nanoparticles templated by supramolecular self-assembly of SDS wrapped on single-walled carbon nanotubes. *Chem. Commun.* 46, 24, 4363–4365.
- TASIS, D., TAGMATARCHIS, N., BIANCO, A., AND PRATO, M. 2006. Chemistry of Carbon Nanotubes. *Chemical Reviews* 106, 3, 1105–1136.
- TIPLER, P.A. 1992. *Elementary modern physics*. Worth Publishers, New York, NY.
- TOBIAS, G., MENDOZA, E., AND BALLESTEROS, B. 2014. Functionalization of Carbon Nanotubes. In: B. Bhushan, ed., *Encyclopedia of Nanotechnology*. Springer Netherlands, Dordrecht, 1–12.
- TURNER, J.A. 1999. A Realizable Renewable Energy Future. *Science* 285, 5428, 687–689.
- UMRAO, S., ABRAHAM, S., THEIL, F., ET AL. 2014. A possible mechanism for the emergence of an additional band gap due to a Ti-O-C bond in the TiO₂-graphene hybrid system for enhanced photodegradation of methylene blue under visible light. *RSC Adv.* 4, 104, 59890–59901.
- URLAUB, R., POSSET, U., AND THULL, R. 2000. FT-IR spectroscopic investigations on sol-gel-derived coatings from acid-modified titanium alkoxides. *Journal of Non-Crystalline Solids* 265, 3, 276–284.
- VIEZBICKE, B.D., PATEL, S., DAVIS, B.E., AND BIRNIE, D.P. 2015. Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system. *physica status solidi (b)* 252, 8, 1700–1710.

- VILATELA, J.J. AND EDER, D. 2012. Nanocarbon Composites and Hybrids in Sustainability: A Review. *ChemSusChem* 5, 3, 456–478.
- WANG, C., PAGEL, R., DOHRMANN, J.K., AND BAHNEMANN, D.W. 2006. Antenna mechanism and deaggregation concept: novel mechanistic principles for photocatalysis. *Conversion photochimique et stockage de l'énergie solaire 2e partie Photochemical conversion and storage of solar energy Part II* 9, 5–6, 761–773.
- WANG, G., ZHANG, L., AND ZHANG, J. 2012a. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* 41, 2, 797–828.
- WANG, L., ZHAO, X., LU, Y., ET AL. 2011. CoMn₂O₄ Spinel Nanoparticles Grown on Graphene as Bifunctional Catalyst for Lithium-Air Batteries. *Journal of The Electrochemical Society* 158, 12, A1379–A1382.
- WANG, Q.H., JIN, Z., KIM, K.K., ET AL. 2012b. Understanding and controlling the substrate effect on graphene electron-transfer chemistry via reactivity imprint lithography. *Nat Chem* 4, 9, 724–732.
- WANG, W., SERP, P., KALCK, P., AND FARIA, J.L. 2005a. Photocatalytic degradation of phenol on MWNT and titania composite catalysts prepared by a modified sol-gel method. *Applied Catalysis B: Environmental* 56, 4, 305–312.
- WANG, W., SERP, P., KALCK, P., AND FARIA, J.L. 2005b. Visible light photodegradation of phenol on MWNT-TiO₂ composite catalysts prepared by a modified sol-gel method. *Journal of Molecular Catalysis A: Chemical* 235, 1–2, 194–199.
- WANG, X., LI, Z., SHI, J., AND YU, Y. 2014. One-Dimensional Titanium Dioxide Nanomaterials: Nanowires, Nanorods, and Nanobelts. *Chemical Reviews* 114, 19, 9346–9384.
- WU, J., XUE, Y., YAN, X., YAN, W., CHENG, Q., AND XIE, Y. 2012. Co₃O₄ nanocrystals on single-walled carbon nanotubes as a highly efficient oxygen-evolving catalyst. *Nano Research* 5, 8, 521–530.
- XIAOPING CHEN, W.S. 2013. Hydrogen production from water splitting on CdS-based photocatalysts using solar light. *Frontiers in Energy* 7, 1, 111.
- XIE, G., ZHANG, K., GUO, B., LIU, Q., FANG, L., AND GONG, J.R. 2013. Graphene-Based Materials for Hydrogen Generation from Light-Driven Water Splitting. *Advanced Materials* 25, 28, 3820–3839.
- XIE, Y., QIAN, H., ZHONG, Y., GUO, H., AND HU, Y. 2012. Facile Low-Temperature Synthesis of Carbon Nanotube/TiO₂ Nanohybrids with Enhanced Visible-Light-Driven Photocatalytic Activity. *International Journal of Photoenergy* 2012, 6.
- XIE, Z., LIU, X., WANG, W., ET AL. 2015. Enhanced photoelectrochemical and photocatalytic performance of TiO₂ nanorod arrays/CdS quantum dots by coating TiO₂ through atomic layer deposition. *Nano Energy* 11, 400–408.

BIBLIOGRAPHY

- XING, M., SHEN, F., QIU, B., AND ZHANG, J. 2014. Highly-dispersed Boron-doped Graphene Nanosheets Loaded with TiO₂ Nanoparticles for Enhancing CO₂ Photoreduction. *Scientific Reports* 4, 6341.
- XU, F., LI, L., AND CUI, X. 2012. Fabrication of Aligned Side-by-Side TiO₂/SnO₂ Nanofibers via Dual-Opposite-Spinneret Electrospinning. *Journal of Nanomaterials* 2012, 5.
- YANG, H., WU, S., DUAN, Y., FU, X., AND WU, J. 2012. Surface modification of CNTs and enhanced photocatalytic activity of TiO₂ coated on hydrophilically modified CNTs. *Applied Surface Science* 258, 7, 3012–3018.
- YANG, S., FENG, X., IVANOVICI, S., AND MÜLLEN, K. 2010. Fabrication of Graphene-Encapsulated Oxide Nanoparticles: Towards High-Performance Anode Materials for Lithium Storage. *Angewandte Chemie International Edition* 49, 45, 8408–8411.
- YEH, J.-M., HUANG, K.-Y., LIN, S.-Y., WU, Y.-Y., HUANG, C.-C., AND LIOU, S.-J. 2009. Noncovalent Interaction between Gold Nanoparticles and Multiwalled Carbon Nanotubes via an Intermediatory. *Journal of Nanotechnology* 2009, 7.
- YU, J., QI, L., AND JARONIEC, M. 2010. Hydrogen Production by Photocatalytic Water Splitting over Pt/TiO₂ Nanosheets with Exposed (001) Facets. *The Journal of Physical Chemistry C* 114, 30, 13118–13125.
- YU, J., YANG, B., AND CHENG, B. 2012. Noble-metal-free carbon nanotube-Cd_{0.1}Zn_{0.9}S composites for high visible-light photocatalytic H₂-production performance. *Nanoscale* 4, 8, 2670–2677.
- YU, Y., YU, J.C., CHAN, C.-Y., ET AL. 2005. Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye. *Applied Catalysis B: Environmental* 61, 1–2, 1–11.
- ZABAN, A., GREENSHTEIN, M., AND BISQUERT, J. 2003. Determination of the Electron Lifetime in Nanocrystalline Dye Solar Cells by Open-Circuit Voltage Decay Measurements. *ChemPhysChem* 4, 8, 859–864.
- ZHANG, H. AND BANFIELD, J.F. 2000. Understanding Polymorphic Phase Transformation Behavior during Growth of Nanocrystalline Aggregates: Insights from TiO₂. *The Journal of Physical Chemistry B* 104, 15, 3481–3487.
- ZHANG, H. AND F. BANFIELD, J. 1998. Thermodynamic analysis of phase stability of nanocrystalline titania. *J. Mater. Chem.* 8, 9, 2073–2076.
- ZHANG, M., ATKINSON, K.R., AND BAUGHMAN, R.H. 2004. Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology. *Science* 306, 5700, 1358–1361.
- ZHANG, X., SUN, Y., CUI, X., AND JIANG, Z. 2012. A green and facile synthesis of TiO₂/graphene nanocomposites and their photocatalytic activity for hydrogen evolution. *11th China Hydrogen Energy Conference* 37, 1, 811–815.

- ZHAO, Y., ZHOU, X., YE, L., AND CHI EDMAN TSANG, S. 2012. Nanostructured Nb₂O₅ catalysts. *Nano Reviews* 3, 1, 17631.
- ZHENG, W., LI, X., HE, G., YAN, X., ZHAO, R., AND DONG, C. 2014. A highly responsive UV photodetector based on hierarchical TiO₂ nanorod/nanoparticle composite. *RSC Adv.* 4, 41, 21340–21346.
- ZHOU, G., WANG, D.-W., LI, F., ET AL. 2010. Graphene-Wrapped Fe₃O₄ Anode Material with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries. *Chemistry of Materials* 22, 18, 5306–5313.
- ZHU, K.-R., ZHANG, M.-S., CHEN, Q., AND YIN, Z. 2005a. Size and phonon-confinement effects on low-frequency Raman mode of anatase TiO₂ nanocrystal. *Physics Letters A* 340, 1–4, 220–227.
- ZHU, Y., YU, F., MAN, Y., TIAN, Q., HE, Y., AND WU, N. 2005b. Preparation and performances of nanosized Ta₂O₅ powder photocatalyst. *Journal of Solid State Chemistry* 178, 1, 224–229.
- ZOU, J., ZHANG, Q., HUANG, K., AND MARZARI, N. 2010. Ultraviolet Photodetectors Based on Anodic TiO₂ Nanotube Arrays. *The Journal of Physical Chemistry C* 114, 24, 10725–10729.