Characterization of electrodeposited zinc oxide/tetrasulphonatedcopper phthalocyanines (ZnO/Ts-CuPc) hybrid films and their photoelectrochemical properties

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A B S T R A C T

Hybrid films of zinc oxide (ZnO) and tetrasulphonatedcopper phthalocyanine (Ts-CuPc) have been prepared by cathodic electro-deposition from aqueous O₂-saturated solutions of ZnCl₂ and Ts-CuPc. The Ts-CuPc content of the films can be varied in a wide range by variation of dye concentration in the electro-deposition bath – from single Ts-CuPc molecules embedded in compact crystalline ZnO to films based on an amorphous Ts-CuPc framework. With increasing dye content the colour of the films changes from light blue to deep blue. All films were characterized by XRD, SEM and AFM. Photoelectro-chemical characteristics of the electrodes were studied by photocurrent spectra and by time-resolved photocurrent measurements in 0.1 M KCl electrolyte. At the same time, changes in the electrical and photoelectrical properties of the films are observed, enabling the tuning of these properties in view of optoelectronic applications. Theoretical calculations based on density functional theory (DFT) models were made to understand the optoelectronic properties of the hybrid films. Different parallel and perpendicular orientations were tested. For the most stable hybrid structure, total and projected densities of states of the system were obtained and the alignment of the levels observed.

1. Introduction

Recently metallo-phthalocyanines complexes have attracted much attention due to their application indifferent areas such as display devices, data storage, solar cell, photo-reduction of water to hydrogen and other UV-vis light driven process [1–3], as well as their role in the photodynamic therapy of cancer [4,5]. Metallo-phthalocyanines such as copper or zinc-phthalocyanines complexes are promising materials for dye-sensitized photoelectrochemical solar cell. The conversion of solar energy into electricity is based on nano-porous–nano-crystalline photo-electrode [6–8]. In such cell, light absorption of the dye is followed by electron injection from the excited adsorbed dye into the conduction band of the semiconductor; the electrons are brought back to the oxidized dye through an external way using a counter electrode (Pt) and a redox system. It is desirable that a dye to be used as a sensitizer [9,17]; should absorb light in the whole solar spectrum, with energy of its lowest unoccupied molecular orbital (LUMO) higher

than the conduction band edge of the semiconductor. Also the dye should be attached strongly to the semiconductor surface to allow the fast electron injection into the conduction band with a quantum yield of unity. It is known that through dye-sensitization of a wide gap semiconductors, like TiO₂ or ZnO, electron can be injected from the excited state of the dye into the semiconductors [10–17], some of the systems investigated are merocyanines-ZnO [18], CuPc/TiO₂ and TiO₂/ZnPc [19]. For a recent review see Ref. [20]. These devices were investigated in the form of bilayer devices. In bilayer heterojunction devices, the photoelectrons generated in organic dye diffuse to the dye/oxide interface in order to achieve charge separation. But the photovoltaic efficiency is limited due to the short diffusion length of excitons (less than 10 nm) in the organic dye. The efficiency of these devices can further be increased by the proper choice of optical band gap and right alignment of donor acceptor molecular orbital. The former will lead to more overlapping with solar spectrum and the latter will result in higher open circuit voltage. In recent years one-step electrodeposition of nanostructured ZnO/dye hybrid films on transparent conducting substrates such as glass covered with ITO or FTO have been deposited and characterized [21–23]. Especially

Fig. 1. Structural formula of $1\alpha3\beta$ (NaSO_3)CuPc.

dye molecules with carboxylic or sulphonic acid groups were found to adsorb strongly on the growing ZnO surface, leading to their co-deposition and a significant influence on the morphology and crystallographic orientation of the ZnO [21,23–26]. The most prominent example is the dye eosin Y, which leads to highly porous and sponge-like ZnO structures that can be described as porous single crystals and proved to be very efficient in dye sensitized solar cells [21,23]. Beside organic dye molecules, tetrasulphonated metal phthalocyanines (Ts-MePc) (Fig. 1) with Zn, Al or Si as metals were also co-deposited with ZnO [24–27]. These films also exhibited some porosity of the ZnO framework, so that the Ts-MePc could act as photo-sensitizers in photo-electrochemical measurements.

In this paper, nanoporous and nanocrystalline hybrid films of ZnO/Ts-CuPc of various thicknesses are electrodeposited on ITO substrate and are characterized by X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The optical and electrical properties of hetero-junction photovoltaic device consisting of hybrid organic (Ts-CuPc)–inorganic (ZnO) structure thin film are presented. Aside from wavelength dependent photocurrent measurements, time-resolved photocurrent measurements are also discussed. Theoretical calculations based on DFT models have been made to study how the dye interacts with the surface and how the bands of the hybrid system are aligned. This is a crucial issue for knowing the possibilities of charge transfer between the donor and the acceptor. Therefore two main goals are addressed in the present paper; the preparation and characterization of hybrid TS-CuPc/ZnO thin films and the understanding of their photoelectronic properties by means of a theoretical level alignment calculation using DFT methods.

2. Experimental

High purity ZnCl_2 , KCl and $1\alpha3\beta$ (NaSO_3)CuPc (here by referred as Ts-CuPc) dye from Aldrich chemicals were taken as starting materials. The experimental setup used to prepare ZnO/Ts-CuPc thin films of various thicknesses by cathodic electrodeposition technique was consisted of a computer-controlled potentiostat/galvanostat and a classical three-electrode electrochemical cell filled with an aqueous solution containing 5.0 mM ZnCl_2 and 0.1 M KCl as supporting electrolyte. Oxygen was bubbled through the solution to make it saturated with oxygen. A glass coated with ITO substrate with sheet resistance of $10\ \Omega/\text{square}$, previously cleaned in an ultrasonic acetone bath for 15 min and then rinsed in distilled water and dried, was the working electrode. Pt and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. The deposition potential was fixed at $-0.9\ \text{V}$ and the solution temperature was kept constant at $70\ ^\circ\text{C}$ by a thermostat. The concentration of dye in solution was varied

from $10\ \mu\text{M}$ to $200\ \mu\text{M}$. The structural characterization of the hybrid films was done by high-resolution XRD using a Rigaku Ultima IV diffractometer through θ – 2θ scans with copper anticathode ($\text{CuK}\alpha$, $1.54\ \text{\AA}$). The morphology of the films was studied by using a JEOL-JSM6300 scanning electron microscope operating at 10 kV. Optical transmittance measurements were performed by means of a deuterium–halogen lamp Ocean Optics DT-MINI-2-GS in association with a 500 nm spectrometer coupled to a back-thinned CCD detector optimised for the UV–vis range. The photoelectrochemical study was performed in a conventional three electrode arrangement in a glass cell with the deposited thin film as a window of the cell illuminated from the glass/ITO side and used as a working electrode, a Pt counter electrode and a Ag/AgCl reference electrode with 0.1 M KCl as solvent. All measurements were performed at a 0.05 V with negligible dark current. The illumination time of the electrode was controlled using a automatic mechanical shutter, for which a controller box had been designed, adjusting the time of illumination to 10 s. The shutter needed about 10 ms to reach a completely open (or closed) position. The photocurrent was measured with a potentiostat/galvanostat and recorded on the PC with proper software. All samples were scanned from 200 nm to 900 nm with an interval of 10 nm.

3. Theoretical

Calculations based on density functional theory (DFT) were made using a PBE-GGA [28] functional. The used code was SIESTA [29], which projects electron wave functions and density onto a real space grid and uses as basis set a linear combination of numerical, finite-range localized atomic orbitals. We also used the DFT+U method [30] included in SIESTA that allows a semi-empirical inclusion of electronic correlations in the description of electronic spectra for systems such as zinc oxide. The used atomic basis set was a double zeta with polarization (DZP) obtained variationally [31] in a bulk ZnO reference, for zinc and oxygen, and using the phthalocyanine molecule itself for the rest of the elements. Core electrons were replaced by norm-conserving pseudo potentials [32]. The mesh cutoffs for real and reciprocal space were such that the energy was converged within 0.001 eV. It is important to keep in mind the limitations of DFT methods related to band gap underestimation. The theoretical results presented here should be taken as qualitative. In any case, DFT calculations are clearly useful in the characterization of the bonding between the dye and the nanostructure. This theoretical study can be seen as a first step to show that charge transfer is possible and to explain the experimental results presented here.

4. Results and discussion

4.1. Crystallinity

XRD patterns of ZnO films prepared with dye of different concentrations in electro-deposition bath varying from $10\ \mu\text{M}$ to $200\ \mu\text{M}$ at $-0.9\ \text{V}$ of deposition potential at $70\ ^\circ\text{C}$ for all samples are shown in Fig. 2a and b. A total charge of 1.5 C was passed in each case. It is well known that pure ZnO films show reflexions corresponding to the wurtzite structure, however, with strong (0 0 2) but weak (1 0 0) and (1 0 1) reflexions (Fig. 2a). The intensity of (0 0 2) peak increases with the rise of deposition temperature and it maximizes at $60\ ^\circ\text{C}$ and $70\ ^\circ\text{C}$. This has been reported before for electrodeposited ZnO films [33,34]. The same orientation is still seen for the hybrid films deposited with $10\ \mu\text{M}$ – $60\ \mu\text{M}$ concentration of dye in the electro-deposition bath. Going to high dye concentrations ($100\ \mu\text{M}$ and $200\ \mu\text{M}$) in the electro-deposition bath leads to the formation of amorphous films noticeable in

disappearance of all ZnO peaks. But a more careful examination of the XRD patterns of the films grown at high concentration of dye (Fig. 2b) shows the retention of crystalline character. The size of crystallites for the films fabricated with different concentrations

of dye was calculated by Scherrer's formula from the full width at half maximum (FWHM) of (0 0 2) diffraction peaks (Fig. 3a). It may be observed that the size of the crystallites decreases as the concentration of dye increases in the film, till it becomes almost

Fig. 2. (a) XRD patterns of ZnO/Ts-CuPc films deposited with 10 μM to 200 μM concentration of dye in deposition bath, $T = 70^\circ\text{C}$, $V = -0.9\text{ V}$, $Q = -1.5\text{ C}$; (b) Zoom of the XRD patterns of hybrid films with high dye content. ITO peaks are labeled as *.

Fig. 3. (a) ZnO crystallite size in ZnO/Ts-CuPc films grown from an electrochemical bath with different dye concentrations calculated from (0 0 2) reflection peak; (b) Variation of distance of crystal planes along the (0 0 2) direction as a function of the dye concentration.

Fig. 4. AFM images of the ZnO/Ts-CuPc hybrid films.

constant about 50 Å with dye concentration more than 100 μM . This clearly indicates that more is the concentration of dye in the electrolytic bath, more porous film of ZnO is formed and which has the more capacity of adsorption of dye on the surface. But the increase of dye concentration beyond 100 μM not affects the porosity of the film. Fig. 3b depicts the interplanar distance between the adjacent crystal planes calculated from the position of the (002) diffraction peak. The interplanar distance between (002) planes varies from 2.606 to 2.613 Å, which are slightly

higher than the standard ZnO crystals (2.600 Å). The distance between the reflection planes decreases as the crystallite size of ZnO decreases. But when the dye concentration is more than 100 μM the increase of distance in the reflection planes is due to the large number of associated dye molecules on ZnO surface.

Fig. 4a and b shows the AFM micrograph of a $5 \times 5 \mu\text{m}$ area for porous ZnO film grown in a bath containing 10 μM concentration of dye. It may be observed that the ZnO surface is porous and most of the pores are interconnected and surface is rough but continuous.

Fig. 5. SEM micrographs of ZnO/Ts-CuPc films with different concentration of dye in deposition bath. (a) 10 μM , (b) 20 μM , (c) 100 μM and (d) 150 μM .

Fig. 6. (a) Absorption structure of pure Ts-CuPc dissolved in water, (b) absorbance spectra of ZnO/Ts-CuPc films prepared with different concentrations of dye in electro-deposition bath at $T = 70^\circ\text{C}$, $V = -0.9 \text{ V}$ and $Q = -1.5 \text{ C}$.

Fig. 5a–d shows top view SEM images of films grown with 10 μM , 20 μM , 100 μM and 150 μM Ts-CuPc in the electro-deposition bath, i.e., the fully crystalline film with the highest crystallographic orientation and almost amorphous film with the large dye content. The crystalline character of the films with lower dye content is clearly seen in Fig. 5a and b in the appearance well defined hexagonal crystallites of similar sizes, but the porosity of the film grown with 20 μM Ts-CuPc is more than that of grown in 10 μM Ts-CuPc. By contrast, the surface of the film with high dye concentration looks more continuous and smoother.

4.2. Optical analysis

In Fig. 6a and b the absorption spectra of pure Ts-CuPc dissolved in water and of ZnO/Ts-CuPc films electro deposited with Ts-CuPc concentrations of 20 μM , 40 μM , 60 μM , 90 μM , 150 μM and 200 μM in the electro-deposition bath are presented and compared. The absorption spectrum of pure Ts-CuPc dissolved in water shows a strong peak of dimeric Ts-CuPc at 620 nm and a shoulder at 660 nm, which indicates the presence of some monomeric Ts-CuPc molecules. The strong p-electron interaction between Ts-CuPc molecules leads to the formation of dimmers by face-to-face arrangement of the phthalocyanine rings in the solution [35,36]. Apart from a blueshift of the strong dimmer peak to 630 nm and monomeric peak to 690 nm, the spectra of ZnO/Ts-CuPc films exhibit the increase of absorption intensity with increase of dye concentration in the electrolytic bath. Strong absorption peaks at 630 nm and 690 nm show the incorporation of both monomer and dimmer form in ZnO. But when the high concentration of dye like 200 μM are used for deposition, there is a decrease of absorption intensity of both peaks showing the presence of aggregates of dye molecules within the crystalline layers and some of them do not contribute to the absorption of light. All films exhibit a high transparency regardless of the dye content.

4.3. Photoelectrochemical study

In Fig. 7 the photocurrent spectra are shown for films prepared in 30 μM , 40 μM , 70 μM and 100 μM dye concentration in the electrolytic bath. The photocurrent spectrum roughly follows the absorption spectrum of the ZnO film and absorption spectrum of dye to contribute to the photocurrent. The longer wavelength absorption at 680 nm dominated the contribution to the photocurrent due to monomeric dye. It is confirmed that the photocurrent is caused by absorption in the adsorbed dye and subsequent sensitization of ZnO. This is well in line with earlier observations that this monomeric absorption provides clearly enhanced quantum efficiency because of a decreased probability of radiationless decay when compared with the aggregate absorption band at 650 nm [27,37].

Only in films with dye concentration lower than 40 μM the contribution of both ZnO and dye to the photocurrent spectra can be observed. For higher dye concentrations the photocurrent due to the dye is not longer observed and the contribution due to ZnO tends to vanish. In Fig. 7a small photocurrent owing to ZnO contribution in the 340 nm region is still observed for 70 μM dye concentration film but no photocurrent is observed in the hybrid film grown with 100 μM concentration of dye in the total range of light scan from 200 nm to 900 nm. This again confirms the total coverage of dimmer or associated species of dye on ZnO surface, of course dye molecules absorb the radiations but the energy is relaxed in the radiation less decay. The surface of ZnO particles is totally covered by the associated dye molecules that no radiation (340 nm) is able to reach the ZnO surface. The hybrid films with high dye content behaves like a thin film of pure Ts-CuPs.

Fig. 7. Photocurrent action spectra of ZnO/Ts-CuPc films electrodeposited with 30 μM , 40 μM , 70 μM and 100 μM concentrations of dye.

Fig. 8. Time-resolved photocurrent measured for the ZnO/Ts-CuPc films electrodeposited with 30 μM concentration of dye.

The films of 30 μM and 40 μM dye concentrations show a far too low photocurrent to be of technical interest. Time-resolved photocurrent measurements were used to further elucidate the origin of such low efficiency (Fig. 8). Hybrid films of ZnO/Ts-CuPc clearly showed an overshoot upon opening of the shutter characteristic of a slow regeneration reaction [27,37] of the oxidized dye molecule following fast injection to ZnO, typically caused by poor accessibility of sensitizers by the redox electrolyte and leading to a steady-state concentration of oxidized sensitizer representing a positively charged interface (electrode negative). Such a situation leads to increased recombination of charge carriers and hence a small photocurrent. Upon shutter closure, this recombination is directly observed in a small cathodic spike, representing the discharge of the positive surface charge by electrons from the electrode (hence opposite direction of current) [38].

4.4. DFT calculations

The theoretical procedure was the following. First, various nano-structures of ZnO and the Ts-CuPc molecule were separately modeled. This was the previous step before studying their interaction. ZnO bulk structure was studied and its lattice parameters and atomic positions were obtained from theory by minimizing the energy. As ZnO and hybrid films have presented a (0 0 2) orientation (see Fig. 2), it was assumed that the available faces for the dye

would be perpendicular to this direction. The selected likely face for docking the dye to ZnO was the wurtzite (1 0 0) face. Thus, slices of different widths were generated in the ZnO (1 0 0) direction, which are periodic in the (0 0 1) and (1-20) perpendicular directions. The band gap width found was 1.1 eV for the ZnO slab, lower than the experimental one, 3.43 eV. This is a well-known underestimation in DFT calculations. However, the valence band levels are correctly placed when using the DFT+U approach, so a rigid shift of conduction band levels would take the proper gap. Parallel to the study of the ZnO structure, the Ts-CuPc molecule (Fig. 1) was studied, finding its optimum geometry and higher occupied molecular orbital energy (HOMO) and lowest unoccupied energy (LUMO). The molecule is flat except the sulphonic groups which can freely rotate. The effect of these groups on the interaction with the nanostructure appeared to be very important for the bonding and not only for the molecule solubility. We then studied the interaction of the two previously converged structures by performing joint relaxations starting from different candidate bound geometries. This analysis is crucial because efficiencies of solar cells depend on organic dyes to bind optimally to the surface of the nano-structure. We have studied three types of interactions between molecule sulphonic acids and the surface. In two of them the Ts-CuPc orientation was parallel to the surface and in the last the interaction was perpendicular. Results showed that the most stable orientation was parallel to the surface with eight sulphonic oxygens, bound to zinc atoms. Furthermore, a Cu-O interaction appeared, moving the metal atom beyond the plane of the molecule. Once the preferential orientation was found, total and projected densities of states were computed for this hybrid system. The Ts-CuPc HOMO was found 0.2 eV above the ZnO valence band. A good estimate of band alignments between adsorbate and substrate was achieved with DFT+U, using the correlation corrections that gave good spectra for both systems separately. Results showed (Fig. 9) that the Ts-CuPc LUMO appears inside the nanostructure gap, so that a direct charge transfer between the donor and the acceptor does not seem possible. The LUMO+1 level appears almost

at the same energy level than the ZnO conduction band, suggesting that, if some charge transfer does happen, it should be small and through a LUMO+1 molecular excitation.

5. Conclusions

Electrodeposited ZnO/Ts-CuPc films represent a hybrid material system that can be varied in its contents in a wide range simply by variation of the Ts-CuPc concentration in the electro-deposition bath. At the same time, the optical as well as the electrical and photoelectrical properties can be tuned. Electrodeposited hybrid films with high phthalocyanine content behave as a thin film of Ts-CuPc. Photocurrent can only be generated in the films having a low concentration of dye. The probable reasons of an over shoot in the photocurrent at the beginning of illumination and a cathodic spike when the illumination was cut off are discussed and related with the low efficiency of photocurrent generation. Theoretical calculations based on DFT models have been made to understand the optoelectronic properties of the hybrid films. Results showed that Ts-CuPc LUMO appears inside the nanostructure gap, so a charge transfer between the donor and the acceptor is not possible. LUMO+1 level appears almost at the same energy level than ZnO conduction band. So if some charge transfer is possible, it should be small and due to a LUMO+1 molecular excitation.

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Fig. 9. DFT Projected Density of states for the ZnO/Ts-CuPc hybrid system. The Fermi level is aligned with ZnO valence band.

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