CaFe₂O₄ as a self-sufficient solar energy converter

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An ideal solar energy to electricity or fuel converter should work without the use of any external bias potential. An analysis of self-sufficiency when CaFe₂O₄ is used to absorb the sunlight is carried out based on the CaFe₂O₄ absorption coefficient. We started to obtain this coefficient theoretically within the experimental bandgap range in order to fix the interval of possible values of photocurrents, maximum absorption efficiencies, and photovoltages and thus that of self-sufficiency considering only the radiative processes. Also for single-gap CaFe₂O₄, we evaluate an alternative for increasing the photocurrent and maximum absorption efficiency based on inserting an intermediate band using high doping or alloying.

I. INTRODUCTION

One of the most promising methods for energy storage is the production of fuels using photoelectrochemical converters (PECs). It permits solar energy to be stored in the form of chemical bonds. For fuel production, the voltage required is supplied from the solar photons absorbed. Of course, the sunlight absorbing semiconductors should produce photovoltages greater than the redox reactions involved in fuel generation because of voltage losses due to electrode overpotentials, resistive and charge transport, etc. In particular, the generation of hydrogen and electric power from water using solar energy has attracted considerable interest.¹ It requires an artificial photosynthesis system with semiconductor electrodes that, when illuminated, breaks water down into hydrogen and oxygen.

In order to be used in solar water-splitting devices, these semiconductors must have a number of characteristics. Because of its properties, the CaFe₂O₄ semiconductor is among the most studied ternary oxide photocathodes for splitting water¹⁻⁴ ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$). The experimental energy bandgap of CaFe₂O₄ is between 1.85 (Ref. 2) and 1.9 (Ref. 4) eV, and the energetic position of the conduction (CB) and valence band (VB) edges is suitable for water splitting: electrons from the CB reduce water (promoting H₂ production) while holes from the VB oxidize water (promoting O₂ production).^{5,6} In addition, it is made up of low-cost materials such as iron and calcium. Because of these properties, this compound has been studied for water splitting induced by solar energy. Connecting p-CaFe₂O₄ and n-type TiO₂ electrodes under illumination has produced hydrogen and oxygen.¹

For a PEC to be self-sufficient (i.e., operating without the use of any external bias potential), it must generate enough photovoltage to split water [$V \geq 1.23$ V (Refs. 6 and 7)]. Otherwise, the PEC needs some external potential and it will become non-self-sufficient. Nevertheless, considering energy losses, the photovoltage V should be greater than 1.6 V.⁶ Furthermore, in order to be self-sufficient, the conduction (CB) and valence band (VB) edges must be above H₂/H₂O

(−4.5 eV from the vacuum zero energy) and below O₂/H₂O (−5.73 eV from the vacuum zero energy) redox potentials, respectively.^{5,6}

From a different aspect, CaFe₂O₄ has been studied because of its magnetic properties. The most stable structure is antiferromagnetic (AFM)^{8,9} and it is a consequence of the antiferromagnetic alignment of the magnetic moments on the two Fe atoms. These magnetic semiconductors are also promising for spintronic and quantum computing if both degree of freedoms, spin and charge of the electrons, are exploited.

In this work, starting with the electronic and optical properties obtained from first principles, we will analyze under which conditions this material can act as a self-sufficient PEC converter. Theoretical methods provide an insight into the material properties from a microscopic level that the experiment cannot provide in general. It also allows basic properties that may be less accessible or more expensive to experiment to be obtained and quantified. In order to quantify the maximum absorption efficiencies, photovoltages, and photocurrents of the PC devices, we will use the absorption coefficients obtained theoretically. After that, the electronic, magnetic, and optical properties will be discussed. Furthermore, we will suggest and evaluate new strategies so that this material can be self-sufficient as a PEC converter.

II. METHODOLOGY

In order to obtain the electronic and optical properties, the calculations were made using the density functional theory (DFT)^{10,11} with periodic boundary conditions to approximate the infinite solid, 140 k -points in the irreducible Brillouin zone and spin-polarization. In order to avoid the characteristic spurious electron self-interactions of the standard DFT methodology, we use the DFT + U¹²⁻¹⁷ method incorporating an effective orbital-dependent, one-electron potential U in accordance with the formalism described in Refs. 14 and 15. The exchange-correlation effects were described through the generalized gradient approximation

within the Perdew-Burke-Ernzerhof¹⁸ formalism. The Troullier-Martins¹⁹ pseudopotentials expressed in the Kleinman-Bylander^{20,21} form and basis set functions made up of localized pseudoatomic orbitals²² have been used.

CaFe₂O₄ has an orthorhombic structure (*Pnma*, *n*° 62) with lattice parameters $a=9.230$, $b=3.024$, and $c=10.705$ Å^{23–25} (Fig. 1). The structure parameters used in the calculation were taken initially from the experimental values. Later, the cell atom positions were relaxed with $U=0$ eV. The self-consistent convergence criterion for the maximal force on atoms is 0.04 eV/Å. The relaxed lattice parameters obtained are $a=9.218$, $b=3.017$, and $c=10.693$ Å. These relaxed parameters were then used for $U \neq 0$.

The optical transition matrix elements,²⁶ proportional to the momentum matrix elements $p_{\mu\lambda}$ between the λ and μ bands, were then calculated. Both the local and non-local parts of the pseudopotentials have been considered in the calculation of the momentum matrix elements. The complex dielectric function as a function of the incident light energy E was evaluated in the independent-particle approximation²⁶ using the transition probabilities, the electronic structure $E_{\mu,\vec{k}}$, and the band occupations $f_{\mu,\vec{k}}$ of the μ bands at $\vec{k}$ points in the Brillouin zone as

$$e_2(E) \sim \frac{1}{E^2} \sum_{\mu} \sum_{\lambda} \int d\vec{k} |p_{\mu\lambda}|^2 [f_{\mu,\vec{k}} - f_{\lambda,\vec{k}}] \times \delta(E_{\lambda,\vec{k}} - E_{\mu,\vec{k}} - E).$$

The other optical properties were obtained using the Kramers-Kronig relationships. Because the optical absorption is calculated in the independent-particle approximation, the excitonic effects are not considered.

FIG. 1. Unit cell of CaFe₂O₄.

The photocurrent J resulting from the VB to CB transitions is obtained as the difference between the absorbed and emitted photons (transformed to current^{27–29}): $J \equiv J_{VC} = J_{VC}^{(a)} - J_{VC}^{(e)}$, where $J_{VC}^{(\kappa)} = q \int a(E, \alpha_{VC}, w) g_{\kappa}(E) dE$ ($\kappa=a, e$ for absorption and emission, respectively). In this expression, $a(E, \alpha_{VC}, w)$ is the absorptivity, α_{VC} is the absorption coefficient corresponding to the VB-CB transitions, w is the thickness of the absorbent material, q is the electron charge, g_a is the incident spectrum photon flux density, and g_e is the photon flux density emitted. In this study, the AM1.5G³⁰ spectrum has been used as the incident spectrum. For the emitted spectrum, we have used the standard approach considering that the device emits radiation as a Black-body at $T_A=300$ K (Refs. 27–29) ($g_e(E) \sim E^2 f_{BE}(E, T_A, \mu_{VC})$), where $f_{BE}(E, T, \mu) = [e^{(E-\mu)/kT} - 1]^{-1}$, k is the Boltzmann constant, and $\mu_{VC} = qV$ is the chemical potential associated with the radiation emitted. Therefore, the emitted radiation depends on the voltage V .

When there are several bands involved, the previous equations must be modified^{27–29} including in the integral $J_{IJ}^{(\kappa)}$ the term (α_{IJ}/α_T) , where α_{IJ} is the absorption coefficient associated with transitions between the I and J bands and α_T is the total absorption coefficient: $\alpha_T = \sum_I \sum_{J>I} \alpha_{IJ}$. Furthermore, the emitted photon flux density is $g_e \sim E^2 \sum_I \sum_{J>I} (\alpha_{IJ}/\alpha_T) f_{BE}(E, T_A, \mu_{IJ})$. The I -band current is then $J_I^{(\kappa)} = \sum_{J \neq I} J_{JI}^{(\kappa)}$ with $J_{JI}^{(\kappa)} = -J_{IJ}^{(\kappa)}$. The carriers are extracted from the VB (holes) and CB (electrons). Therefore, it is necessary to take into account the constraints $J_V = -J_C$ and $J_I = 0$ ($I \neq V, C$) to solve the problem. These constraints agree with the charge conservation $\sum_I J_I = 0$. In the analysis of this case, we have used the absorption coefficient α_{VC} obtained theoretically for the VB-CB transitions. For the coefficients α_{IJ} involving intermediate bands (IB), we have used the conventional approach^{27–29} considering step functions.

III. RESULTS AND DISCUSSION

Under ambient conditions, calcium ferrite CaFe₂O₄ is an antiferromagnetic semiconductor. In the unit cell (Fig. 1), there are two crystallographically non-equivalent Fe atoms (Fe₁ and Fe₂), one Ca atom, and four O atoms. As shown in the figure, the Ca atom is surrounded by eight O atoms, and the Fe atoms are surrounded by six O atoms with a distorted octahedron shape.

The experimental CaFe₂O₄ energy bandgap is between 1.85 (Ref. 2) and 1.9 eV (Ref. 4) eV. We have determined the U values using the GGA+ U methodology semi-empirically by limiting the best agreement with the experimental bandgap range. Of course, in general, self-consistent GW calculations would be more appropriate for quasiparticle bandgaps. However, this method is very expensive computationally and, in some cases, presents delicate convergence issues. Furthermore, we have considered the ferromagnetic (FM) and antiferromagnetic (AFM) spin alignment of the two Fe magnetic moments. For the AFM order, the initial spin-polarization is up and down (or vice versa) for the Fe₁ and Fe₂ atoms (Fig. 1), respectively. The final result is the

AFM structure with a zero total cell magnetic momentum and the spin-polarization of the two Fe magnetic moments aligned in opposite directions. On the other hand, the same initial spin-polarization for the Fe atoms leads to the FM structure with the Fe magnetic moments aligned in the same direction and with a total magnetic moment of $5 \mu_B$ per Fe atom according to the $\text{Fe}^{3+}(\text{d}^5)$ configuration. From the results, the AFM alignment is the more stable energetically in accordance with other theoretical results found in the literature.⁹ In this configuration, the Fe_1 and Fe_2 atoms in Fig. 1 have an AFM spin configuration. With $U = 2$ and 2.5 eV for the $\text{d}(\text{Fe})$ states, the energy bandgaps obtained are 1.86 and 2.03 eV for the down-spin states. The experimental bandgap range is well represented with these values. The main effect of relaxing the cell atoms positions is for $U = 0$ with a reduction of the bandgap of 0.26 eV.

In Fig. 2(a), the band-structure diagram along high symmetry lines in the Brillouin-zone of the spin-down AFM CaFe_2O_4 is shown for several U values. An analysis of the projected density of states [Fig. 2(b)] indicates that the states of the edge of the VB are derived mainly from the $\text{p}(\text{O})$ states

FIG. 2. (a) Band-structure diagram along high symmetry lines in the Brillouin-zone of the spin-down AFM CaFe_2O_4 for several U values. (b) PDOS on species states with more contribution to the VB and CB edges. The thin and thick lines correspond to $U = 0$ and 2.5 eV, respectively.

whereas the CB edge states are derived mainly from the $\text{d}(\text{Fe}_2)$ and $\text{d}(\text{Fe}_1)$ states for the spin-up and -down components.

The main property determining the sunlight radiation absorption capacity is the absorption coefficient. Therefore, we have additionally obtained the optical properties from theoretical calculations. In Fig. 3(a), the absorption coefficient is shown for several U values. The differences with U are small when the energy is scaled by the bandgap. Therefore, the main difference is due to the value of the bandgap. It justifies, *a posteriori*, the use of U values with energy bandgap closer to the experimental data.

These absorption coefficients are used to quantify photocurrents (Sec. II), efficiencies, and photovoltages in order to analyze the self-sufficiency of the PEC converter. Our treatment is characterized by: (i) the losses due to the light emitted by radiative recombination being considered. Therefore, the output photocurrent J is the difference between that absorbed from the solar spectrum J_a and that emitted due to the radiative recombination J_e , i.e., $J = J_a - J_e$; (ii) The absorbed photons depend on the absorption coefficient. In many cases, it is considered that all incident photons above the bandgap are absorbed, whereas those of lower energy are not. It implies that the absorption coefficients are 0 for $E < E_g$ and a constant for $E > E_g$. This approach is unable to

FIG. 3. (a) Absorption coefficient for U from 0 eV ($E_g \sim 1.22$ eV) and $U = 2.5$ eV ($E_g \sim 2.1$ eV). The bandgap energy E_g has been chosen as the origin of the energy. (b) Spectral irradiance of the AM1.5G spectrum. The shaded area represents the range of the AM1.5G spectrum that could be absorbed by a semiconductor with a bandgap greater than 1.9 eV.

justify why two semiconductors with the same bandgap absorb solar radiation in different ways. Furthermore, with these approximations, the absorption would not depend on the thickness of the device. For all these reasons, we use the absorption coefficient as the criterion for absorption instead of the bandgap. In our analyses, we have used the AM1.5G solar spectrum³⁰ [Fig. 3(b)] with an irradiance of 1 kW.m^{-2} ($=1 \text{ sun}$). Nevertheless, the spectral intensity can be modified by the concentration factor X , where $X=1$ ($X>1$) corresponds to the spectra without (with) concentration.

The efficiency of a solar converter to electricity (PVC) or fuel (PEC) is similar: $\eta = VJ/P_{inc}$, where J and V are the photocurrent and photovoltage extracted from the device, and P_{inc} is the irradiance of the incident spectrum. The main difference between the two converters is that for a PEC, J is different from zero if $V > V_{redox} + \zeta_{red} + \zeta_{oxd}$, where V_{redox} is the difference between the half-cell potentials of the fuel production, and ζ_{red} and ζ_{oxd} are the overpotentials for the oxidation and reduction, respectively. For water splitting, $V \geq 1.60 \text{ V}$.⁶

The overall conversion efficiency depends fundamentally on (i) the absorption, (ii) the charge separation and transport, and (iii) the collection at the contacts or electrocatalytic fuel production. The processes (ii) and (iii) depend on the device structure, contacts, transport properties, interfacial barriers, doping, manufacture, etc. However, the absorption process only depends on the material absorption properties. Therefore, before optimizing processes (ii) and (iii) for each particular case, the absorption efficiency is a first filter. If the absorption efficiency is small with respect to the absolute maximum absorption efficiency, then the total efficiency, product of efficiencies of the three processes, will be low. Then, the absorbent material will be not suitable for any solar energy converter. For example, for single-gap semiconductors, the absolute maximum absorption efficiency^{27,28} is $\sim 33\%$ for the AM1.5G spectrum and $\sim 31\%$ for the spectrum of a 5760 K blackbody reduced by the factor 46 200.

In order to obtain the absorption efficiency, we have used other standard approximations:^{27–29} an ideal system without non-radiative recombination, without ohmic losses, and with ideal contacts. For a PEC solar energy converter, this model assumes that carrier transfer to the liquid is infinitely fast (Ohmic) and that the corresponding surface reactions are much faster than all non-radiative recombination processes. With these approximations, the results are independent of the architecture and of the energy band alignment structure.

The efficiencies, photovoltages, and photocurrents have been calculated using the absorption coefficients obtained previously from theoretical calculations. The efficiencies and photocurrents for $U=2 \text{ eV}$ ($E_g \sim 1.8 \text{ eV}$) and 2.5 eV ($E_g \sim 2.0 \text{ eV}$) are detailed in Fig. 4. The maximum efficiencies and photocurrents are reached with just a few μm of absorbent material. Therefore, for bandgap energies of between 2.0 eV ($U=2.5 \text{ eV}$) and 1.8 eV ($U=2 \text{ eV}$), the efficiencies and photocurrents are within the ranges of $22.9\% \leq \eta \leq 26.2\%$ and $14.5 \text{ mA.cm}^{-2} \leq J \leq 19.2 \text{ mA.cm}^{-2}$, respectively. The photovoltages corresponding to the maximum power (efficiency) for

FIG. 4. Efficiency η_U (%) (left y axis) and photo-current J_U (right y axis) extracted from the solar cell converter as a function of the cell thickness w using the AM1.5 G spectra and with $U=2$ and 2.5 eV .

$U=2$ and 2.5 eV ($E_g \sim 1.8$ and 2.0 eV) are 1.46 eV and 1.60 eV , respectively.

The sunlight concentration with a factor X , i.e., multiplication of the incident irradiance spectral by X , changes the efficiency η , photocurrent J , and slightly the output photovoltages V . Nevertheless, the ratio J/X is almost independent of X . For the concentration factors $X = 1/10^2/10^3/10^4$, the photovoltages and the efficiencies for the maximum power (efficiency) and $E_g \sim 1.8 \text{ eV}$ ($U \sim 2 \text{ eV}$) are $V = 1.45/1.51/1.57/1.63/1.68$ and $\eta = 26.2\%/27.3\%/28.3\%/29.4\%/30.5\%$, respectively. Similarly, for $E_g \sim 2.0 \text{ eV}$ ($U \sim 2.5 \text{ eV}$), the output photovoltages and the efficiencies are $V = 1.59/1.65/1.71/1.77/1.82 \text{ V}$ and $\eta = 22.9\%/23.7\%/24.6\%/25.4\%/26.3\%$, respectively. As has been previously mentioned, for a PEC to be self-sufficient $V \geq 1.60 \text{ V}$.⁶ Therefore, X should be larger than 10^3 if $E_g \sim 1.8 \text{ eV}$ and $X > 1$ if $E_g \sim 2.0 \text{ eV}$.

An alternative for increasing the PEC efficiency is to use doping. Experimentally doping CaFe_2O_4 with Ag, Na, and Mg increases the photocurrent density under several illumination sources.^{3,31} Upon doping, the bandgap and the electronic structure of the semiconductor are altered by inserting new states into the bandgap. These states can be characterized as a function of the position and charge as: donor, acceptor, or with amphoteric behavior. They are donors (acceptors) when they correspond to occupied (empty) states and amphoteric when they are partially full. The amphoteric states are simultaneously donor and acceptor states. Of course, the donors and acceptors will only be of practical use when they are below the CB and above the VB. Their role in the radiative and non-radiative recombination processes of these states in the bandgap has been discussed for many years. The deep levels are considered as a negative effect because they act as effective Shockley, Read, and Hall recombination centers^{32,33} via the lattice relaxation multiphonon emission mechanism (MPE).³⁴ It reduces the efficiency of the solar converters. Nevertheless, if the amphoteric states form an intermediate band (IB) in the semiconductor's bandgap,^{27–29} the negative non-radiative recombination is suppressed.^{35–37} From the technological point of view, it permits the output current and efficiency³⁸ of the solar energy converters to be increased with respect to the host

FIG. 5. Efficiency η_U (%) (left y axis) and photovoltage V_U (right y axis) extracted from the IB- CaFe_2O_4 solar converter as a function of the decimal logarithm of the concentration factor X for $U=2$ and 2.5 ($E_g \sim 1.86$ and 2.1 eV, respectively).

semiconductor. It is because the photons with energy lower than the bandgap host semiconductor are absorbed in the VB-IB, and the IB-CB transitions increasing the carriers (holes in the VB and electrons in the CB). These carriers, created via IB transitions, are added to those already produced via the usual VB-CB transitions.

The efficiencies, photovoltages, and photocurrents of CaFe_2O_4 with an IB have been obtained using the calculate absorption coefficient, a cell thickness $w > 4 \mu\text{m}$, and the AM1.5G spectrum. The efficiencies and photovoltages with respect to the concentration factor X are presented in Fig. 5. Although the efficiencies and photocurrents are much larger than those of the single gap CaFe_2O_4 semiconductor, only that corresponding to the shaded area in the figure satisfies the requirement of $V \geq 1.60$ V so that a PEC becomes self-sufficient. The results from the figure indicate that for $E_g \sim 2.0$ eV ($U \sim 2.5$ eV) and with $X \geq 10^2$, the photovoltage $V \geq 1.6$ V. For this case, the efficiencies and photocurrents are presented in Fig. 6 with respect to the energetic IB position as regards the edge of the VB. Therefore, solar converters with an IB and $X \geq 10^2$ are self-sufficient, more efficient, and generate more current than traditional ones based on single gap CaFe_2O_4 . For example with $X=10^2$, the

FIG. 6. Efficiency η_X (%) (left y axis) and photo-current J/X (right y axis) extracted from the IB- CaFe_2O_4 ($U = 2.5$ eV and $E_g \sim 2.1$ eV) solar converter as a function of the difference between the IB energy (e_I) and the VB edge energy (e_V) and with $X=10^2$ and $X=10^3$.

efficiency could increase from 24.6% to $\sim 60\%$ and the photocurrent from 14.5 to 35.0 mA.cm^{-2} . Note that when the IB is in the middle of the gap, the VB-IB and IB-CB transitions compete for the photons of the same energy, thus reducing the overall efficiency. This corresponds to removing the carriers that come from transitions involving the IB, i.e., only the usual VB-CB transition is able to generate carriers.

IV. CONCLUSIONS

The efficiencies, photovoltages, and photocurrents have been obtained from the theoretical absorption coefficients using the GGA + U methodology. We have obtained U values that limit the best agreement with the experimental bandgap range. It is justified because the differences in the absorption coefficients with U mainly come from the bandgap.

These absorption coefficients have later been used to quantify different parameters. It allows the interval of possible values of photocurrents, efficiencies, and photovoltages obtained with a PEC converter based on the CaFe_2O_4 as an absorbent semiconductor to be fixed and the self-sufficiency to be evaluated. Furthermore, we evaluate an alternative for increasing the PEC photocurrent and efficiency based on inserting an intermediate band using high doping or alloying. The operating conditions and the main parameters of this PEC have been quantified.

ACKNOWLEDGMENTS

This work was supported by the National Spanish projects MADRID-PV (S2013/MAE-2780, FEDER FUNDS) and INVENTA-PV (TEC2015-64189-C3-1-R, MINECO/FEDER).

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