Determination of electron and hole energy levels in mesoporous nanocrystalline TiO$_2$ solid-state dye solar cell

Jorge García-Cañadas a, Francisco Fabregat-Santiago a, Henk J. Bolink b, Emilio Palomares b, Germà Garcia-Belmonte a,*, Juan Bisquert a

a Departament de Ciències Experimentals, Universitat Jaume I, E-12071 Castelló, Spain

b Institut de Ciència Molecular Universitat de València, Políгон La Coma s/n, E-46980 Paterna, València, Spain

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Abstract

A study of a hybrid heterojunction solar cell based on nanocrystalline mesoporous TiO$_2$ and the hole conductor spiro-OMeTAD (2,2'7,7'-tetrakis(N,N'-di-p-methoxyphenyl-amine)-9,9'-spiro-bifluorene) has been realized. Impedance and cyclic voltammetry techniques were used to measure the interfacial properties of the hybrid heterojunction and establish the energy levels of the solid-state electrolyte. It was observed that the energy levels of the organic hole transport material are changed when it forms a film deposited onto indium-doped tin oxide (ITO). Moreover, the HOMO level of the mono oxidized spiro-OMeTAD is well coupled with the HOMO level of the dye N719 (Ru(4,4'-dicarboxy-2,2'-bipyridyI)$_2$(SCN)$_2$) which implies that it is not convenient to increase the doping of the hole conductor much further than this first oxidized state. This doping level ($n \approx 10^{19} \text{ cm}^{-3}$) also assures a high enough hole conductivity. The implications of our results to the solid-state dye solar cell performance are discussed.

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1. Introduction

Mesoporous nanocrystalline TiO$_2$ dye sensitized solar cells are promising for the success of low cost photovoltaic devices. Efficiencies of ca. 11% have been achieved using liquid electrolytes containing iodine/iodide red-ox couple. However the commercial development of such solar cells has been delayed by technological problems, some of them related to inconveniences caused by the use of volatile liquid electrolytes. In this regard, several efforts have been devoted to the replacement of the liquid electrolyte by a non-volatile solvent such as ionic liquids or solid-state hole transport materials (HTM). The former have achieved high efficiencies and impressive stability and the latter is an interesting approach towards large-scale flexible hybrid device preparation.

Hybrid heterojunctions must meet a number of requirements for the achievement of efficient light-to-energy conversion. For example, (i) the HTM has to be transparent in the visible range, (ii) it must have excellent hole mobility, and (iii) good regioregularity to avoid problems due to the HTM penetration into the voids of the mesoporous semiconductor. Moreover, the HOMO energy level of the HTM must accept holes from the oxidized dye before the electron recombination takes place between the photoinjected electrons at the semiconductor and the dye.

Despite the increasing number of publications on hybrid dye sensitized heterojunctions so far (see for instance [1–5]) the best efficiency reported is $\sim 4\%$ [6] (under 100 mW/cm$^2$ 1.5 AM illumination) using a hole transport molecule named spiro-OMeTAD (chemical name: 2,2'7,7'-tetrakis (N, N'-di-p-methoxyphenyl-amine)-9,9'-spiro-bifluorene). Needless to say that an important piece of information to optimize the solid-state dye sensitized solar cell device (s-DSSC) is the distribution of electron and hole energy levels both in the HTM and the dye. It is also well known that the densities of states place constraints over the maximum photovoltage attainable and also play a dominant role in the charge transfer kinetics that govern the injection of carriers from the dye and the recombination at the TiO$_2$/hole conductor interface. Recently, a large number of studies, includ-
ing our own, have discussed the determination of the electronic densities of states by electrochemical methods in mesoporous nanocrystalline TiO₂ [7,8] and in conducting polymers [9,10]. In the present work, we aim to apply these methods to study the position of the energy levels of each component of a s-DSSC analyzing (i) the TiO₂/dye electrode and (ii) the spiro-OMeTAD electrochemical response.

The results obtained here will be interpreted and combined to provide a general overview of the energetics of the solid-state dye sensitized solar cell.

2. Experimental conditions

The OMeTAD studied was used as received from Merck OLED Materials GmbH. Anhydrous propylene carbonate (99.7%), anhydrous dichloromethane (99.8%) and tetrabutylammoniumtetrafluoroborate were purchased from Aldrich. Potassium hexafluorophosphate was provided by Alfa Aesar. All the reagents were used as received.

Cyclic voltammetry (CV) was performed using a potentiostat–galvanostat AutoLab PGSTAT30 system. All the experiments were carried out in a three-electrode cell under N₂ atmosphere inside a Faraday box at room temperature. Electrolytic solutions were deoxygenated by dry nitrogen flow through the solution prior the experiments. For CV experiments having OMeTAD in solution, a two-compartment electrochemical cell was used. Pt wire was employed as working electrode, large area Pt wire as counter electrode and Ag/AgCl in KCl (3 M) electrode as reference. The counter electrode compartment was filled with 0.1 M tetrabutylammoniumtetrafluoroborate in dichloromethane. The reference and working electrode compartment contained the same electrolytic solution plus OMeTAD with concentration 2.5 × 10⁻³ M. In electrochemical measurements using OMeTAD film deposited onto indium-doped tin oxide (ITO) substrate (area ∼ 0.65 cm² and 100 nm-thick confirmed by profilometry techniques) as working electrode, 0.1 M KPF₆ in propylene carbonate was used as electrolytic solution. In this case Pt wire was used as counter electrode and Ag/AgCl/KCl (3 M) electrode connected to the cell by means of a salt bridge containing the electrolytic solution as reference. This last configuration was used in CV and impedance spectroscopy measurements of fresh dye sensitized nanoporous TiO₂ films of 4.6 μm thick. The dye used was Ru(4,4′-dicarboxy-2,2′-bipyridyl)₂(SCN)₂ (N719 from Solaronix).

3. Results and discussion

Cyclic voltammetry of spiro-OMeTAD in solution is shown in Fig. 1. As can be observed, there are two oxidation peaks located at ∼0.65 and ∼0.75 V versus Ag/AgCl/KCl. The first one is related to the withdrawal of one electron, i.e., the formation of the spiro-OMeTAD⁺ species, and the second peak is assigned to the extraction of a second electron from the previously formed spiro-OMeTAD⁺. A positive background current is appreciated in the voltammograms due to the diffusion of spiro-OMeTAD and spiro-OMeTAD⁺ species towards the work-
spiro-OMeTAD film switches from an insulating to a conducting state.

The cyclic voltammetry technique usually monitors the current \( j(V) \) as the potential \( V \) varies at a constant scan rate, \( s = \text{d}V/\text{d}t \). At slow enough scan rates and thin films, kinetic processes can be neglected so that the doping of the film practically occurs in quasi-equilibrium conditions. Therefore the current involved is proportional to the chemical capacitance \( C_\mu \) [9]:

\[
j = sC_\mu
\]

which is related to the change of doping induced by a potential variation as

\[
C_\mu = \varepsilon^2 \frac{\text{d}c}{\text{d}\mu}
\]

where \( \mu \) is the elementary charge, \( c \) stands for the concentration of the acceptor species, and \( \mu \) represents the electrochemical potential of electronic species. The electrode potential relates to the electrochemical potential \( \mu \) as \( V = -\frac{\mu - \mu_{\text{ref}}}{e} \), with respect to the electrochemical potential of the reference electrode \( \mu_{\text{ref}} \). So the features of the CV can be readily interpreted in terms of the chemical capacitance dependence on potential \( C_\mu(V) \). For nernstian species adsorbed onto an electrode, \( C_\mu \) shows a peak at the standard potential with slopes of \( \alpha \) 60 mV/decade, being \( \alpha \) the number of electrons transferred. Therefore, the expected width at half height must be \( \alpha \times 90 \) mV [9].

In the first oxidation peak of the cyclic voltammetry of spiro-OMeTAD adsorbed onto ITO a width at half height of \( \sim 160 \) mV has been obtained. Such value is unusually high when compared to the nernstian width for one-electron transfer. We have then interpreted this result assuming that the oxidation energy levels, \( \varepsilon = \mu \), corresponding to \( N \) molecules per unit volume are distributed according to a Gaussian expression [11–13] with mean energy \( \varepsilon_0 \) and deviation \( \sigma \) (energetic disorder):

\[
g(\varepsilon) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left[\frac{-(\varepsilon - \varepsilon_0)^2}{2\sigma^2}\right]
\]

Assuming that the holes follow the zero-temperature Fermi distribution [9] the overall result is that the chemical capacitance monitored by cyclic voltammetry is proportional to the density-of-states as [9]:

\[
C_\mu = \varepsilon^2 g(\mu).
\]

Hence, the shape of the oxidation peak is directly related to the shape of the electronic state distribution [10], the correction of finite temperature in determination of the one-particle DOS is described in [8], but for a smooth distribution as that obtained here the correction can be neglected in a first approximation. As observed in Fig. 3, an excellent fit is obtained for the anodic part of the oxidation peak. From this graph, values of 154 meV width at the half height of the peak (\( \sigma = 65 \) meV) and \( N = 2.9 \times 10^{19} \) cm\(^{-3} \) are obtained. The integration of Eq. (3), or equivalently Fig. 3, yields a value for the density of holes as a function of the voltage in equilibrium (electrochemical potential \( \mu \)). For instance at potentials corresponding to the oxidation peak the doping level results of the order of \( 10^{19} \) cm\(^{-3} \). It should be noted that a density-of-states value higher than that obtained was expected taking into account the density of spiro-OMeTAD. Several factors might have influence in the density reduction, such as the porosity of the sample, irreversible impurity chemical doping, and the existence of inactive molecules. Moreover, the analysis assumes equilibrium measurement conditions, which are likely not fully reached at the scan rate employed.

We remark that, in this analysis it has been assumed that the second oxidation peak does not perturb the shape of the left part of the first oxidation peak. Since the second oxidation peak represents a second oxidation of species previously oxidized, a complete analysis should consider the equilibrium distributions for both sets of energy levels [9,14]. However, the information extracted from the first peak suffices for our purposes.

From the previous results we have obtained the potential positions of the spiro-OMeTAD respect to the Ag/AgCl reference electrode. However, to scrutinize the possible energetic limitations of the s-DSSC it is convenient to determine the corresponding energy levels of the dye/TiO\(_2\), the HTM and of the conduction band edge of TiO\(_2\). To this end, the position of the HOMO level of the dye adsorbed onto the nanocrystalline particles of TiO\(_2\), was studied by electrochemical means. Cyclic voltammetry of sensitized TiO\(_2\) film in the same electrolyte solution as that employed for the experiments described above were used. The redox potential of the HOMO orbital of the dye was determined by oxidation from the TCO at positive potentials where the TiO\(_2\) is an insulating material and remains electrochemically inert. The LUMO energy level was obtained by adding the energy of absorption data at 750 nm.

The position of the conduction band edge of the TiO\(_2\) film was calculated following the method described in a previous paper [7]. First the chemical capacitance of the TiO\(_2\) film was measured by impedance spectroscopy. This chemical capacitance (per volume unit) follows a straight line in a semi logarithmic
Fig. 4. Chemical capacitance of dye sensitized TiO₂ film obtained from impedance measurements. The regression line provides a slope of $-3.6 \text{ V}^{-1}$, related with the factor, $-e\alpha_0/k_BT$, of Eq. (5) while the intercept of the ordinate axes, $-6.6$, is equal to $\log C_a$.

plot versus applied potential, Fig. 4, and it has a value of:

$$C_{\text{TiO}_2} = C_a \exp \left( -e\alpha_0 V \right)$$ \hspace{1cm} (5)

with

$$C_a = \frac{\alpha_0 e^2 N_t}{k_BT} \exp \left( -\frac{-\alpha_0 (\varepsilon_{cb} - \varepsilon_{F_0})}{k_BT} \right)$$ \hspace{1cm} (6)

being $N_t$ the total volume density of traps, $\alpha_0$ a factor regarding the distribution of the traps, $\varepsilon_{cb}$ the position of the conduction band edge and $\varepsilon_{F_0}$ the equilibrium Fermi level. The expression for the electronic density of states in the exponential tail below the conduction band is given by

$$g(\varepsilon) = \frac{\alpha_0 N_t}{k_BT} \exp \left( -\frac{-\alpha_0 (\varepsilon_{cb} - \varepsilon)}{k_BT} \right).$$ \hspace{1cm} (7)

From the fit of the data in Fig. 4 and taking $N_t = 2.2 \times 10^{19} \text{ cm}^{-3}$ [7] a value of $\varepsilon_{cb} - \varepsilon_{F_0} = 1.2 \text{ eV}$ has been obtained. $\varepsilon_{F_0} = -0.4 \text{ eV}$ has been estimated from the measurement of the open circuit potential versus the reference after immersion in the electrolyte. Then we can approximate the value of $\varepsilon_{cb} = 0.8 \text{ eV}$. Similar values for the capacitance were also obtained previously for TiO₂ films in aqueous solutions [7].

The results of the sets of data obtained, provide the energy levels of these different components as pictured in Fig. 5. The energy level of the spiro-OMeTAD and the HOMO level of the dye are energetically well coupled for the two first oxidation peaks observed. However, it is suggested that for a good regeneration rate of the dye an extra electrochemical potential (of at least 0.2 V) is needed as driving force for the extraction of the photogenerated holes [15]. Thus it will not be convenient to dope the spiro-OMeTAD much further from the first oxidized state. Moreover, the optimal configuration would be reached by limiting the spiro-OMeTAD doping near the energy of the oxidation peak (see Fig. 5b). This doping level ($n \approx 10^{19} \text{ cm}^{-3}$) assures a high enough hole conductivity as concluded from the mobility value of spiro-OMeTAD reported at room-temperature, $\mu_h \approx 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [16]. From these values we obtain $\sigma_h \approx 1.6 \times 10^{-4} \text{ S cm}^{-1}$, what it yields resistances of the order of 1 $\Omega \text{ cm}^2$ for 1 $\mu$m-thick hole transport layers.

On the other side, although the absorption peak of the dye matches well with the position of the conduction band of TiO₂ nanoparticles, the results obtained suggest that the LUMO level of the dye is not very far from $\varepsilon_{cb}$ in the electrolyte used. As nanostructured TiO₂ films have the property of displacing their conduction band position due to ions attached onto its surface [17–19], it is needed to choose carefully the additives that will form the environment of the TiO₂ matrix in order to avoid a mismatch between the levels of $\varepsilon_{cb}$ from TiO₂ and LUMO from dye.

In this work we have not explored if the deposition of OMeTAD over the TiO₂ film may lower the conduction band edge of TiO₂. However, due to the size of OMeTAD molecules compared with K ions, it seems very unlikely that this effect may occur. On the other side, it is clear that the addition of Li salt to the standard OMeTAD [20,21] cells has another benefi-
cial effect apart from screening of the charge: it compensates the conduction band rise due to addition of tert-butyl-piridine (TBP) [18,22]. Other ways to diminish the conduction band position and thus assure an efficient injection, are the synthesis of the TiO$_2$ nanoparticles in a more acidic media or, alternatively, to subdue the film to a protonation treatment [23], using an acidic coating such as SiO$_2$ or silanes that, at the same time prevent recombination of electrons injected in TiO$_2$, as TBP does [24].

4. Conclusions

Calculations indicate that energy levels of hybrid heterojunction solar cell based on nanocrystalline mesoporous TiO$_2$ and the hole conductor, spiro-OMeTAD are initially well positioned to obtain good efficiency. However, to avoid mismatches between the energetic levels of dye and TiO$_2$ by one side and OMeTAD on the other it is required to have a good control over the additives that are added. Care should be taken to avoid overoxidation of OMeTAD, while at the same time TiO$_2$ conduction band needs to be kept at a low enough position.

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