

# Influence of Electron Solvation at the Surface of Nanostructured Semiconductors on the Electronic Density of States

Vladimir G. Kytin, José Pablo González-Vázquez, Juan A. Anta, and Juan Bisquert

(Invited Paper)

**Abstract**—The energetics of electrons at the surface of a nanostructured semiconductor in contact with an electrolyte are analyzed in this paper. The solvation of electrons produces a gap in the density of states, which separates the occupied states from empty states by solvation energy. The dynamic effects of the solvation, with respect to the relaxation time of the electrolyte, are discussed. A calculation by random-walk numerical simulation of the diffusion coefficient of electrons moving in the surface of nanoparticles shows the reduction of the rate of transport by the polarization effect.

**Index Terms**—Electron transport, metal oxides, nanostructured semiconductors, random walk simulation.

THERE is a great interest in the electronic properties of nanostructured semiconductors prepared by low-temperature chemical routes, since these materials can provide cheap and efficient devices such as dye-sensitized solar cells (DSCs). A wide number of studies on the electronic conductivity in nanostructured metal oxides (TiO<sub>2</sub>, ZnO) surrounded with electrolyte have been summarized recently [1]. It is well known that the solvation of ions in solution produces important constraints on the rate of charge transfer [2], and reorganization energy also markedly affects the rate of charge transport in organic conductors [3]. A very important topic is the interaction of the electron at the localized state in TiO<sub>2</sub> with the electrolyte. This interaction alters the electron energy and may produce important effects on both electronic conductivity and electron transfer rate. The latter determines the rate of recombination in a DSC [4], [5]. Experimental evidence shows that the concentration and kind of ions in the electrolyte largely modify electron diffusion coefficients and activation energies of

the conductivity [6], [7]. Accounting of these effects requires considering a set of dynamical phenomena (screening charge formation, solvent polarization, electron hopping, etc.).

The starting point of our consideration is the statement that the energy of the state occupied by an electron is reduced by the solvation energy  $\delta$  with respect to the empty state (see Fig. 1). This can be viewed as the modification of the density of electronic states. Let  $E$  denote the energy of the occupied (solvated) state. The modified density of states (DOS)  $g^*(E)$  is the sum of the density of occupied states,  $g(E)f(E)$ , and the density of empty states,  $g(E - \delta)[1 - f(E - \delta)]$ . The shift of the energy is due to the fact that empty states with energy  $E$  are not solvated, while the functions  $g(E)$  and  $f(E)$  describe the density and mean occupation number for filled, and therefore, solvated states correspondingly. If the empty states are solvated, their energy will be  $E - \delta$ . Therefore, this shifted energy has to be substituted in the functions  $g$  and  $f$  for empty states. Thus

$$g^*(E) = g(E - \delta)(1 - f(E - \delta)) + g(E)f(E). \quad (1)$$

In the majority of equilibrium situations,

$$f(E) \equiv f_0(E) = \frac{1}{\exp(E - E_F/k_B T) + 1}. \quad (2)$$

Here,  $E_F$  is the Fermi energy of electrons,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. Charging and spectroscopic measurements showed that the DOS in the bandgap of nanostructured TiO<sub>2</sub> films is well described by an exponential distribution of trap energies [1]

$$g(E) = N_L/k_B T_0 \exp[(E - E_c)/(k_B T_0)]. \quad (3)$$

Here,  $N_L$  is the full number of localized states per unit volume,  $E_c$  is the conduction band edge, and  $k_B T_0$  is the width of the decay of the exponential DOS from the band edge toward the center of the gap.

A typical view of the modified DOS [see (1)] is shown in Fig. 2. In the framework of the presented analysis, we can also introduce a modified occupation number  $f^*(E)$  as follows. The number of occupied states with energy  $E$  is equal to  $g(E)f(E)$ , while the total number of states with energy  $E$  is given by (1). The modified mean occupation number of the state with energy  $E$  is equal to the number of occupied states with this energy

Manuscript received November 23, 2009; revised January 1, 2010; accepted January 1, 2010. Date of publication February 18, 2010; date of current version December 3, 2010. This work was supported by the Ministerio de Ciencia e Innovación of Spain under Project Consolider HOPE CSD2007-00007 and Project MAT2007-62982 and by Generalitat Valenciana Project 091179 PROMETEO.

V. G. Kytin is with the Low Temperature Physics and Superconductivity Department, Faculty of Physics, M. V. Lomonosov Moscow State University, 119992 Moscow, Russia (e-mail: kytin@mig.phys.msu.ru).

J. P. González-Vázquez and J. A. Anta are with the Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Seville, Spain (e-mail: jpgonzalez@upo.es; anta@upo.es).

J. Bisquert is with the Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain (e-mail: bisquert@fca.uji.es).

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Digital Object Identifier 10.1109/JSTQE.2010.2040065

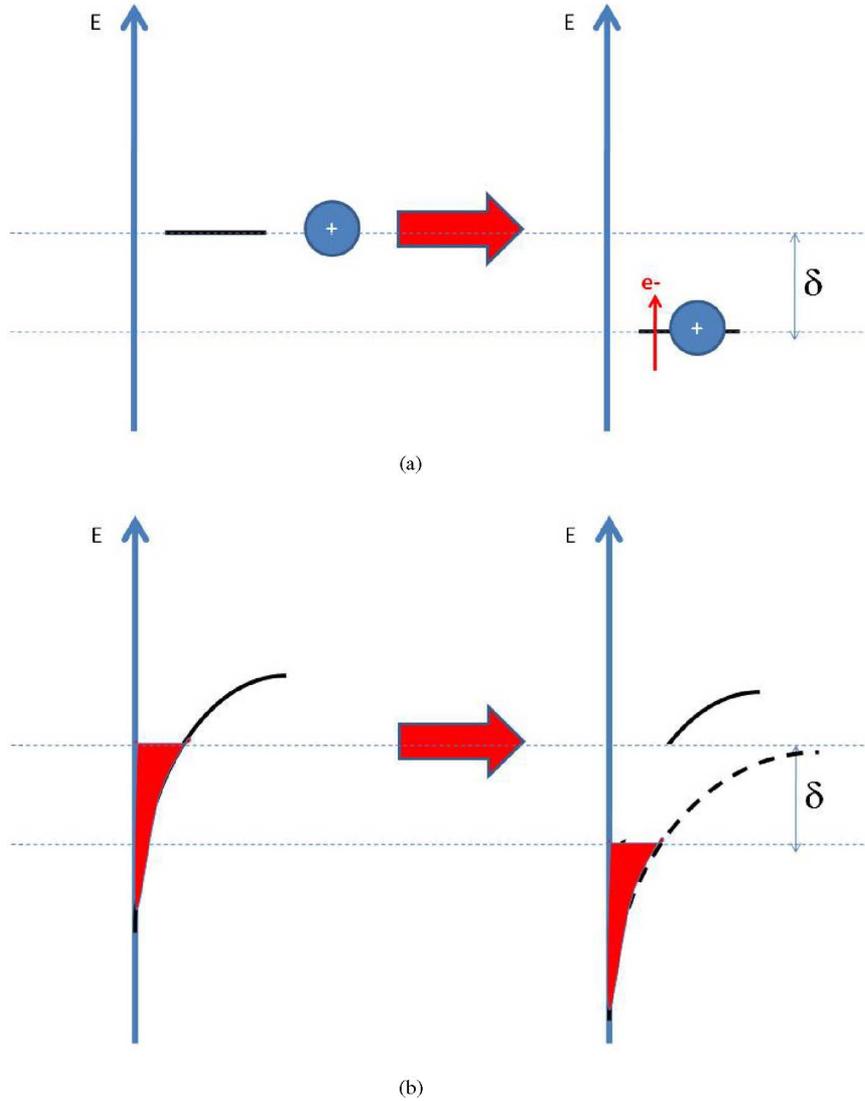


Fig. 1. Illustration of the electron solvation effect due to (a) positive ions in the electrolyte and (b) effect on the trap energy distribution.

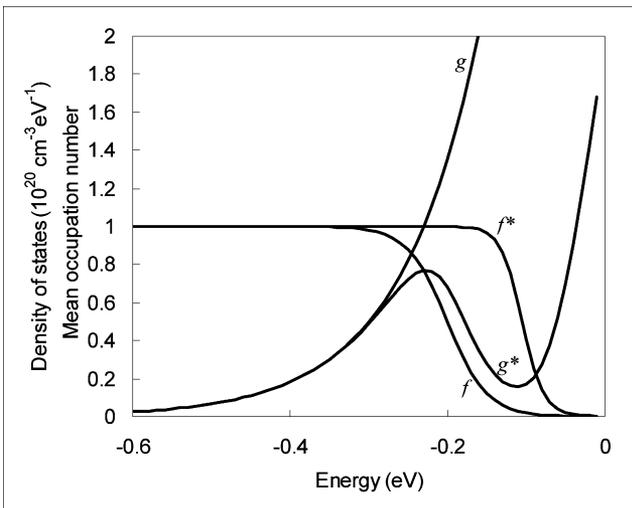


Fig. 2. DOS  $g^*(g)$  and mean occupation number  $f^*(f)$  for exponential DOS given by (1) with following parameters:  $N_L = 10^{20} \text{ cm}^{-3}$ ,  $E_c = 0$ ,  $k_B T_0 = 0.1 \text{ eV}$ ,  $E_F = -0.2 \text{ eV}$ , and  $T = 293 \text{ K}$ .

divided by  $g^*(E)$

$$f^*(E) = \frac{g(E)f(E)}{g(E-\delta)(1-f(E-\delta)) + g(E)f(E)} \quad (4)$$

The difference between functions  $g$  and  $g^*$ , and  $f$  and  $f^*$  is that DOS and the mean occupation number marked by an asterisk have real energy as an argument, while nonmarked functions have the energy of solvated state as an argument.

As can be seen from Fig. 2, a minimum appears at the DOS  $g^*$  and the mean occupation number  $f^*$  is close to 0.5 at this minimum. The width of the minimum is equal to the solvation energy  $\delta$ . The presence of this minimum increases the activation energy of electron transfer between localized states as well as activation energy of electron transfer from localized state in semiconductor to electrolyte. The latter could be an explanation of the large activation energies of conductivity observed in electrochemical gating measurements [7]. Note, however, that the capacitance measured by impedance spectroscopy is related to

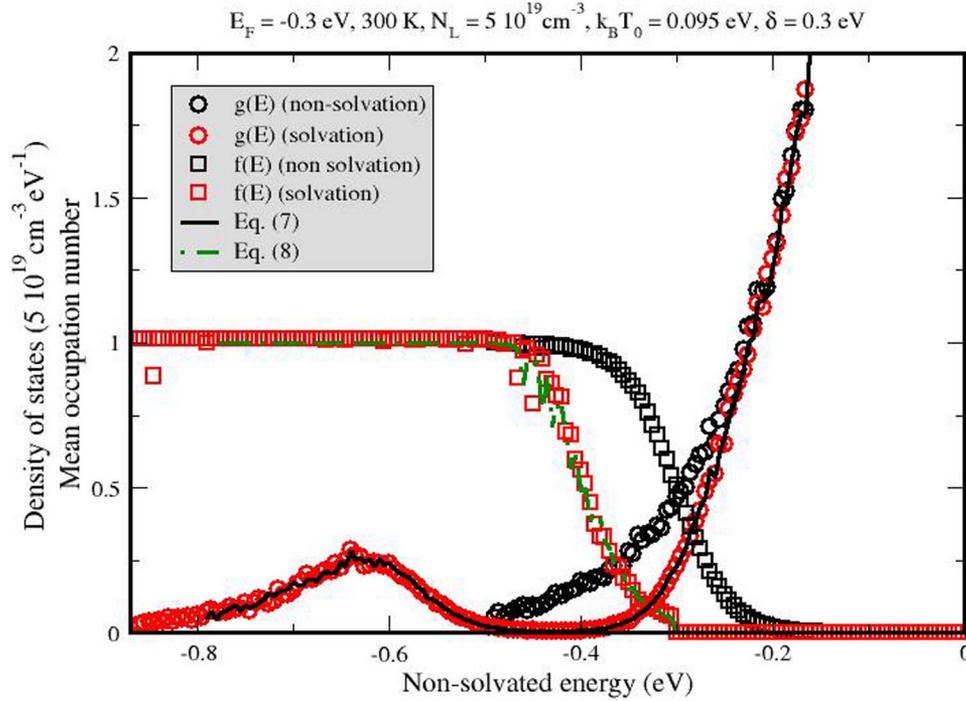


Fig. 3. Trap energy distribution and occupation probability as obtained from RWNS calculations with and without solvation effects. The simulations were performed with 50 particles in a random network of traps  $10 \times 10 \times 10 \text{ nm}^3$  (trap density  $5 \times 10^{19} \text{ cm}^{-3}$ , average trap distance = 1 nm).

the integral [8]

$$C_{\mu}(E_F) = e^2 N_L \int g(E) \frac{df(E, E_F)}{dE_F} dE \quad (5)$$

and is not modified by the solvation effect.

The value of solvation energy can be relatively large for the electronic states at the interface of the electrolyte and the semiconductor. For Debye electrolyte with mobile ions in the static limit, the value of  $\delta$  can be given by [9]

$$\delta = \int \rho_e \varphi_p dV = \frac{1}{\varepsilon_0} \int \mathbf{D}(\mathbf{r})^2 dV \approx \frac{e^2}{4\pi\varepsilon_{p\infty}\varepsilon_0 r_0} \quad (6)$$

where  $r_0$  is the radii of electronic state,  $e$  is the electron charge,  $\varepsilon_0$  is the electric constant,  $\varepsilon_{p\infty}$  is the high-frequency dielectric constant of electrolyte,  $\rho_e$  is the density of electron charge,  $\varphi_p$  is the potential created by polarization and screening charge in electrolyte, and  $\mathbf{D}(\mathbf{r})$  is the electrical displacement. For  $r_0 = 1 \text{ nm}$ ,  $\varepsilon_{p\infty} = 4.8$  (water at room temperature [10]) and  $\delta \approx 0.3 \text{ eV}$ . This value is essentially greater than thermal energy at the same temperature (26 meV).

Electron solvation in the electrolyte is a dynamical process that consists of polarization (orientation) of solvent molecules and redistribution of mobile ions (screening). Therefore, the value of  $\delta$  depends on the dynamical characteristics of the electrolyte. These characteristics can be described by the frequency dependence of dielectric constant of the electrolyte. Qualitatively, one can expect that solvation energy is equal to its static limit if the electron resides at the localized state longer than the longest time of electrolyte relaxation, and is smaller than the static limit if electron solvation becomes slower than electron

transfer. For diluted electrolytes, the slowest relaxation time is close to the screening time,  $\tau_s = \varepsilon\varepsilon_0/\sigma_{\text{ion}}$ , where  $\sigma_{\text{ion}}$  is the ionic conductivity. For example, for pH = 2 aqueous solution of  $\text{H}_2\text{SO}_4$ ,  $\sigma_{\text{ion}} = 4.3 \times 10^{-3} \Omega^{-1}\cdot\text{cm}^{-1}$  and  $\tau_s = 20 \text{ ps}$  at room temperature. However, in solid-state DSC based in organic hole conductors, the conductivity of hole conductor can have much lower values [11] of the order  $\sigma_p = 10^{-9} \Omega^{-1}\cdot\text{cm}^{-1}$ , which sets the relaxation time on the 90- $\mu\text{s}$  scale. The electron solvation is a self-consistent process: the longer the electron resides at the localized state, the larger is the reduction of its energy. This dynamics should contribute to the frequency dependence of impedance measured on porous electrodes and DSC.

To provide further confirmation of the effects predicted by this formalism due to electron solvation, we carried out random-walk numerical simulations (RWNS) in an exponential distribution of trap energies. To implement this in the simulation, we modified the algorithm described in [12]–[15] in such a way that when a trap is occupied, its energy is reduced by  $E = E' - \delta$ , where  $E'$  is the original energy of the trap. This affects the transition probability for electrons since they become more deeply trapped with respect to the original energy of the traps.

Hence, we have performed RWNS calculations with and without solvation effects and computed histograms for the trap energy distribution  $g(E)$  and the occupation probability  $f(E)$  of the traps. The simulations were performed on a random network of traps [16] such that the average distance between traps equals  $1/N_L^{1/3}$  and the number of particles is adjusted to reproduce the desired value of the Fermi level. Results are shown in Figs. 3 and 4 for the low-density case ( $E_F = -0.3 \text{ eV}$ ) and the high-density case ( $E_F = -0.2 \text{ eV}$ , same as Fig. 2), respectively.

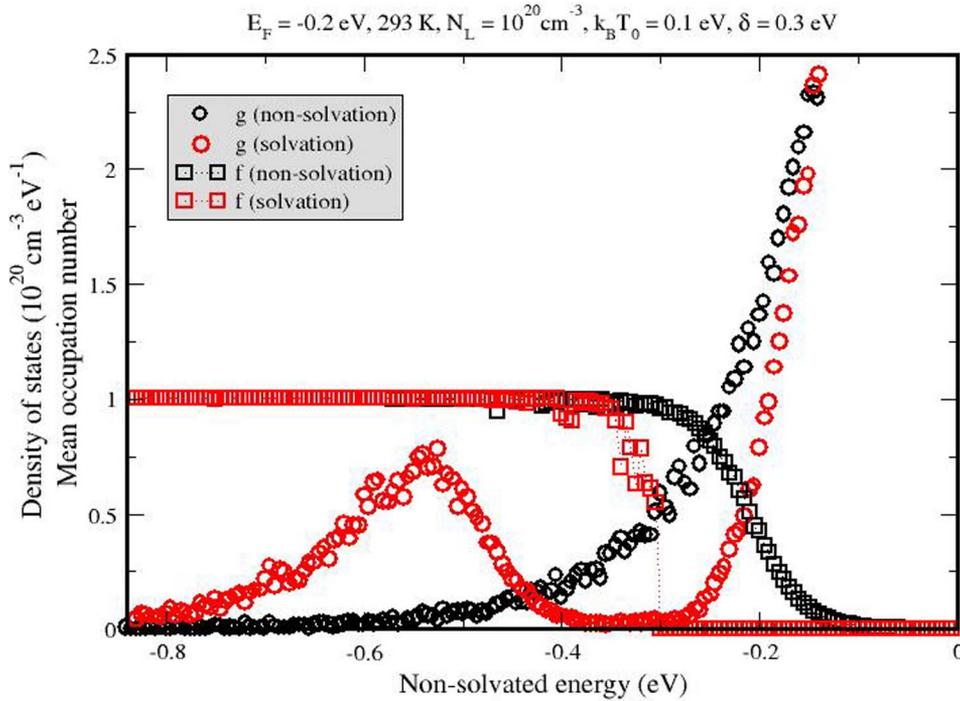


Fig. 4. Trap energy distribution and occupation probability as obtained from RWNS calculations with and without solvation effects. The simulations were performed for a trap density of  $10^{20} \text{ cm}^{-3}$ , average trap distance = 2.15 nm).

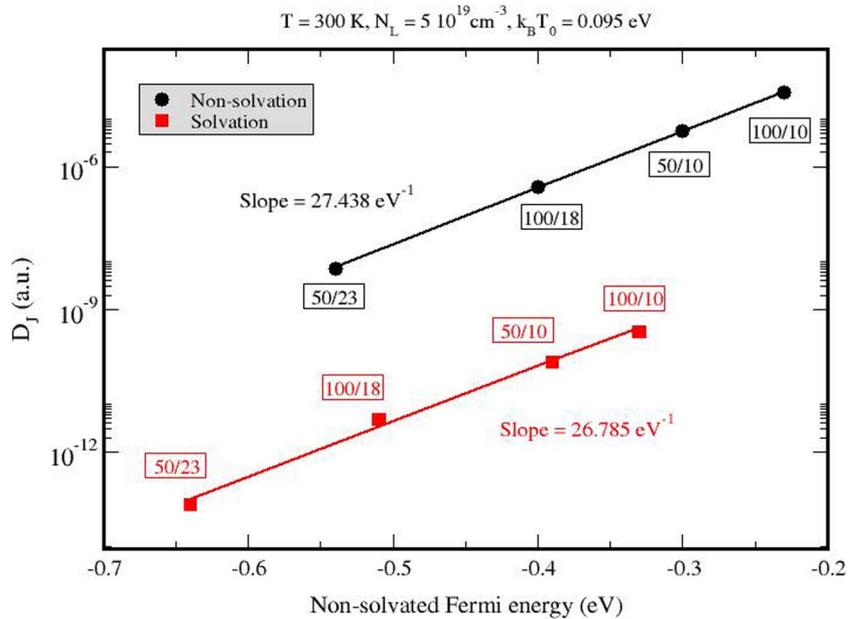


Fig. 5. Electron diffusion coefficient as obtained from RWNS calculations with and without solvation effects. The labels stand for  $N/L$ , where  $N$  is the number of electrons employed in the simulation and  $L$  the size of the simulation box in nanometers. Note that the solvation data are plotted with respect to the displaced (solvated) Fermi level.

We observe that solvation has two main effects. On one hand, the trap distribution for the occupied traps is displaced by  $\delta$  toward the tail of the distribution and then there is a gap with no traps (as illustrated in Fig. 1). On the other hand, the occupation probability is also displaced to lower energies and so is

the Fermi level. The obvious consequence of this is that the diffusion coefficient is reduced by a factor of  $\exp(-\delta/k_B T)$  (see Fig. 5).

With the simulation data, it is interesting to perform the same analysis as before to derive the “solvated” quantities from the

“nonsolvated” ones. For a fixed energy scale (non-solvated energy  $E'$ ), (1) and (4) become

$$g^*(E') = g(E')(1 - f(E')) + g(E' + \delta)f(E' + \delta) \quad (7)$$

$$f^*(E') = \frac{g(E' + \delta)f(E' + \delta)}{g(E')(1 - f(E')) + g(E' + \delta)f(E' + \delta)}. \quad (8)$$

Since “occupied traps” shift toward lower energies by  $\delta$ , in the scale of nonsolvated energies, the change of variable  $E = E' - \delta$  should apply for the term accounting for occupied traps instead of the empty traps.

To verify these equations, we use the terms  $g(E)$  and  $f(E)$  that are obtained from the simulations *with no solvation effects* to compute the quantities  $g^*(E)$  and  $f^*(E)$ . The resulting quantities coincide accurately with the results obtained in the simulation with solvation effects, as shown in Fig. 3. Note that in the high-density case of Fig. 4, the maximum of  $g(E)$  for the solvated case appears at  $-0.53$  eV, which is 0.3 eV below the maximum of  $g^*(E)$  in Fig. 2. However, in Fig. 2, the quantities are represented in a scale of solvated energies  $E$ .

Important evidence for the changes of diffusion coefficient with the concentration of cations in the electrolyte was given by Kambe *et al.* [6]. However, later, it was shown that the electron diffusion coefficient in DSC is strongly affected by the multiple trapping mechanism [1]. At given position of the Fermi level, the diffusion coefficient is strongly modified by a change of the position of the conduction band. The shift of the conduction band can affect both the rate of transport and charge transfer [17]–[20]. Further experiments are therefore necessary to separate the shift of the conduction band from solvation effects in the coefficients for transport and interfacial charge transfer.

In summary, the calculations show an important role of the reduction of the energy of occupied surface states in nanostructured semiconductors used in DSC. These results have important implications for the understanding of recombination in a DSC. It is believed that recombination in a DSC is related to the charge transfer from electrons at surface levels of  $\text{TiO}_2$  to the acceptor states in the electrolyte or a solid hole transport medium [5], [18], [20], [21]. The solvation effect should produce a charge transfer from effectively lower states than those recorded by capacitance spectroscopy. This effect may have a large impact on the recombination resistance and should be further investigated experimentally.

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**Vladimir G. Kytin** was born in Ioshkar-Ola, Russia, in 1967. He graduated from the Faculty of Physics, M. V. Lomonosov Moscow State University, Moscow, Russia, in 1992, and received the Ph.D. degree in 1995 from the same University.

During 1995–2003, he was an Assistant Professor in the Low Temperature Physics and Superconductivity Department, Faculty of Physics, M. V. Lomonosov Moscow State University, where he is employed as Associated Professor since 2004. During 2000–2002, he was a Humboldt Fellow at the Technische Universität, Munich, Germany. His research interests include metal oxides, thermoelectric materials, organic conductors, and superconductors.



**José Pablo González-Vázquez** received the B.A. degree in physics from the Universidad de Seville, Seville, Spain, in 2007. He is currently working toward the Ph.D. degree at the Universidad Pablo de Olavide, Seville.

During 2008, he was a Programmer at Accenture. He is currently supported by the Consolider project "Hybrid optoelectronic and photovoltaic devices for renewable energy (HOPE)." His research interests include solar cell modeling and computer simulation.



**Juan Bisquert** received the B.Sc. and Ph.D. degrees in physics in 1985 and 1992, respectively, from the Universitat de València, València, Spain.

He is currently a Full Professor of applied physics at the Universitat Jaume I, Castelló, Spain. His research interests include nanoscale devices for production and storage of clean energies, in particular photovoltaic devices and organic LEDs based on nanostructured metal oxides and organic conductors. He is a specialist in theoretical modeling and interpretation of impedance spectroscopy of electroactive

films, transport in disordered materials, interfacial charge transfer, and glass transition.



**Juan A. Anta** received the B.A. degree in chemistry from the Universidad Complutense de Madrid, Madrid, Spain, and the Ph.D. degree from the Physical Chemistry Institute, National Research Council of Spain, Madrid.

In 1997 and 1998, he was a Postdoctoral Fellow in the Department of Theoretical Chemistry, University of Oxford. From mid-1999 to mid-2000, he was a Research Assistant in the Department of Chemistry, Imperial College, London, U.K. He is currently an Assistant Professor at the Universidad Pablo de

Olavide, Seville. His research interests include solar cell modeling, computer simulation, and nanostructured solar cells.