Hybrid molecular materials for optoelectronic devices

Eugenio Coronado* and Emilio Palomares*

Received 25th May 2005, Accepted 28th June 2005
First published as an Advance Article on the web 28th July 2005
DOI: 10.1039/b507453n

Hybrid molecular materials based on semiconductor nanocrystalline metal oxides are a subject of intense research for the development of optoelectronic devices. Such devices follow the strategy of combining high surface area mesoporous materials with optically and electrochemically active molecules. Photovoltaic devices, molecular sensors and biosensors are some of the examples discussed in this paper.

Introduction

Molecular electronics is recognized as the new challenge for this century. Arising from the collaboration between chemistry, biology, physics and materials science, molecular electronics has passed from the development of synthetic methods to obtain supramolecular materials—conducting polymers, for example—to the control of functionality at the atomic scale for the development of functional nanodevices. This step forward has been, in part, possible thanks to the efforts made in supramolecular and supermolecular chemistry. Rapid progress has been made towards the demonstration of redox switches and light driven molecular machines as well as self-assembling nanostructures. However, after almost thirty years there are still only few examples of technological applications in this field. The reality is that the demonstration of operational supramolecular structures has only been observed in solution, and that the integration and organization of such structures into solid-state electronic or optoelectronic devices has been very limited to date. Networks of nanometer-sized metal or semiconductor particles combined with functional molecules may be the first step towards the understanding on a variety of the new phenomena arising at the interface. It is the control, at the nanometer scale, of such interfaces where most efforts is now directed, since the processes taking place at the interfaces govern device performance.

Nanocrystalline metal oxides electrodes are well established as attractive materials for the integration of molecular and supramolecular components with potential applications in optical devices, nanometer scale sensors and biosensors. The fabrication of nanocrystalline semiconductor particles with nanoscale precision is already well known. Typical sol–gel methods offer the potential of low-cost mass fabrication of a wide range of semiconductors such as SnO_2, ZnO, TiO_2 and Nb_2O_5. These methodologies have the potential to synthesize mesoporous films of semiconductor metal oxides with different band gaps and good optical properties. However, to date a few examples of molecular devices using these materials have received attention.

We will give here an insight about the use of these mesoporous nanocrystalline materials in different hybrid molecular devices, ranging from the use of such hybrid structures to obtain energy from sunlight, to the development of new hybrid bio- and molecular sensors.

Hybrid materials for molecular solar cells

Functional hybrid materials consisting of inorganic mesoporous semiconductors and organic components form an exciting, recent research area in modern material science. Perhaps, the most appealing application of such hybrid

---

Instituto de Ciencia Molecular-Universidad de Valencia. Dept. de Química Inorgánica. Facultad de Química. Bloque F. Burjassot, 46100, Valencia, Spain. E-mail: eugenio.coronado@uv.es; Fax: +34 96 354 48 59; Tel: +34 96 354 48 59

Eugenio Coronado

Eugenio Coronado, born in Valencia in 1959, has been Professor of Inorganic Chemistry at the University of Valencia since 1993 and Director of the University's Institute of Molecular Science (ICMol) . He is author of numerous contributions in the area of multifunctional materials, with particular interest in magnetic and optoelectronic properties.

Emilio J. Palomares

Emilio J. Palomares received his PhD in Chemistry from the University Politécnica de Valencia in 2001. He worked as a Marie Curie Postdoctoral Fellow at the Centre for Electronic Materials and Devices at Imperial College in London. Since 2002 he has been a research fellow (Ramon y Cajal Program) at ICMol-UV in Valencia working on the development of optoelectronic molecular and bio-molecular devices.

materials is the conversion of sun light into electrical current. Since the breakthrough of the dye-sensitised photoelectrochemical cells (DSSC),[1] the research activities on organic–inorganic photovoltaic devices have increased enormously. Hybrid molecular DSSC comprises a dye-sensitised mesoporous, high surface area, nanocrystalline TiO_2 film interpenetrated by a hole transport material (HTM). Upon light excitation of the dye an electron is injected into the conduction band (CB) of the semiconductor. Thus, the electron is collected at the contacts and transferred to an external circuit. The dye cation regeneration is achieved by the hole transport material (HTM) by transferring one electron to the oxidized dye. Fig. 1 illustrates the architecture of a DSSC and the electron transfer reactions tacking place at the device.

It is widely known that the main charge-transfer events take place at the nc-TiO_2/dye/HTM interfaces.[2] For this reason, the efficient operation of these hybrid photovoltaic devices will depend upon the minimization of the possible recombination pathways occurring at such interfaces.

Two interfacial recombination processes are of primary importance on these devices: (1) the injected electrons, which might recombine with the oxidized dye, and (2) the injected electrons recombining with the oxidized redox couple. Most efforts to minimize the recombination processes have been focused towards the control of the distance between the highest occupied molecular orbital (HOMO) of the excited dye and the nc-TiO_2 surface. It is obvious that increasing the distance between these two parameters will decrease the electron recombination rate and, therefore, an increase in the device performance has to be expected. An approach that has been investigated is to conformally coat the nanocrystalline semiconductor particles with a thin layer overcoat of a different metal oxide with a higher conduction band edge.[3] This overcoat is designed not only to increase the physical separation between the injected electrons and the oxidized dye but also to be an efficient barrier for the oxidized electrolyte.[4] Fig. 2 shows the high resolution transmission electron microscopy (HRTEM) image for the Al_2O_3 coated and non-coated nanocrystalline particles of TiO_2 in a mesoporous film. Using this approach several groups have reached higher efficiency device performance. Moreover, the low-temperature hydrolysis of Al_2O_3 onto the surface of the nanocrystalline TiO_2 allows achieving multi-structured nanolayers.[5] This novel strategy facilitates the immobilization of several molecular species in an ordered heterosupermolecular fashion that allows electron transfer cascades, achieving vectorial movement of the oxidized species away from the semiconductor surface and therefore retarding the interfacial charge recombination process.

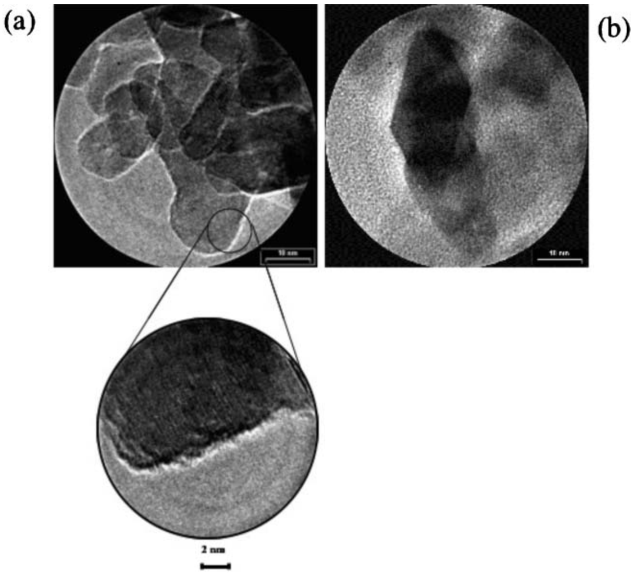

Fig. 2 HRTEM of TiO_2 nanoparticles in the presence of (a) Al_2O_3 coating and (b) without the coating.

By employing this coating route it has also been possible to prepare a highly efficient quasi-solid flexible hybrid DSSC. In such case a polymer electrolyte hole-transporting material system is used as HTM. The polymer is a matrix where the I^-/I_3^- redox couple is directly solubilized. Haque *et al.*[6] have

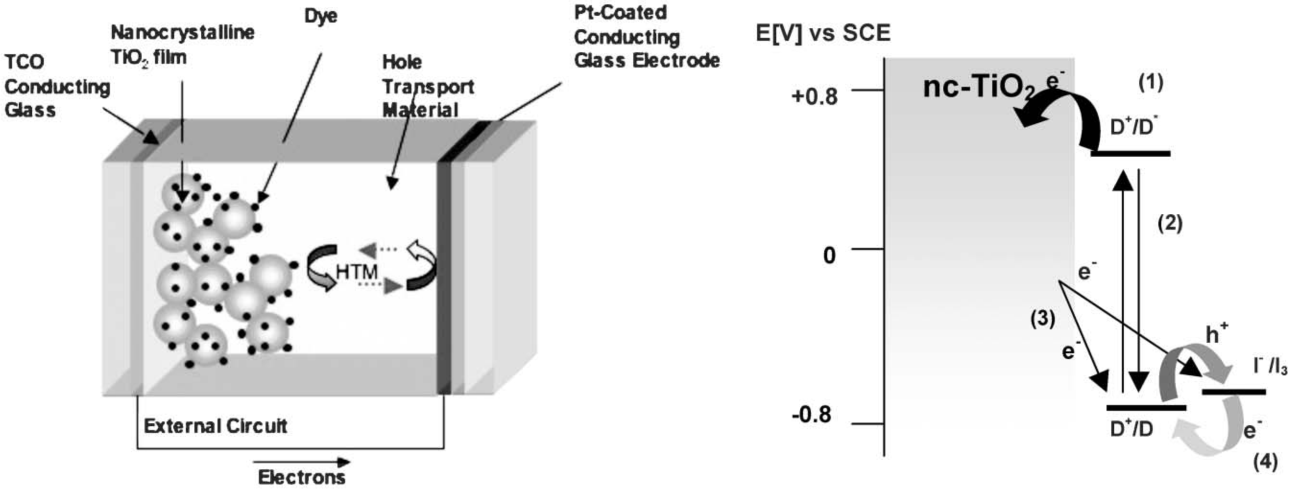

Fig. 1 Architecture of a hybrid photovoltaic device (left). On the right, a schematic representation of the interfacial charge transfer processes at the DSSC: (1) electron injection, (2) and (3) electron recombination and (4) dye regeneration. The hole transport material (HTM) is usually a liquid I^-/I_3^- electrolyte.

demonstrated that a simple 60 °C degree casting procedure results in a high penetration of the polymer electrolyte into the mesoporous nc-TiO_2/Al_2O_3 film enhancing the efficiency of the hybrid flexible DSSC.

Another strategy to control the "distance dependence" factor involves the design of new supermolecular dyes. The objective is the synthesis of dyes containing subunits that can translate, within the dye molecule, the hole away from the surface, therefore increasing the distance for the electron recombination pathway.[7] However, in this process it is critical to maintain the efficient electron injection from the dye excited states into the CB of the semiconductor. That means that the lowest unoccupied molecular orbital (LUMO) has to be close to the nc-TiO_2 particles. Hirata *et al.* have previously shown that it is possible to retard the electron recombination from milliseconds to 0.8 seconds without decreasing the electron injection rate.[7] More recently, Torres *et al.*[8] have achieved a route to anchor phthalocyanine dyes onto nanocrystalline TiO_2 particles using an axial ligand. Phthalocyanine dyes are of great interest since they have high molar extinction coefficients near to the IR region (*ca.* 700 nm). The axial ligand approach allows the control of the distance between the dye and the nc-TiO_2 surface retarding the recombination and also avoids the formation of molecular aggregates onto the surface of the nanocrystalline semiconductor particles. Due to the potential of this approach, there is no doubt that the distance control between the dye molecules and the semiconductor particles will be the focus of much interesting research on hybrid molecular solar cells in the near future.[9]

More recently, a new focus on the development of hybrid molecular solar cells is the combination of nanostructured metal oxides composites with small organic hole conductor molecules or conjugated polymers. In this case, the target is the replacement of the liquid electrolyte by a solid one. To date, the most efficient devices are based on a liquid electrolyte containing the redox couple I^-/I_3^- however; to improve the stability of the device there are increasing efforts towards a hybrid solid-state photovoltaic device.[10] A breakthrough on this issue was the use of spyro-OMETAD (chemical name: 2,2′,7,7′-tetrakis(*N*,*N*-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene) as solid electrolyte. Regardless of the low conductivity of the spyro-OMETAD when compared with other hole molecular conductors, the photovoltaic devices based on this approach are still nowadays the record cells with an efficiency of *ca.* 4% under 100 mW cm^{-2} 1.5 AM irradiation.[11] The interface between a nanocrystalline semiconductor particle and a solid organic hole conductor is currently the subject of intense research. Little is known about the charge separation processes at these interfaces as well as other important factors which control the photovoltaic device performance such as: The HTM pore penetration, self-assembly of the HTM domains inside the mesoporous semiconductor film, *etc.* All these circumstances make the solid-state hybrid molecular cells an attractive challenge for researchers.

Despite these initial problems, several groups have published excellent efficiencies for hybrid solid-state devices compared with pure organic photovoltaic cells. The use of a thin high surface area metal oxide film increases the charge separation yield and therefore the efficiency on these devices. In fact the use of thin layers (*ca.* 2 μm), which in principle seems to be a problem for efficient light harvesting, has been recently overcome with the use of organic dyes with higher molar extinction absorption coefficients.[12] The use of thin mesoporous semiconductor films is still necessary to facilitate the transport of holes by the HTM. In fact, the mobility of the positive charges through the HTM is the main issue to date. There is not doubt that new HTM with higher mobility will improve the device performance. In fact, a new type of hybrid molecular solar cell has been developed in the last years. These new devices are based on a *ca.* 100 nm mesoporous semiconductor film interpenetrated with a polymer. In this new device the polymer acts as a light absorber as well as the hole transport material (Fig. 3). Although the efficiencies of such hybrid photovoltaic devices are still low, compared to the organic fullerene based solar cells, their stability, low cost and easy-to-prepare features will make them very attractive for large-scale preparation. Furthermore, the appealing approach of using high surface area mesoporous nanocrystalline semiconductors has also attracted the attention in the development of new hybrid light-emitting devices.[13]

Hybrid materials for molecular sensors and biosensors

The immobilization of active molecules on electrodes is currently attracting widespread attention. For example protein immobilisation onto electrode surfaces is a key point for the development of a broad range of bioanalytical devices.[15] Moreover, the electronic coupling of a redox protein to a transparent electrode is of fundamental importance in the design of optical-based nanodevices. On the other hand molecular sensors based on specific receptors for the selective recognition of harmful analytes such as mercury, cyanide, *etc.* are focusing the attention not only of researchers but also of many industries.

Mesoporous metal oxide electrodes combine properties of high surface area, optical transparency in the visible range, non-toxicity, ease to handling and chemical stability, with

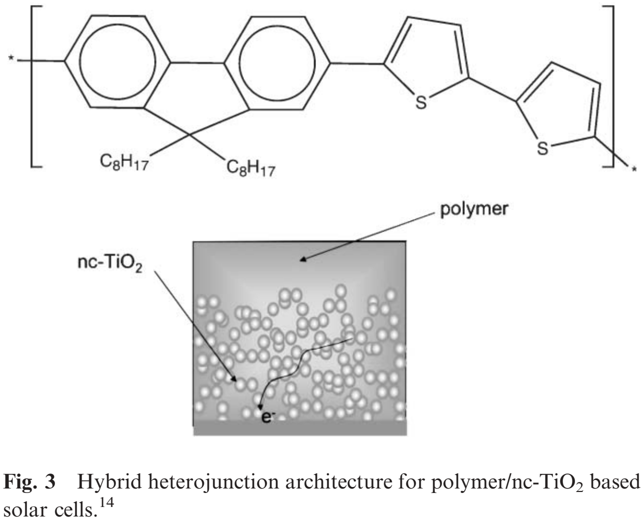

Fig. 3 Hybrid heterojunction architecture for polymer/nc-TiO_2 based solar cells.[14]

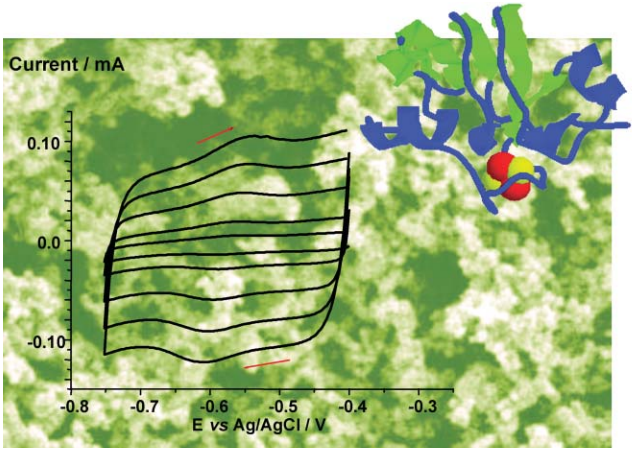

Fig. 4 Cyclic voltammogram for a 4 μm thick nc-SnO_2 film sensitivized with a 2Fe : 2S (red and yellow respectively) ferredoxin protein.

electrochemical activity at potentials negative to their conduction band edge. In addition, the mesoporous structure of the nanocrystalline films enhances the active surface area, by a factor of almost 800 for an 8 μm thick film. For example, the immobilisation and redox activity of several negatively charged proteins on modified nanocrystalline metal oxide electrodes have been demonstrated.[16] Thus, proteins such as ferredoxin (Fig. 4) can be easily studied by spectroelectrochemical means when adsorbed onto the surface of mesoporous SnO_2 films.

Moreover, direct sensing of the presence of nitric oxide can be measured using this approach. The use of hybrid biointerfaces formed by heme proteins, such as cytochrome C (Cyt C) and hemoglobin (Hb), immobilised in a transparent mesoporous SnO_2 film allows the electrochemical sensing of nitric oxide with a detection limit of 1 μM.[17]

As mentioned before, not only the high surface area of the mesoporous semiconductor film, but also the transparency in the visible spectrum are remarkable properties of such material. The optical studies of photoinduced charge separation between zinc-substituted Cyt C and a nanocrystalline TiO_2 electrode can be investigated by transient optical spectroscopy and the photocurrent action spectra measured to demonstrate the charge separation on these electrodes.[18] This is of special relevance, since optoelectronic devices are based on electron transfer reactions and therefore, the "bottom-up" approach for the development of nanoscale optically active structures, using hybrid biomaterials, will have to study the fundamental charge transfer reactions taking place at the interface.

On the hand, heterogeneous molecular sensors present several advantages when compared with solution-based probes. Heterogeneous anions or cations sensors, based upon the adsorption of specific receptors to solid supports, are technologically attractive as they are easy to use and reusable. Moreover, colorimetric sensors that do not require the use of any spectroscopic instrumentation (the so-called "naked-eye-sensors") are particularly appealing due to their simplicity in measuring the presence of the analyte. A breakthrough in this area has been the use of open mesoporous high surface area films.[19] In some cases, the film not only acts as a passive support but also controls the surface pH, due to the high hydroxylated surface area, being a self-buffering material for the receptors anchored onto the nanocrystalline particles. In the past, applications of hetereogeneous sensors were seriously limited by their low sensitivities and slow response times. However, by the use of these mesoporous transparent films it has been demonstrated that these problems can be overcome. For example new molecular sensors have been recently reported where their selectivity towards the analyte, for example mercuric ions[20] (Fig. 5), their stability, low cost fabrication and easy-to-prepare properties makes them a interesting target for not only materials chemists but also for the analytical industry.

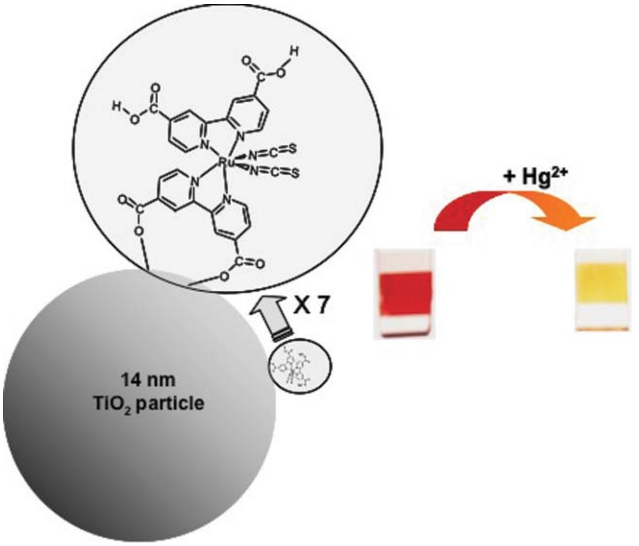

Fig. 5 Reversible heterogeneous colorimetric sensing of mercury using nanocrystalline semiconductor particles sensitivized with ruthenium dyes.

Conclusions

There are striking advances being made in designing and synthesizing new molecular dyes, organized mesoporous nanocrystalline and molecular semiconductors. Enormous efforts are also being made towards handling and introducing polymers at inorganic semiconductor interfaces, where properties are tailored for increasing device performance. As both streams of research come together in multidisciplinary research, the future looks bright for hybrid photovoltaic molecular devices. Still, potential approaches in materials research to optimize the electron transport and control the charge separation process are being explored. Thus, nanostructures with high surface area as those provided by oriented semiconductor metal oxide rods, are good candidates as working electrodes. Moreover, the molecular ordering of the organic/inorganic interface appears to be also crucial to improve the device performance. The use of molecules with high molecular extinction coefficient in the IR region, such as phthalocyanines, with self-assembling motifs may induce molecular ordering in donor-acceptor nanostructured domains controlling the charge transport trough the interface of the device. Furthermore, the interface between biology and materials science allows us to create a discipline with attractive applications of immobilized redox proteins to drive nano-biocatalytic processes that can generate a specific product of interest or detect a toxic analyte and transform them into a harmless product. As for the molecular receptors adsorbed onto mesoporous semiconductor films, such films allow high loading, enabling optical sensing for analyte binding. The semiconductor character of titanium dioxide also can allow the anchored molecular receptor to be cycled between their oxidized and reduced states on application of positive and negative potentials, without the use of mediators. Repetitive cycling of immobilized molecular redox active sensors on mesoporous nanocrystalline semiconductors may enable the reversible sensing of species in a near future.

Acknowledgements

Financial support from the Spanish Ministerio de Educación y Ciencia (Project MAT2004-03849 and EP Ramón y Cajal Fellowship) is acknowledged. EP would like to thank Dr James R. Durrant and Dr Saif A. Haque for their help and useful comments.

References

1 B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737–749.
2 James R. Durrant, Saif A. Haque and E. Palomares, *Coord. Chem. Rev.*, 2004, **248**, 1247–1257.
3 E. Palomares, John N. Clifford, Saif A. Haque, T. Lutz and James R. Durrant, *J. Am. Chem. Soc.*, 2003, **125**, 475–482.
4 F. Fabregat-Santiago, J. García-Cañadas, E. Palomares, John N. Clifford, Saif A. Haque, James R. Durrant, G. García-Belmonte and Juan Bisquert, *J. Appl. Phys.*, 2004, **96**, 6903–6907.
5 John N. Clifford, E. Palomares, Md. K. Nazeeruddin, R. Thampi, M. Gratzel and James R. Durrant, *J. Am. Chem. Soc.*, 2004, **126**, 5670–5671.
6 Saif A. Haque, E. Palomares, Hari M. Upadhyaya, L. Otley, Robert J. Potter, Andrew B. Holmes and James R. Durrant, *Chem. Commun.*, 2003, 3008–3009.
7 N. Hirata, Jean-Jacques Lagref, E. Palomares, James R. Durrant, M. K. Nazeeruddin, M. Gratzel and Davide Di Censo, *Chem. Eur. J.*, 2004, **10**, 595–602.
8 E. Palomares, M. Victoria Martínez-Díaz, Saif A. Haque, Tomas Torres and James R. Durrant, *Chem. Commun.*, 2004, 2112–2113.
9 *Materials Chemistry Forum Newsletter Royal Society of Chemistry Highlights*, 2004, **7**, 6.
10 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature*, 1998, **395**, 583.
11 J. Kruger, R. Plass, M. Gratzel and H.-J. Matthieu, *Appl. Phys. Lett.*, 2002, **81**, 367.
12 L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida and M. Gratzel, *Adv. Mater.*, 2005, **17**, 813–815.
13 Md. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli and M. Gratzel, *J. Am. Chem. Soc.*, 2003, **125**, 8790–8797.
14 P. Ravirajan, Saif A. Haque, James R. Durrant, Donald D. C. Bradley and J. Nelson, *Adv. Funct. Mater.*, 2005, **15**, 609–617.
15 Gianfranco Gilardi and Andrea Fantuzzi, *Trends Biotechnol.*, 2001, **19**, 468–476.
16 E. Topoglidis, E. Palomares, Y. Astuti, A. Green, Colin J. Campbell and James R. Durrant, *Electroanalysis*, 2005, **17**, 1035.
17 E. Topoglidis, Y. Astuti, F. Duriaux, M. Gratzel and James R. Durrant, *Langmuir*, 2003, **19**, 6894–69001.
18 E. Topoglidis, Colin J. Campbell, E. Palomares and James R. Durrant, *Chem. Commun.*, 2002, 1518–1519.
19 E. Palomares, James R. Durrant and Ramón Vilar-Compte, *Adv. Funct. Mater.*, 2004, **14**, 111–115.
20 E. Palomares, Ramón Vilar-Compte and James R. Durrant, *Chem. Commun.*, 2004, 362–363.