

Solar energy harvesting in photoelectrochemical solar cells†

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Received 11th December 2006, Accepted 28th February 2007

First published as an Advance Article on the web 20th March 2007

DOI: 10.1039/b618065e

Here we study different approaches for increasing energy harvesting in titania based photoelectrochemical solar (PES) cells. We study the light harvesting of PES cells when photonic crystal and photonic sponge architectures are used. We also report on the influence of the surface corrugation of the metal electrode on the harvesting of photocarriers in solar cells

Introduction

Nanostructured semiconductor films have attracted increasing attention, since their physical and chemical properties can provide new materials for efficient and cheap photovoltaic solar cells. The introduction of dye-sensitized photoelectrochemical solar (PES) cells¹ opened the possibility of a promising alternative to conventional silicon based solar cell technology. This approach takes advantage of the large surface area of nanoparticles for increasing light harvesting, and maximizing the number of dye molecules to extend the spectral response of PES cells. Moreover nanoparticles show new properties different from those of the bulk that can enhance photochemical response as has recently been shown for mesostructured CeO₂ based PES cells.²

Nevertheless, there are two main obstacles to the development of high efficiency PES cells. They concern the maximum light harvesting of sunlight and the efficient collection of photocarriers at electrodes. For these purposes, researchers have focused on optimization of the chemical composition of titania³ and electrolyte,⁴ as well as the development of new sensitized dyes able to extend the spectral response or enhance charge separation.⁵ Indeed, device response improvement would allow the use of thinner TiO₂ layers that would reduce the recombination of photoexcited carriers and therefore increase PES cell efficiency.

Dyes with red absorbance usually have low molar extinction coefficients that reduce charge injection into the main semiconductor layer. This problem has been partially solved by the synthesis of sensitizers with an increased molar extinction coefficient, and also by tuning the HOMO and LUMO levels.⁶

The strategy to improve PES cell efficiency is directly related to light scattering phenomena in the photoactive material. Indeed, nanoparticles employed in PES cells have the

advantage of ensuring high surface areas to maximize photoelectrochemical processes. However, the resulting nanocrystalline TiO₂ films are poor light scatterers.^{7,8} The introduction of scattering centres in the device electrode should lead to an enhancement of the light harvesting. In such a way, scattering layers formed by large titania particles^{7,9,10} have been deposited on nanostructured TiO₂ film, or spherical voids (around 200–300 nm) inserted in the electrodes.⁷ Nevertheless, only modest enhancement factors have been reported. Another approach, first introduced by Mallouk *et al.*,¹¹ and then studied by several groups,^{12,13} was to localize photons into the active material by using TiO₂ inverse opal based photonic crystals (PC). Also they have used a disordered scattering layer¹⁴ coupled to a conventional nanocrystalline TiO₂ film, resulting in an enhancement of the red region of the solar spectrum. In spite of the fact that this approximation is very attractive, light localization effects are still restricted to small frequency regions of the solar spectrum. It would be desirable to find new photonic architectures able to localize photons of the whole solar spectrum near the photoactive medium. In this way, knowledge of strongly scattering systems¹⁵ can help in the design of new solar cells able to harvest light in broad spectral regions. Most of the work published so far concerns materials formed by isolated or interconnected high refractive index particles (titania,¹⁶ GaAs,¹⁷ GaP,¹⁸ Ge,¹⁹ *etc.*) with a porosity value below 60%. TiO₂ is a very appropriate scattering material, as it is transparent to visible light and possesses a high refractive index value ($n = 2.7$).²⁰

Our strategy to enhance light harvesting in PES cells consists of designing an architecture able to harvest efficiently photons from a broad optical region. We have recently reported a new solar cell architecture, based on the photonic sponge (PhS) concept,²¹ able to localize photons from the whole solar spectrum. This new structure is formed by a quasi-Apollony fractal distribution of interconnected spherical cavities in the TiO₂ active material.²²

In this paper, we present a comparison between PES cells with PC¹³ and PhS²² topologies recently reported by our group. Finally, it would be very interesting to increase the metal surface area to enhance the harvesting of photo-generated charge carriers (electrons and holes). We will also report on the influence of the surface corrugation of metal electrodes on PES cells.

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† This paper is part of a *Journal of Materials Chemistry* theme issue on New Energy Materials. Guest editor: M. Saiful Islam.

Experimental

Synthesis of TiO₂ inverse photonic crystal

In the following we will describe the components of the photoelectrochemical cell. The electrode is made of nanoparticles of TiO₂ with inverse opal topology. We have used thin film opal templates with a thickness of 8 µm, grown by the method of Xia *et al.*²³ The latex opals that were grown on ITO electrodes have a particle size of 245 nm. Substrates were cleaned successively with deionized water, acetone, isopropanol and ethanol and dried with a stream of N₂. Latex particles (IKERLAT polymers) were cleaned with deionized water and submitted to several cycles of sonication/centrifugation prior to form the PC described above. We have synthesized TiO₂ in the template pores by using titanium isopropoxide (Aldrich, 99.9%) as precursor. Several cycles of infiltration and temperature treatment at 50 °C of the samples were employed until full infiltration was achieved. Then, the latex template was selectively removed to obtain the inverse structure, either by firing the sample at high temperature (450 °C) or through a gentle chemical attack with toluene. An improvement of the electrical connectivity between nanoparticles and the titania–anatase phase was obtained by firing the samples at 450 °C. For comparison purposes, we also prepared reference photoelectrochemical cells with the same thickness and chemical method as for the PC. It is important to stress the much higher porosity of the inverse opal topology (with 76% void volume).

Synthesis of TiO₂ inverse photonic sponge (PhS)

Our PhS samples were prepared in a similar manner as those of inverse PC. However we used completely different colloidal templates with the following steps. Firstly, we built a random colloidal template, 23 µm thick, made from a suspension of monodisperse latex spheres of 1500, 400, 300 and 150 nm diameter with volume proportions of 82 : 12 : 4 : 2 respectively to favour the Apollony architecture.²⁴ Colloidal packaging was prepared following the customary methods used for thin film colloidal crystals. Colloidal suspensions of polydisperse particles as well as ITO substrates were submitted to the same preparation processes as used for the PC case. The aqueous suspension with a concentration of 10% by weight was introduced into the cell. As the particles have very different size values they were sedimented very quickly to favour fractal ordering in the colloid. The method to obtain the inverse structure is the same as used for the inverse TiO₂ opal topology. For the sake of comparison, we also made twin reference samples of titania nanoparticle paste produced with the same physico-chemical method but lacking the PhS architecture. Both PhS and reference samples have the same thickness value (23 micrometres).

Solar cell assembly

The PES cell was made as follows. The electrode is composed of nanoparticles of TiO₂ with PhS or inverse opal topology as described above. For the standard solar cell, we employed a paste of titania nanoparticles synthesized according to the same procedure as in the case of PhS or inverse opal.

The cell was assembled by sandwiching a 50 micrometre thick Surlyn (Dupont) spacer between the inverse opal, sponge, or standard TiO₂ electrode and the counter electrode. The counter electrode was made by sputtering platinum over an ITO substrate. The redox couple electrolyte solution consisted of 0.5 M of LiI and 0.05 M of I₂ with 0.4 M of *tert*-butylpyridine.

Preparation of PES cells with corrugated metal electrodes

We also studied the influence of the roughness of the metal back electrodes on the photoelectrochemical response of standard PES cells. In this study, metal electrodes were fabricated by depositing a layer of platinum layer over the structured surface of commercial DVDs. The objective was to increase the contact surface from the corrugated electrode.

To make the back electrode, a commercial DVD was opened and cut into pieces of 2.5 × 2.5 cm. Then, the inner surface was cleaned with ethanol and NaOH to remove the aluminium layer. Once cleaned, a ~160 nm layer of platinum was sputtered over the structured surface of the DVD sample. Reference electrodes were fabricated by using the method above described but performed on the flat surface of a DVD.

TiO₂ nanoparticles and PES cell fabrication were performed with the well known method reported by Grätzel and colleagues.³ Here the new element is the platinum corrugated back electrode and also the solvent used in the electrolyte. The electrodes have an active area of 0.7 × 0.7 cm² and a thickness value of 10 micrometres. The electrolyte used was a solution of I[−]/I₃[−] in polyethylene glycol. Acetonitrile electrolytes, of customary use for PES cells, are not valid for this configuration because they react with the polycarbonate of DVDs, destroying the surface of the electrode.

Sample characterization

The morphology of the samples was examined by scanning electron microscopy (SEM) with a JEOL 6300 microscope using an accelerating voltage of 20 kV. The samples were covered by a sputtered thin gold layer before imaging.

We also performed optical experiments on different types of titania electrodes. Those experiments, concerning absorption, transmission and reflectance, are not reported here, but they can be found in ref. 13 and 22.

Photoelectrochemical characterization was carried out in an Oriel solar simulator. Solar cell characterization was performed using a global AM1.5 filter equivalent to a solar intensity of 1000 W m^{−2}.

Results and discussion

Photonic harvesting of PCs and PhSs

For the sake of comparison, we firstly prepared a titania solar cell electrode with an inverse photonic crystal topology.

Fig. 1 shows the SEM image of the TiO₂ inverse opal made of a periodic distribution of spherical voids. One can see the periodic distribution of spherical voids of 170 nm diameter with a porosity value of 76%. The periodicity of the structure has been carefully selected to tune the adsorption edge of the (111) photonic pseudogap. In this region the group velocity of

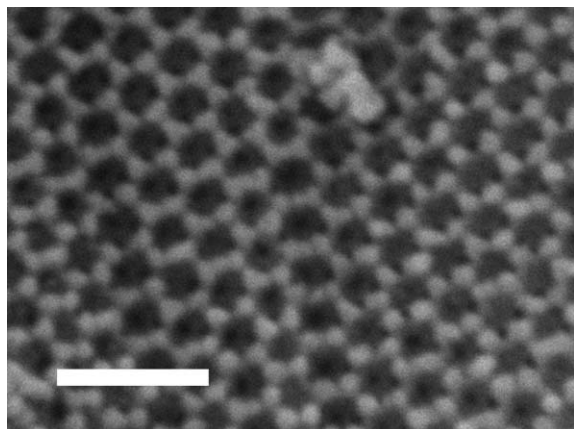


Fig. 1 SEM image of a titania inverse opal 8 μm thick electrode used for a PES cell. The void size is 170 nm and the bar corresponds to 500 nm.

photons is very small and consequently the light localization is much higher than that of the bulk material.

Fig. 2 shows the SEM images of the PhS. Unlike the PC case, PhS presents a random distribution of spherical air cavities (from 0.1 to 1.5 micrometres) surrounded by a high refractive medium formed by connected TiO_2 nanoparticles.

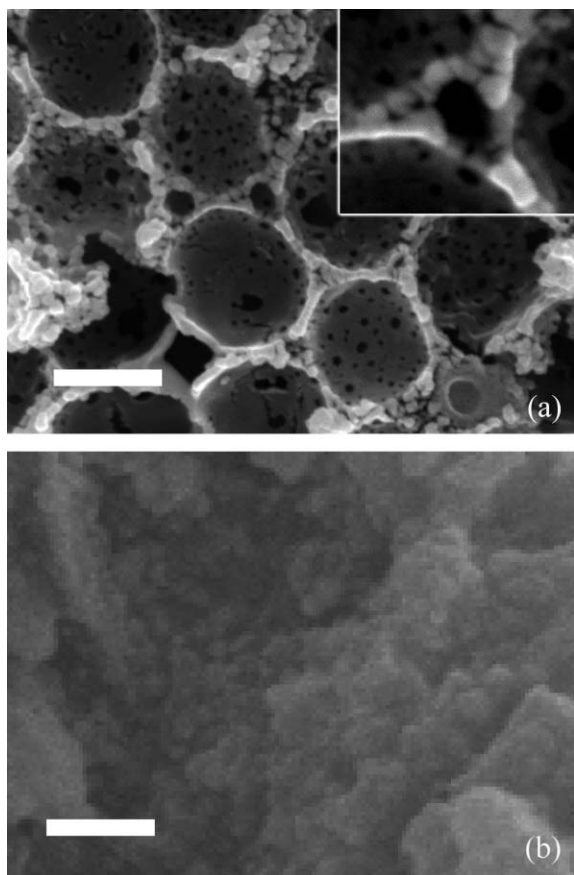


Fig. 2 SEM images of titania nanoparticles arranged in a PhS architecture (a) or in a packed manner (b). One can see in (a) how the smaller cavities are arranged in the regions between the larger ones. Scale bars: 1 μm .

The pores are interconnected resulting in a macroporous membrane with a high porosity value of 85%. Also, in some regions (see inset in Fig. 2a), one can see the tendency towards quasi-Apollony fractal ordering,²¹ with smaller pores located at the intersection of three neighbouring large cavities. In Apollony packing, smaller cavities are located at the intersection of four larger ones. In both PC and PhS cases, titania nanoparticles are organized around cavities. However there are two main differences between them. Firstly, PhS has a larger porosity value. More importantly, at variance with the PC case, cavities in the PhS architecture have a very large range of diameter values. Therefore, PhS is able to scatter photons, not from a single frequency region as PC does, but from the whole UV and VIS regions. One can also see huge differences compared with the standard titania film shown in Fig. 2b. The plain thin film is composed of titania nanoparticles with a much smaller porosity value (23%).

In what follows we will report on the photoelectrochemical response of PC and PhS PES cells and their comparison to the reference cells. Reference PES cells were fabricated with the same thickness and chemical methods used for the colloidal templated (PC and PhS) ones. Fig. 3a shows the I - V photovoltaic response of both the PC and the reference PES cells. One can see that the PC cell presents a better response in both open circuit voltage (V_{oc}) and short circuit current (I_{sc}), the total power being 35% more efficient than that from the reference cell. Fig. 3b shows the spectral response that in both cases peaks at the adsorption edges of titania. Such an

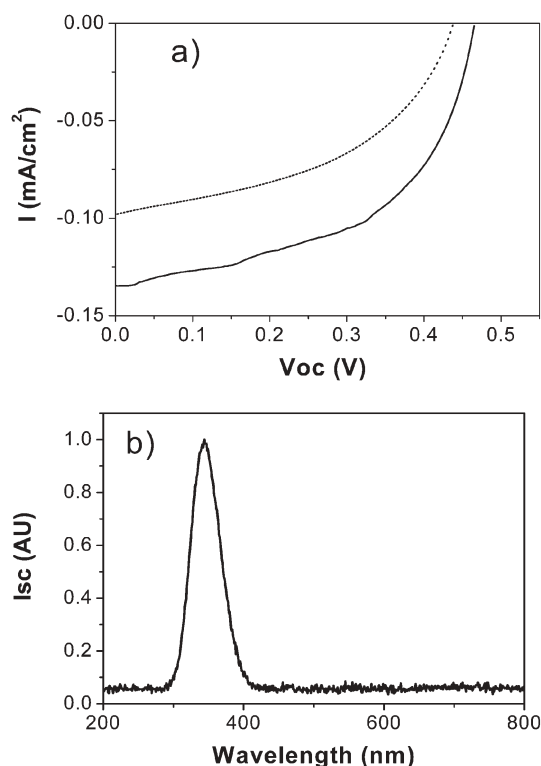


Fig. 3 a) Current-voltage (I - V) characteristic curves for both the inverse titania (continuous curve) and the standard titania (broken curve) PES cells. b) Spectral response of the PC PES cell as a function of the light wavelength.

enhancement in the efficiency of photoelectrochemical solar cells has been reported by Mallouk *et al.*¹¹ in devices made of electrodes composed of a TiO₂ inverse opal coupled to conventional nanocrystalline TiO₂ film. In a previous hypothesis, it was proposed that the amplification of the optical absorption comes from the anomalous propagation of light through the photonic crystal part of the cell. In fact, recent studies^{12,14} point out that efficiency enhancement comes mainly from the localization of light (within the nanocrystalline TiO₂ film) due to multiple scattering caused by disordered regions of both ordered and disordered inverse opals. In conclusion different groups agree that light harvesting in PC like PES cells is mostly induced by disordered regions of samples. These conclusions are particularly interesting as they bring us to systems like the PhS with which we are concerned, and will show next.

Fig. 4a shows the *I*-*V* characteristics for both the reference and the PhS based solar cells. All parameters that determine the solar cell characteristics, *I*_{sc}, *V*_{oc} and the fill factor, are much better in the case of the PhS topology. The PhS architecture improves the total efficiency value of dye sensitized PES cells by a factor of 5. Fig. 4b shows the spectral response of both cells. One can see that PhS electrodes induce a large amplification of the photocurrent in the whole range of the cell response (300–800 nm). However the amplification effect is more important in the optical region where titania is active (see peak around 350 nm). At the absorption edge of titania, the refractive index value increases and consequently, light scattering effects are enhanced. As the

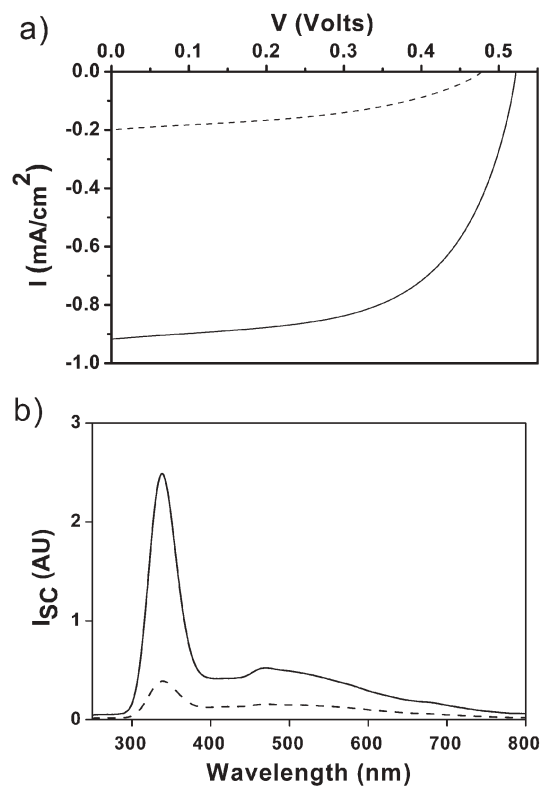


Fig. 4 a) *I*-*V* characteristic of dye sensitized PES cells under AM 1.5 conditions, and b) photocurrent spectra for standard (dashed line) and PS (continuous line) titania electrodes.

processing method for both types of samples is identical, we infer that the much higher efficiency in PhS electrodes can only be ascribed to the different topology of the titania network.

Electronic harvesting of corrugated metal electrodes

Fig. 5 shows SEM images of the upper surface of a commercial (read-only) DVD (Fig. 5a), the lower surface of a commercial DVD (Fig. 5b), and the surface of a DVD-R (Fig. 5c), all of them covered with a platinum layer with a thickness value of 160 nm. In the images, the platinum surface appears cracked, but these cracks are due to the action of the electron flux of the SEM, and appear only when samples are seen with the electron microscope. Read-only DVD electrodes show (see Fig. 5a and b) either tips (upper surface) or dips (lower surface). The

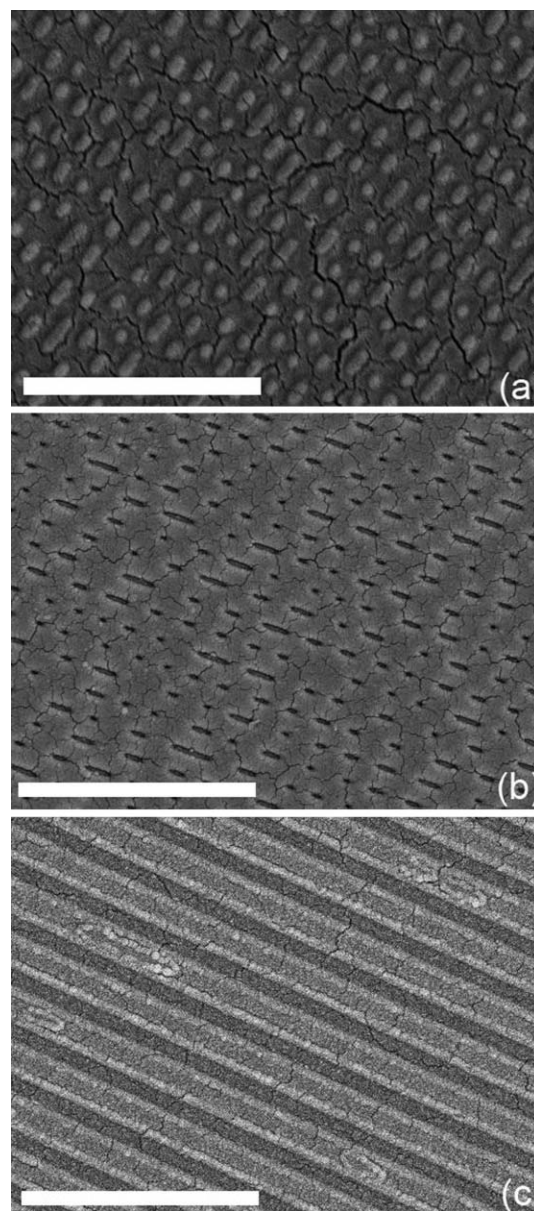


Fig. 5 SEM image of different surface profiles employed for metal electrode in TiO₂ PES cell. DVD inner-upper side surface: (a) tips, (b) holes and DVD-R (c). All surfaces are covered with platinum.

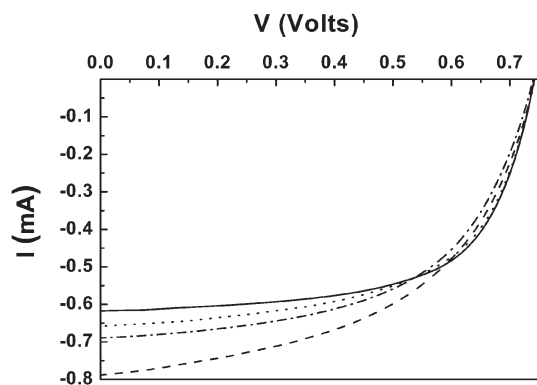


Fig. 6 Influence of the PES back electrode configuration on the I - V characteristics under AM 1.5 conditions. The same TiO_2 electrode was employed with a Pt flat (solid line), DVD tips (dashed line), DVD holes (dashed dotted line) and DVD-R (dotted line) electrode.

dimensions of tips (dips) are ~ 470 – 500 nm thick and ~ 125 – 140 nm high. The length of the pits depends on the number of bits coded. Tracks separation is about 750 nm. The DVD-R shows continuous tracks formed by periodic distribution of ridges and grooves with a periodicity value of 1400 nm. The grooves are 130 nm deep and 400 nm wide.

Results of I - V characterization taken with a solar simulator are shown in Fig. 6. The best behaviour is obtained with the DVD inner-upper side surface (tips) that corresponds to the electrode image of Fig. 5a. Fig. 6 shows an increment of about 28% in the short-circuit current for the electrode with tips configuration. It also shows that, unfortunately, DVD electrodes show a poorer fill factor than flat electrodes, which reduces the increment in the overall efficiency. This may be due to the effect of higher resistance of the nanostructured electrodes as compared to the flat ones. Surface resistance of reference flat electrodes was about $9 \Omega \text{ sq}^{-1}$ while for a “read-only” DVD surface it was $30 \Omega \text{ sq}^{-1}$. It is also noticeable that the cell is short-circuited more easily when corrugated metallic electrodes are used. This makes us think that local electric fields are enhanced around the tips or ridge edges of the corrugated electrodes.

It is important to stress that the electrode corrugation is very small as compared to the thickness of the titania electrode (10 micrometers). Therefore small corrugation values produce noticeable effects in the cell efficiency. Carrier collection would be more efficient for more strongly corrugated surfaces of electrodes. Moreover, this effect would further be enhanced if the corrugation of both the back (Pt) and front (ITO) electrodes were attained.

Conclusions

To summarize, we have demonstrated that PES cells show much better photoelectrical performances when the titania electrode is structured to localize photons. From all topologies so far used, PhS shows the best performance. The low absolute

efficiency problem could be solved either by researching other gentler synthesis routes or by using more robust templates. Finally, we have shown that corrugation of the metal back electrode enhances the photoelectrochemical response of PES cells in spite of the small aspect ratio value of the corrugation. It would be desirable to find methods to produce high aspect ratio corrugation factors for both front (ITO) and back (Pt) electrodes to maximize harvesting of photoexcited carriers.

Acknowledgements

This work has been partially supported by the Spanish CICYT (project MAT2003-04993-C04-01) and by CSIC under contract 200480F0210. I. R. thanks the Spanish Ministry of Education and Science for a Ramón y Cajal Fellowship.

References

- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737;
- M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry Backer, E. Mueller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 638.
- A. Corma, P. Atienzar, H. Garcia and J.-Y. Chane-Ching, *Nat. Mater.*, 2004, **3**, 394.
- C. J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover and M. Grätzel, *J. Am. Ceram. Soc.*, 1997, **80**, 3157.
- M. Grätzel, *J. Photochem. Photobiol., A*, 2004, **164**, 3.
- S. A. Haque, S. Handa, K. Peter, E. Palomares, M. Thelakkat and J. R. Durrant, *Angew. Chem., Int. Ed.*, 2005, **44**, 5740.
- C. Klein, M. K. Nazeeruddin, P. Liska, D. Di Censo, N. Hirata, E. Palomares, J. R. Durrant and M. Grätzel, *Inorg. Chem.*, 2005, **44**, 178.
- J. Ferber and J. Luther, *Sol. Energy Mater. Sol. Cells*, 1998, **54**, 265.
- A. Usami, *Sol. Energy Mater. Sol. Cells*, 1999, **59**, 163.
- A. Usami, *Chem. Phys. Lett.*, 1997, **277**, 105.
- G. Rothenberger, P. Comte and M. Grätzel, *Sol. Energy Mater. Sol. Cells*, 1999, **58**, 321.
- S. Nishimura, N. Abrams, B. A. Lewis, L. I. Halaoui, T. E. Mallouk, K. D. Benkstein, J. van de Lagemaat and A. J. Frank, *J. Am. Chem. Soc.*, 2003, **125**, 6306.
- A. Mihi and H. Míguez, *J. Phys. Chem. B*, 2005, **109**, 15968.
- I. Rodríguez, P. Atienzar, F. Ramiro-Manzano, F. Meseguer, A. Corma and H. Garcia, *Photonics Nanostruct. Fundam. Appl.*, 2005, **3**, 148.
- L. I. Halaoui, N. M. Abrams and T. E. Mallouk, *J. Phys. Chem. B*, 2005, **109**, 6334.
- P. Cheng, *Introduction to Wave Scattering, Localization and Mesoscopic Phenomena*, Academic Press, New York, 1995.
- J. M. Drake and A. Z. Genack, *Phys. Rev. Lett.*, 1989, **63**, 259.
- D. S. Wiersma, P. Bartolini, A. Lagendijk and R. Righini, *Nature*, 1997, **390**, 671–673.
- F. J. P. Schuurmans, D. Vanmaekelbergh, J. van de Lagemaat and A. Lagendijk, *Science*, 1999, **284**, 141.
- J. Gómez-Rivas, R. Sprik, A. Lagendijk, L. D. Noordam and C. W. Rella, *Phys. Rev. E*, 2001, **63**, 046613–1.
- A. Z. Genack, *Phys. Rev. Lett.*, 1987, **58**, 2043.
- A. Lagendijk, J. Gomez Rivas, A. Imhof and R. Sprik, Propagation of light in disordered semiconductor materials, in *Photonic Crystals and light localization in the 21st century*, ed. C. M. Soukoulis, Kluwer, Dordrecht, 2001, pp. 447–473.
- F. Ramiro-Manzano, P. Atienzar, I. Rodríguez, F. Meseguer, H. Garcia and A. Corma, *Chem. Commun.*, 2007, **3**, 242.
- S. H. Park, D. Qin and Y. Xia, *Adv. Mater.*, 1998, **10**, 1028.
- J. Duran, *Sand, Powders, and Grains*, Springer, New York, 2000.