ADVANCED MATERIALS

Increase of the Efficiency of Quasi-Solid State Dye-Sensitized Solar Cells by a Synergy between Titania Nanocrystallites of Two Distinct Nanoparticle Sizes**

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Nanocrystalline titanium dioxide electrodes are standard choice for the construction of Dye-sensitized Solar Cells (DSC). Nanocrystallinity, small number of defect sites, optimized electrical conduct between nanoparticles and sufficient active surface area are crucial factors, which determine the quality of the electrodes and, subsequently, the overall efficiency of the cell. The maximum efficiency of DSC ever reported[1] was around 10.4 % and referred to cells based on a liquid electrolyte and on non-transparent Light-Scattering Electrodes (LSE) of 18μm thickness. For several years, we have made efforts to reach comparable cell efficiencies with DSC's employing thinner transparent TiO_2 electrodes by optimizing the synthesis and deposition procedures. The motive of these efforts is related with the prospect of utilizing such transparent cells as photovoltaic windows. LSEs do not offer this possibility but, instead, they entrap light and result in higher cell efficiencies. In order for Transparent Electrodes (TE) to reach performance of LSE, it is necessary that the former are deposited with optimized parameters: good quality nanocrystals without defects, compact enough films to allow sufficient electric contact between nanoparticles and sufficient mesoporosity to allow dye-sensitizer and electrolyte filling. We have achieved this goal by synthesizing titania through the sol-gel procedure in the presence of surfactant templates under ambient conditions. Spatially isolated self-organized entities seem to encourage formation of good quality nanosrystalline particles. For example, reverse micelles dispersed in an organic solvent, originally used to synthesize CdS nanocrystals[2] proved excellent templates for TiO_2 nanocrystals as well.[3] However, reverse micelles are rather costly and less environmentally friendly systems. It has been found that simpler systems can offer similar results and more handy experimental procedures. Thus organic acid solvolysis of titanium isopropoxide in the presence of the non-ionic surfactant Triton X-100 (polyoxyethylene-(10) isooctylphenyl ether), can assist nanocrystalline anatase deposition[4] with nanoparticle size of around 12 nm and active surface area around 110 $m^2 g^{-1}$. About 2 μm thick TE were made by subsequent layer deposition by dipping under ambient conditions. Organic acid solvolysis in the absence of water has the advantage of slow sol-gel evolution that allows surfactant assembling and shell formation around titania core. The choice of this route was rewarding. Indeed, as it has been previously reported,[4] such electrodes gave DSCs with efficiency >9 %, i.e., not far from the reported maximum. The DSC of ref. [4] was a non-optimized cell employing *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) [abbreviated $RuL_2(NCS)_2$] as dye sensitizer and I_3^-/I^- in acetonitrile as liquid redox electrolyte. When the same electrodes were used to construct quasi-solid state DSCs, where the redox couple I_3^-/I^- was incorporated into a sol-gel nanocomposite organic-inorganic gel, efficiency dropped[5] but it was still at satisfactory levels of 5.3 %. This efficiency decrease was due to current decrease, which in turn was due to lower ionic mobility in the gel. Gel electrolytes based on nanocomposite organic-inorganic materials is our approach to ensure cell stability and avoidance of electrolyte leakage.

In the present work we are testing an alternative method of titania deposition, in which we try to further increase cell efficiency by producing LSEs, using new organic templates or combined templating methods.[6] It will be seen that indeed LSEs do increase cell efficiency by an important percentage, however, this increase should be appreciated by also taking into account the disadvantages related with the loss of transparency. The cell described in the following paragraphs is made by using a titania electrode that consists of two layers: a rough nanocrystalline titania film making a light-scattering layer and a compact nanocrystalline titania layer filling the voids and standing on the top of the lower layer. As a matter of fact, the deposition of the second layer did not produce a separate stratum and did not increase the thickness of the film but it was accommodated within the voids and the pores of the first layer. The assembly made a LSE. The efficiency of this cell climbed to 6.9 %, a value that is more than 20 % higher than that of the corresponding cell employing a single transparent layer. This efficiency is very high, if we take into account the fact that it concerns a solid-state device. Another interesting feature of this cell is the employment of a silica-based nanocomposite organic-inorganic gel as host for the $I_3^-/$

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I^- redox couple. The cell is easily assembled by sandwiching one drop of the gel between the titania and the counter electrode. Details about electrode deposition and cell assembling are given in the Experimental Section.

The simple and straightforward procedure to assemble a cell described in the Experimental section is sufficient to make a functional and durable cell. This is the great advantage of the present approach for cell construction. Three different types of cells are described for comparison. In the first case, the titania electrode was deposited by using Polyoxypropylene-2000 (PEG2000) templates. XRD analysis showed that the film consists of Anatase nanocrystals. AFM analysis of the same film showed a rough surface with many voids and nanoparticles of about 50 nm diameter, as can be seen in Figure 1A. The thickness of this titania film was extracted by recording a SEM image of the cross section of the film and it was about 2 μm. In the second case, the titania electrode was deposited by using Triton X-100 templates. Several layers of the same material were deposited so as to make a film of about 2 μm thick. The appearance of the top of this film is now shown by the AFM image of Figure 1B. It is seen that the film is compact and contains small nanocrystallites of about 12 nm size. XRD analysis again showed the presence of Anatase nanocrystals. Finally, in the third case, the titania electrode was made of two layers, one deposited by using PEG2000 templates (base layer) and the second by using Triton X-100 templates (top layer). As already said, the thickness of the film remained practically the same. The fact that the deposition of the top layer did not increase the film thickness led to the conclusion that the top layer did not make a separate stratum but it was accommodated within and filled the pores of the first layer. This is possible, since we are concerned with the deposition of a fluid material. The three cells had all the rest of the parameters the same, i.e., the same dye-sensitizer, gel electrolyte and counter electrode.

Figure 2 shows *I–V* curves for the above three types of cells. The cell of Figure 2a, based on a titania electrode made exclusively with PEG2000 templates (cf. Fig. 1A) gave the poorest

performance of 4.8 %. The cell of Figure 2b, based on a titania film exclusively made with Triton X-100 templates, similar to that of Ref. [5], gave a performance of 5.5 %. It is interesting to note that this efficiency was the same as in the case of the previously constructed cell,[5] and this shows that the procedures used to make the present cells give consistent and reproducible results. The highest efficiency was obtained with the two-layer cell of Figure 2c, i.e., 6.9 %. This efficiency is very high, if we take into account the fact that that it was obtained with a quasi-solid DSC. It was previously reported[7] that a cell using a viscous electrolyte containing fumed silica nanoparticles dispersed in 1-methyl-3-propylimidazolium iodide and methoxypropionitrile gave an efficiency of 7 %, i.e., higher than the present one. However, this cell is not quasi-solid state cell in a strict sense. On the contrary, the cell of the present work contains only solid materials including the electrolyte, which is a solid gel with a silica network extending over the whole structure. The corresponding photocurrent action spectrum (IPCE) is shown in Figure 3. This high performance is a contribution of all three factors affecting cell efficiency, i.e., Short Circuit Current J_{sc}, Open-circuit Voltage V_{oc} and Fill Factor ff. All three were the highest in the third cell. J_{sc} was higher in the case of the cells, which contained compact titania films (cases (b) and (c)). Apparently, the compact film provides better electrical communication between titania nanocrystals and this results in higher current densities. Furthermore, the highest active surface area of nanomaterials made of smaller nanocrystallites is expected to enhance photocurrent. It is also interesting to note that the cells based on titania films that included the rough LSE layer (cases (a) and (c)) gave higher V_{oc}. This result was not expected and it is hard to explain in a straightforward manner. Other researchers, who have constructed cells based on combinations of titania nanoparticles of two distinct sizes[8,9] also found an increase in V_{oc}. This was explained by the longer residence time of electrons in the nanocrystallites, which results to an increase of the Fermi level of the semiconductor. Longer residence time of electrons in the present case could, of course, be justified by the two different sizes of the nanoparticles that could create electron traps. Electron trapping has, of course, adverse effects on conductivity. However, it seems that the benefits overcome the disadvantages leading to a positive outcome.

In conclusion, we have found that two layers of titania films made by two different templates and sol-gel procedures, which produce nanoparticles of two distinct sizes, leads to the construction of a Quasi-Solid state DSC with very high efficiency of 6.9 %. One layer is made by using PEG2000 templates where sol-gel hydrolysis and condensation proceeds by ambient humidity. This layer makes a rough LSE with relatively large
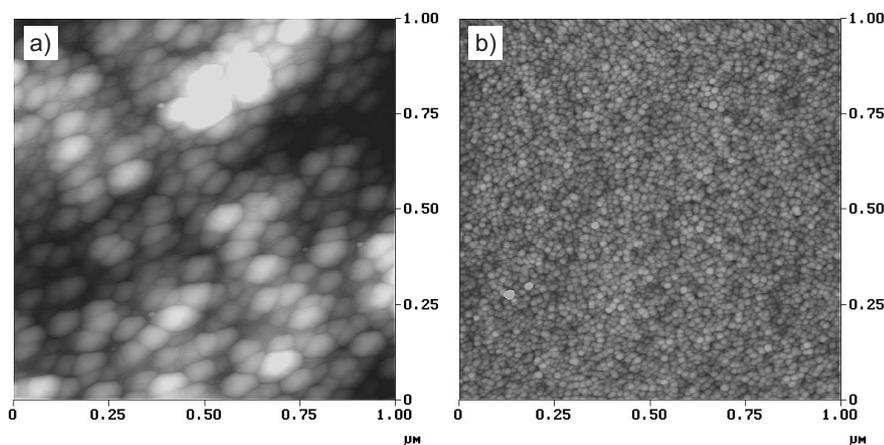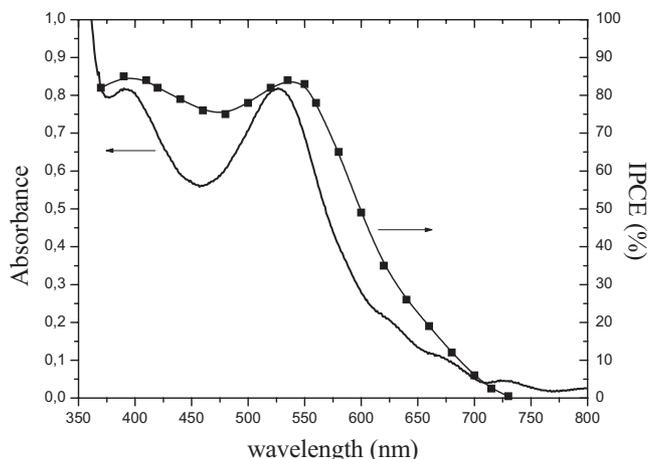
Figure 1. AFM image of a titania film made by using PEG2000 templates (A) and Triton X-100 templates (B)
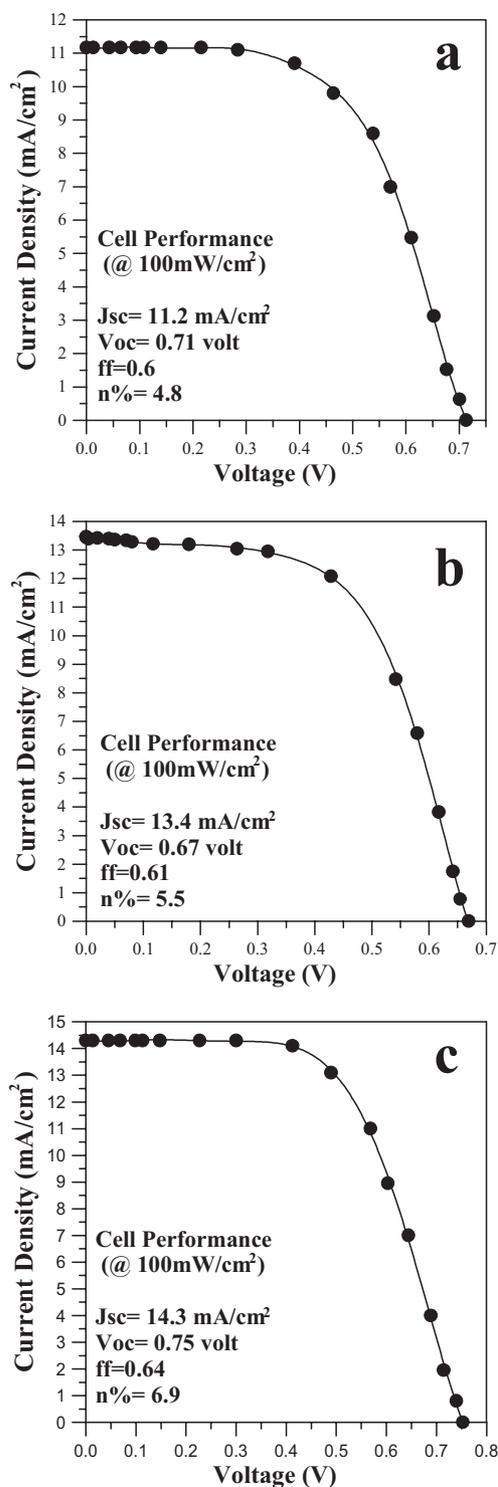
Figure 2. I–V curves for cells based on tree different titania electrodes: a) titania film made with PEG2000 templates only; b) titania film made with Triton X-100 templates only; and c) two-layer titania film.

Figure 3. Photocurrent Action spectrum of the cell made of the two-layer Titania film together with the absorption spectrum of the dye-sensitizer adsorbed on a transparent Titania film.

nanocrystallites. A second layer is deposited by using Triton X-100 templates and AcOH solvolysis in the absence of water. In this case the film becomes compact and contains small size nanocrystallites. The synergy between the two materials re-sults in increasing all main factors affecting overall efficiency, i.e current, voltage and fill factor. The beneficial combination of Titania nanoparticles of distinct sizes has been previously observed by other researchers,[10] even though, the size differ-ence was in that case more pronounced.[10] The present case shows that the combination of template techniques provides a simple and handy means of constructing an efficient cell si-multaneously carrying all the advantages of a quasi-solid-state construction.

Experimental

The following experimental procedures were used to make titania electrodes and to assemble DSCs. All materials were from Aldrich ex-cept $RuL_2(NCS)_2$, which was provided by Solaronix, Switzerland. 1 g of polyethylene glycol MW 2000 (PEG2000) was dissolved in 8 g of EtOH and then 1 g titanium isopropoxide was added under vigorous stirring. After five minutes, a fluorine-doped SnO_2 transparent con-ductive electrode (8 Ω/square, Hartford glass TCO8) was dipped in the above sol and left to dry in air. Only one side (the conductive side) of the electrode was covered with material. The other side was pro-tected by an adhesive tape, which was subsequently removed. Then the solvent evaporates while ambient humidity leads to alkoxide hy-drolysis and condensation. The obtained film was a non-transparent light-scattering material that is composed of a mixture of PEG2000 with large colloidal titania nanoparticles. Finally, the film was put in an oven and calcined at 550 °C. After taking it out of the oven, the film was still a non-transparent light-scattering material. The proce-dure was repeated once, again offering a LSE. This was a rough film with many voids as already discussed and shown in Figure 1A. On the top of this rough film we deposited nanocrystalline TiO_2 made by a different procedure, similar to that previously described [4]: 1.4 g of the non-ionic surfactant Triton X-100 was mixed with 7.6 ml ethanol. Then we added 1.36 ml glacial acetic acid (AcOH) and 0.72 ml of Ti-tanium isopropoxide under vigorous stirring. After a few minutes stir-ring, the above fluorine-doped SnO_2 transparent conductive electrode covered on one side with the above described film was dipped in the sol and left to dry in air for a few minutes. Finally, it was calcined at 550 °C. The temperature was raised at a pace of 20 °C min^{-1} to 550 °C and then it was left for about 10 min at that temperature. When the film was taken out of the oven it made a LSE, i.e., it was a non-trans-

parent light-scattering material. Its thickness was measured by recording the SEM image of a cross-section of the film. It was approximately 2.3 μm when the first rough layer was deposited and remained approximately the same when the second material was deposited on the top (cf. image in Supporting Information). This result undoubtedly suggests that the top material is accommodated within the voids and the pores of the base material. Alternative titania electrodes were made by depositing layers made only with PEG2000 templates (LSE) or only with Triton X-100 templates (TE), the rest of the procedure being the same. Adsorption of the dye sensitizer was made by immersing still hot titania film in an 1 mM ethanolic solution of $RuL_2(NCS)_2$ for several hours.

The gel electrolyte was synthesized by the following procedure. 0.7 g of the functionalized alkoxide precursor (Ureasil) [5] were dissolved in 2.4 grams of sulfolane [5] under vigorous stirring. Then we added 0.6 ml glacial AcOH followed by 0.3 M 1-methyl-3-propylimidazolium iodide, 0.1 M KI, 0.05 M I_2 and 0.6 M 1-methylbenzimidazole. 1-Methyl-3-propylimidazolium iodide was used in order to avoid crystallization of KI [11], while the presence of KI was necessary since these small mobile ions allow increase of ionic conductivity. The presence of 1-methylbenzimidazole is known to increase the open-circuit voltage V_{oc} of the cell [12,13]. After six hours stirring, one drop of the obtained sol was placed on the top of the titania electrode and a slightly platinized F:SnO$_2$ counter electrode was pushed by hand on the top. Platinization was made by exposing the electrode to a Na_2PtCl_4 solution (5 mg/1 ml of EtOH) followed by heating at 550 °C. The two electrodes tightly stuck together by Si–O–Ti bonds developing, thanks to the nanocomposite gel.

I–V curves have been recorded by connecting the cell to an external variable resistor and by measuring the current flowing through the resistor and the corresponding voltage across the resistor. Cell active area for these measurements was 0.9 cm^2. An Oriel 450 W Xenon lamp was used for the illumination of the samples. Illumination intensity was controlled by multiple wire grids and it was 100 mW cm^{-2}.

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