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C. R. Chimie 9 (2006) 622–626



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Preliminary communication / Communication

## TiO<sub>2</sub> sol–gel blocking layers for dye-sensitized solar cells

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Received 2 July 2004; accepted after revision 14 February 2005

Available online 13 September 2005

### Abstract

The application of a thin, compact layer of TiO<sub>2</sub> on the conductive glass substrate in a dye-sensitized solar cell can prevent short-circuits in the solar cell and, therefore, prevent the back transfer of electrons by blocking direct contact between the electrolyte and the conductive substrate. In this work, it has been found that compact films of TiO<sub>2</sub>, produced by a sol–gel method and applied by dip-coating, increased the short-circuit current and efficiency of the solar cells. As the number of TiO<sub>2</sub> coatings increased, the solar cell efficiency increased, due to the film becoming thicker and more smooth and uniform. **To cite this article:** *J.N. Hart et al., C. R. Chimie 9 (2006).*

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### Résumé

Le dépôt d'une couche mince et dense de TiO<sub>2</sub> sur un substrat de verre conducteur peut bloquer le transfert inverse des électrons du substrat vers l'électrolyte et, par conséquent, empêcher les courts-circuits au sein des cellules solaires photovoltaïques. Il a été démontré dans ce travail que la présence de films denses de TiO<sub>2</sub>, préparés par la méthode sol–gel et déposés par *dip-coating* améliore le courant de court-circuit ainsi que l'efficacité des cellules solaires. L'efficacité de ces photopiles est de plus accrue grâce à la présence de plusieurs couches de TiO<sub>2</sub>, le film devenant plus lisse, uniforme et épais. **Pour citer cet article :** *J.N. Hart et al., C. R. Chimie 9 (2006).*

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**Keywords:** Dye-sensitized solar cell; TiO<sub>2</sub>; Sol–gel; Blocking layer

**Mots clés :** Cellule solaire photovoltaïque ; TiO<sub>2</sub> ; Sol–gel ; Couche bloquante

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## 1. Introduction

Dye-sensitized solar cells are an attractive alternative to conventional solar cells, since they are cheaper and simpler to produce [1]. The working electrode of these solar cells consists of a nanostructured film of titanium dioxide ( $\text{TiO}_2$ ) coated on a conductive glass substrate. A dye is adsorbed on to the surface of this  $\text{TiO}_2$  film; under illumination, electrons are injected from the excited state of the dye to the conduction band of the  $\text{TiO}_2$  and transported through an external circuit to the counter-electrode. The circuit is completed within the cell by an electrolyte [1].

The nanostructured films used in these solar cells often contain small holes that allow direct contact between the electrolyte and the conducting layer on the glass [2], and these points of contact act as short-circuits in the cell. The use of a compact, thin layer of  $\text{TiO}_2$  coated directly on to the glass substrate, applied by spray pyrolysis, has been found to prevent the back transfer of electrons to the electrolyte from the conductive glass substrate [3–5]. The use of a phenol/2-allylphenol copolymer as a blocking layer, applied by electrodeposition, has also been investigated [2]. In this work, the effect on solar cell performance of applying a compact film of  $\text{TiO}_2$  by a simple dip-coating method has been investigated.

## 2. Experimental

$\text{TiO}_2$  nanoparticles were produced by a sol–gel method. Following the method of Shklover et al. [6], 300 g of dilute (0.1 M) nitric acid solution was placed in a round-bottom flask. Titanium isopropoxide (48 g, Aldrich, 97%) was added drop-wise over a 1-h period under constant stirring. Peptization was then achieved by heating at 80 °C for ~8 h, followed by filtering through a glass frit to remove any remaining agglomerates.

F:SnO<sub>2</sub> glass (Hartford Glass Company, sheet resistance 15  $\Omega$  per square) was cleaned by an ultrasonic treatment in ethanol and dried at 70 °C. Compact  $\text{TiO}_2$  blocking layers were applied by dip-coating using the  $\text{TiO}_2$  sol; samples were produced with 1, 3 and 5 coatings, allowing the films to dry at room temperature for 30 min and at 70 °C for 10 min between each coating. The films were subsequently heat treated at 450 °C for 30 min.

A slurry of a commercially available  $\text{TiO}_2$  powder (Degussa P25) was made using 4 g  $\text{TiO}_2$ , 8 g distilled water and 250 g poly(ethylene oxide) (Aldrich). A thorough dispersion of the  $\text{TiO}_2$  was achieved using an ultrasonic horn (Sonics and Materials VCX-750, 750 W, 20 kHz), with treatments for 5 min being applied both before and after adding the PEO to the slurry. Films of this slurry were then coated on the blocking layers by doctor blading. Control samples were also produced with no blocking layer. These films were heat treated at 450 °C for 30 min and stored in a desiccator until used in solar cell construction.

The thickness and roughness of both the sol–gel blocking layer and the P25 nanostructured film were measured by profilometry (Cotec Altisurf 500). Scanning Electron Microscope (SEM) images were obtained at 25 kV (Hitachi S570).

Prior to dye adsorption, the  $\text{TiO}_2$  films were heated again at 450 °C for 10 min and then immersed in a ruthenium dye solution (0.3 mM solution of  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ , where dcbpy is 4,4'-dicarboxylic acid-2,2'-bipyridine, in 1:1 butanol and acetonitrile) for 24 h. Excess dye solution was removed by rinsing in acetonitrile.

The counter-electrode was produced by coating F:SnO<sub>2</sub> glass with a thin layer of a 5 mM solution of  $\text{H}_2\text{PtCl}_6$  in isopropanol. This coating was dried at 50 °C for 15 min and heated at 385 °C for 15 min, with a heating rate of 2 °C min<sup>-1</sup>.

The two electrodes were sealed together with Surlyn polymer film (200  $\mu\text{m}$  thick, DuPont) and the electrolyte (0.5 M LiI (Lancaster), 0.04 M I<sub>2</sub> (Lancaster) and 0.05 M 4-*tert*-butylpyridine (Aldrich) in acetonitrile) was injected through a hole in the counter-electrode, which was then sealed with Surlyn and glass.

The photovoltaic properties of the solar cells were characterized under illumination of a 21-V, 80-W tungsten lamp (Phillips 13160). A source meter (Keithley 2400) was used to measure the current between -0.2 and 0.9 V, under a light intensity of 1 Sun (determined by an externally calibrated photodiode).

## 3. Results and discussion

The thickness of the nanostructured  $\text{TiO}_2$  layer (applied on top of the compact layer) was consistently ~10  $\mu\text{m}$ . Electron micrographs of these films are shown

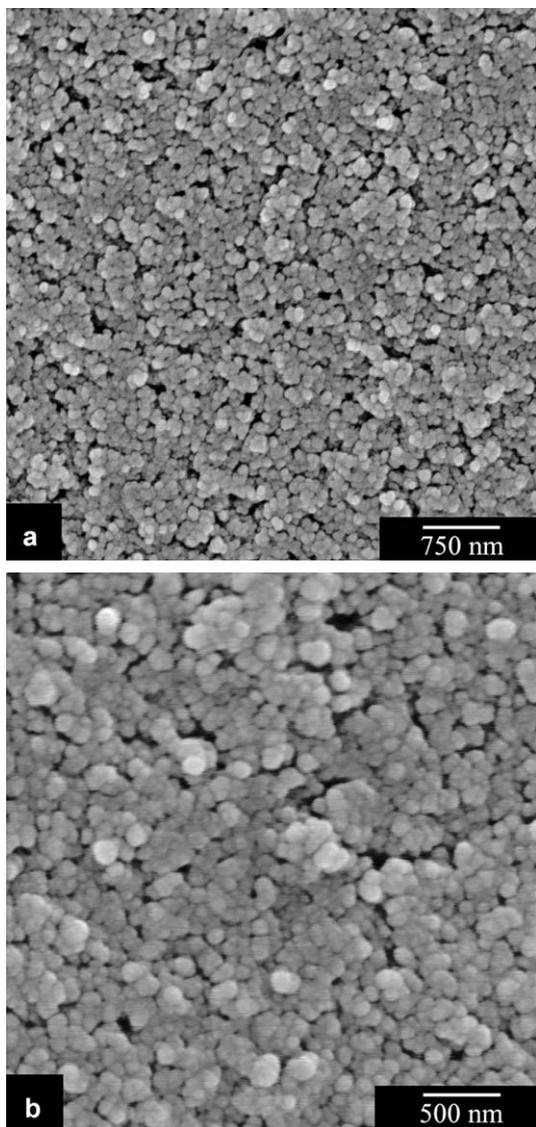


Fig. 1. SEM micrographs of nanostructured  $\text{TiO}_2$  layer for samples with three compact  $\text{TiO}_2$  blocking layers (a) and five compact  $\text{TiO}_2$  blocking layers (b).

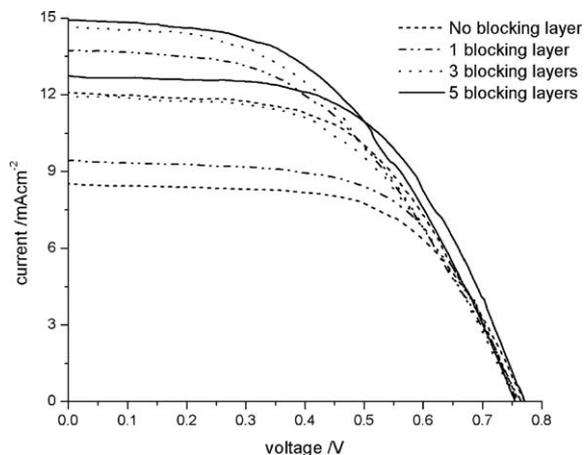


Fig. 2. Current–voltage curves for solar cells with no blocking layer and with 1, 3 and 5  $\text{TiO}_2$  sol–gel blocking layers.

in Fig. 1; there was no significant difference in the microstructure of these films for different numbers of blocking layers.

The photovoltaic properties of the solar cells without a blocking layer and with 1, 3 and 5  $\text{TiO}_2$  sol–gel blocking layers are shown in Table 1 and the current–voltage curves for the cells that produced the highest and lowest short-circuit current for each number of blocking layers are shown in Fig. 2. It can be seen that, with increasing the number of coatings of sol–gel  $\text{TiO}_2$ , the short-circuit current and the efficiency of the solar cell increased. This indicates that the back transfer of electrons is suppressed by the blocking layer. There was no significant change in either the open-circuit voltage or the fill factor, which is in agreement with previous work, in which it was found that compact  $\text{TiO}_2$  blocking layers, applied by spray pyrolysis, prevent the back transfer of electrons to the electrolyte under short-circuit conditions but have little effect under open-circuit conditions [4].

The thickness and mean-square-roughness of the compact  $\text{TiO}_2$  layers are shown in Table 2 and electron micrographs of these films are shown in Fig. 3. The

Table 1

Photovoltaic properties of solar cells with no blocking layer and with one, three and five compact  $\text{TiO}_2$  sol–gel blocking layers. Uncertainties are given as the 70% confidence interval

	Short-circuit current ( $\text{mA cm}^{-2}$ )	Open-circuit voltage (mV)	Fill factor	Efficiency (%)
No blocking layer	$10.7 \pm 0.8$	$764 \pm 2$	$55 \pm 3$	$4.5 \pm 0.2$
One blocking layer	$11.9 \pm 1.1$	$755 \pm 4$	$54 \pm 3$	$4.8 \pm 0.2$
Three blocking layers	$13.1 \pm 1.0$	$757 \pm 1$	$51 \pm 3$	$5.0 \pm 0.2$
Five blocking layers	$13.8 \pm 0.9$	$762 \pm 6$	$52 \pm 3$	$5.49 \pm 0.02$

Table 2  
Thickness and root-mean-square roughness of compact TiO<sub>2</sub> blocking layers

	Thickness (nm)	Roughness (nm)
One blocking layer	30–100	25–45
Three blocking layers	200–400	10–25
Five blocking layers	250–500	10–25

thickness and roughness of the films varied between samples and the range in which the values for the majority of samples were found are given in Table 2. As the

number of blocking layers that were applied increased, the thickness of this compact TiO<sub>2</sub> layer increased. This increase in thickness is the most likely explanation for the improvement in solar cell performance when the number of blocking layers is increased, since a thicker film will more effectively block the back transfer of electrons.

As the number of blocking layers was increased from 1 to either 3 or 5, the roughness of the film decreased (Table 2). It is likely that the first layer does not com-

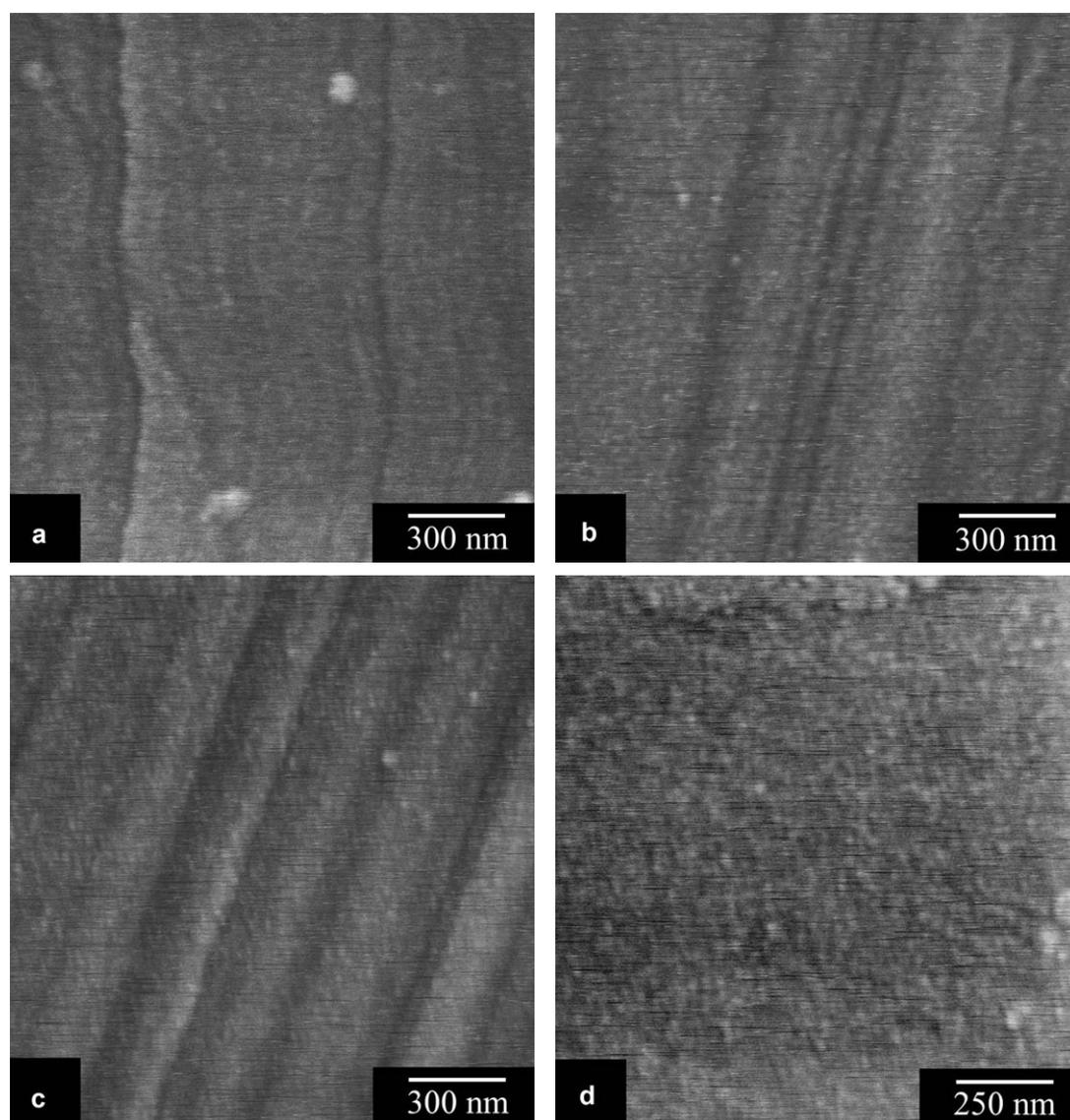


Fig. 3. SEM micrographs of compact TiO<sub>2</sub> blocking layers for samples with one blocking layer (a), three blocking layers (b) and five blocking layers (c and d).

pletely cover the substrate and still contains some small holes. When further layers are deposited, the film becomes smooth and uniform and the holes are filled, leading to complete coverage of the substrate. This increase in the uniformity and smoothness of the compact TiO<sub>2</sub> films probably also contributed to the improvement in solar cell performance when the number of blocking layers increased.

In this work, it has been found that the solar cell performance continued to improve up to the maximum number of blocking layers that were used, suggesting that further work is required to determine if the performance continues to improve as the number of layers is increased and to establish the optimum thickness for the compact TiO<sub>2</sub> film.

#### 4. Conclusions

The application of compact TiO<sub>2</sub> films to the substrate of the working electrode of dye-sensitized solar cells by dip-coating increased the efficiency of these solar cells. This increase in efficiency was largely due to an increase in the short-circuit current, resulting from the prevention of the back transfer of electrons from the conducting layer on the glass substrate to the electrolyte. As the number of coatings increased, the efficiency of the solar cells also increased, due to the compact TiO<sub>2</sub> film providing better coverage of the substrate and due to the thickness of the film increasing, thus providing a greater barrier to the back transfer of electrons.

Further work will include microwave processing of both the TiO<sub>2</sub> sol–gel blocking layers and the nanostructured TiO<sub>2</sub> films. It is hoped that the use of microwave processing will allow a relatively high efficiency to be achieved with heat treatment at lower temperatures than those used in this work.

#### Acknowledgements

The authors acknowledge the financial support for this work provided by a Monash University Engineering Research Grant and the Australian Research Council. J.N.H. gratefully acknowledges the assistance provided by Monash University through the Sir James McNeill Foundation Scholarship. The assistance of Dr. Sophie Cerneaux with the French translation is also gratefully acknowledged.

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