

Enhanced Efficiency of a Dye-Sensitized Solar Cell Made from MgO-Coated Nanocrystalline SnO₂

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2001 Jpn. J. Appl. Phys. 40 L732

(<http://iopscience.iop.org/1347-4065/40/7B/L732>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 132.174.255.116

This content was downloaded on 11/11/2014 at 20:06

Please note that [terms and conditions apply](#).

Enhanced Efficiency of a Dye-Sensitized Solar Cell Made from MgO-Coated Nanocrystalline SnO₂

Kirithi TENNAKONE*, Jayasundara BANDARA, Priyangi Konara Mudiyanseelage BANDARANAYAKE, Gamaralalage Rajanya Asoka KUMARA¹ and Akinori KONNO¹

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

¹Department of Materials Science, Shizuoka University, Hamamatsu 432-8561, Japan

(Received February 23, 2001; accepted for publication May 23, 2001)

Nanocrystalline SnO₂-based dye-sensitized photoelectrochemical solar cells have very low open-circuit voltages of 325–375 mV and efficiencies of ~1%. However, on coating the SnO₂ crystallites with a thin film of MgO, the voltage and efficiency are increased to 650–700 mV and ~6.5%, respectively. Evidence is presented to show that the photoexcited dye on the outer MgO shell could tunnel electrons to SnO₂ and that the low probability of reverse tunneling suppresses recombinations, thus increasing the efficiency. An explanation is also given as to understand why dye-sensitized TiO₂ cells are more efficient than those made from SnO₂ alone.

KEYWORDS: solar cells, photoelectrochemical cells, semiconductor electrodes, dye-sensitization, electron tunneling, electron traps, carrier recombination, electron effective mass, tin (IV) oxide, magnesium oxide

Dye-sensitized (DS) photoelectrochemical cells (PECs) based on nanocrystalline semiconductor films and the mechanisms of charge separation, transport and recombinations involved have attracted much attention.^{1–8} The performance of these devices depends on the film material, film morphology, photophysical and structural properties of the sensitizer and the redox couple used. PECs with Ru-bipyridyl dye-coated TiO₂ films in I⁻/I₃⁻ redox electrolyte generate short-circuit photocurrents (I_{sc}) at nearly 100% incident photons to photocurrent conversion efficiencies (IPCEs) and energy conversion efficiencies (η) ~ 10% have also been achieved.³ Despite optimization by variation of the film characteristics, we found that η comparable to DS TiO₂ PECs could not be obtained with DS SnO₂ cells, although they have similar light absorption cross sections. However, on coating the SnO₂ crystallite surfaces with a thin layer of MgO, an obvious enhancement of I_{sc} , open-circuit voltage (V_{oc}) and η was noted. Recombinations of the electrons (injected into the conduction band (CB) by the photoexcited dye) with the dye-cations (D^+) or I₃⁻ ions in the electrolyte are the main dissipative processes limiting the η of a DS cell. In this letter, we describe the construction and characteristics of a DS SnO₂/MgO PEC and explain how the MgO layer on SnO₂ could improve the cell by suppressing the leakage of trapped electrons to the electrolyte interface.

SnO₂/MgO films were deposited on conducting tin oxide (CTO) glass plates (1.5 × 0.5 cm², sheet resistance ~ 15 Ω□⁻¹) as follows: colloidal SnO₂ aqueous solution (1 ml, 15% SnO₂) and 50–100 μl of acetic acid (sufficient to dissolve MgO) are mixed and ground with a weighed amount of MgO, gradually adding 10 ml of ethanol. The dispersion is then sprayed onto CTO glass plates heated to 150°C and sintered at 550°C for 20 min. All films used for the measurements had a thickness of ≈ 8 μm. PECs were constructed in the usual manner (i.e., a platinized CTO glass counterelectrode interposing the electrolyte⁹) after depositing the dye cis-dithiocyanato-bis(2,2' bipyridyl 4,4' dicarboxylate) Ru(II) and I_{sc} ; V_{oc} was recorded at a constant intensity of ~ 1000 W·m⁻² (tungsten filament lamp). The variation of these quantities with the MgO% (w/w) presented in

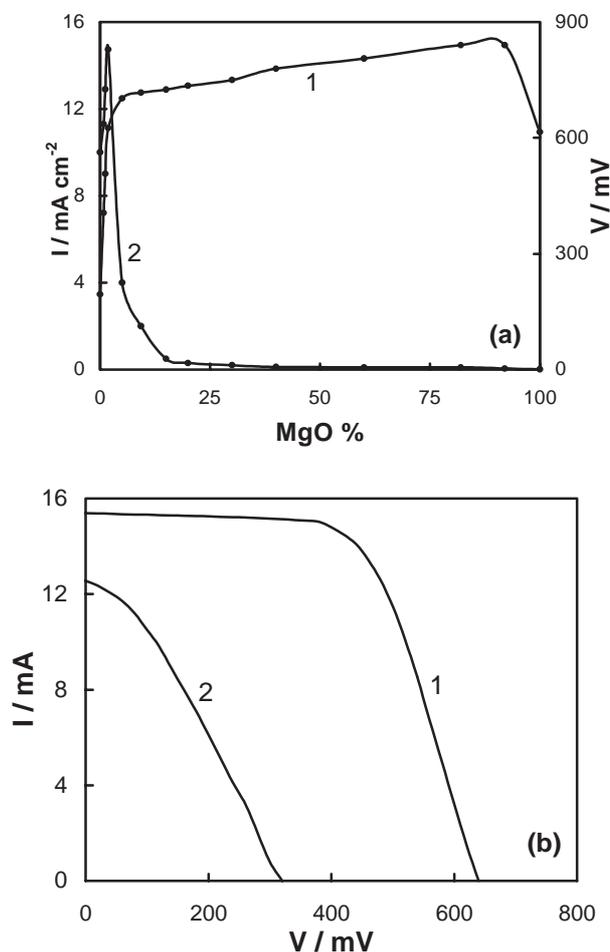


Fig. 1. (a) Variation of V_{oc} (curve 1) and I_{sc} (curve 2) of cells made from SnO₂/MgO films with the MgO% (cell area 0.25 cm²). (b) I - V characteristics of the DS cells made from (1) SnO₂/MgO(4.1%) and (2) SnO₂.

Fig. 1(a) shows a sharp peak for I_{sc} when MgO% = 4.1, thereafter I_{sc} decreases rapidly. V_{oc} slowly increases, with the MgO% reaching a peak at ~87%. The maximum value of η also corresponds to the positions of maximum I_{sc} . Scanning electron microscopy (SEM) examination did not reveal any distinguishable differences between SnO₂/MgO(4.1%) and

*Corresponding author. E-mail address: tenna@ifs.ac.lk

SnO₂ films. Interconnected SnO₂ crystallites (4–10 nm) appeared clearly in both SEM images. The only distinction seen in the transmission electron microscopy (TEM) was a slight haziness around SnO₂ crystallites in the SnO₂/MgO films, which we attribute to a coating of MgO. Energy dispersive X-ray (EDX) microanalysis detected MgO as homogeneously distributed (resolution 100 nm) and atomic absorption spectroscopy confirmed that the amount of Mg in the film is almost the same as that used for the preparation. When the MgO% = 4.1, X-ray diffraction (XRD) did not resolve Mg peaks. However, on increasing the MgO% (i.e., 15%), only MgO and SnO₂ peaks appeared, indicating the absence of mixed oxides. Digestion of the SnO₂/MgO(4.1%) films in HCl leached all MgO. Surface areas of SnO₂/MgO(4.1%) and SnO₂ (determined by desorption of adsorbed dye) were found to be ~750 and 800 times the geometrical area. Based on the above experiments we conclude that the SnO₂ crystallites in the SnO₂/MgO(4.1%) films are covered with a MgO layer of ~0.1 nm thickness. We are not certain whether the intercrystallite contacts are also interposed by a MgO film; if all such contacts incorporate a MgO film, the resistance may be too excessive to yield the observed *I*_{sc}. Sintering possibly fuses SnO₂ to SnO₂. The dye coated on SnO₂/MgO(4.1%) films is completely desorbed on digestion in 0.25 M HCl whereas the dye on SnO₂ films was resistant. From these observations we infer that in SnO₂/MgO(4.1%), the dye becomes anchored to the MgO surface.

Figure 1(b), (curve 1) shows the *I*–*V* characteristic of the DS SnO₂/MgO(4.1%) cell at 1000 W·m⁻² illumination, as measured by a solar-cell evaluation system (JASCO, CEP-25BX). For comparison, the characteristics of the DS SnO₂ cell are also included (Fig. 1(b), (curve 2)). We observe a dramatic enhancement of *V*_{oc}, *η* and fill factor (FF) in the SnO₂/MgO(4.1%) system with an increase in *I*_{sc} as well (Table I). The photocurrent action spectra of SnO₂/MgO(4.1%) and SnO₂ cells yield peak (~535 nm) IPCEs of 59% and 48%, respectively (not corrected for losses). We conducted another experiment by sensitizing SnO₂/MgO(4.1%) and SnO₂ films with hematoxylin (H). This dye, adsorbed on SnO₂ and MgO, have different spectral characteristics owing to surface complexing. H-adsorbed SnO₂ (brownish red) and MgO (blue) have absorption peaks at ~533 and 600 nm, respectively and we observed that H-adsorbed SnO₂/MgO(4.1%) has the same color and peak absorption position as H-adsorbed MgO (Fig. 3), again confirming that SnO₂ crystallites in SnO₂/MgO(4.1%) have an outer shell of MgO. Furthermore, the photocurrent action spectra of H-sensitized SnO₂ and SnO₂/MgO(4.1%) cells (where a neutral electrolyte is used) showed peaks at ~533 nm and 600 nm, respectively (Fig. 3), proving that in the latter cell, sensitization had occurred *via* dye deposited on MgO. Therefore, we conclude that the photoexcited dye

on the outer MgO shell on SnO₂ could tunnel electrons to the CB of SnO₂. Tunneling of electrons across the MgO barrier becomes energetically feasible as the excited level of the dye (S*) is located well above the CB (inset Fig. 2). As the MgO film thickness is small, direct tunneling transfer occurs easily.¹⁰⁾ Although recombinations are better suppressed by thicker films of MgO, increase in the film thickness reduces the tunneling probability. We believe that the origin of the sharp peak in the variation of *I*_{sc} with MgO% at 4.1% of MgO (Fig. 1(a)) originates from the presence of these two competing effects. *V*_{oc}, which is dependent on the height of the electron quasi-Fermi level (QFL) is more sensitive to recombinations. Thus, thicker MgO films favor higher *V*_{oc} and the limitation here is the insulating action of very thick films of MgO. Consequently, *V*_{oc} slowly increases with the MgO%, giving a peak at 87% of MgO (Fig. 1(a)).

The final questions that need to be answered are: (1) How does a thin film of MgO on SnO₂ improve the performance of the cell? (2) Why do DS TiO₂ cells deliver

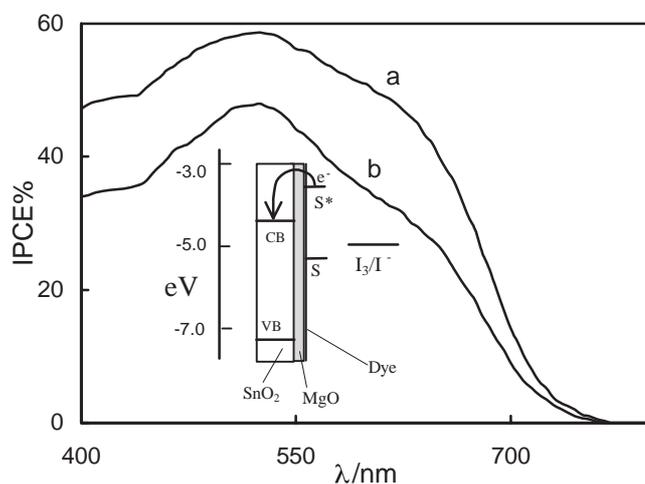


Fig. 2. Photocurrent action spectra of DS cells made from (a) SnO₂/MgO(4.1%) and (b) SnO₂ films. Inset: Schematic energy level diagram indicating the positions (eV/vacuum scale) of the bands of SnO₂, ground and excited levels of the dye (S, S*) and the I₃⁻/I⁻ redox level.

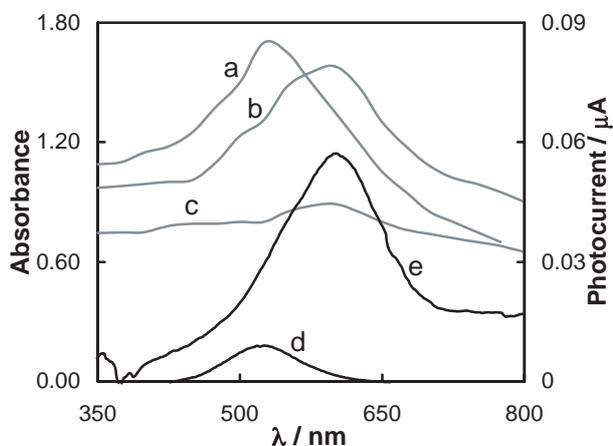


Fig. 3. Absorption spectra of hematoxylin-coated (a) SnO₂, (b) SnO₂/MgO(4.1%) and (c) MgO films and photocurrent action spectra DS cells made from (d) SnO₂ and (e) SnO₂/MgO(4.1%) films sensitized with hematoxylin.

Table I. Short-circuit photocurrent, open-circuit voltage and fill-factor of DS cells made from SnO₂/MgO(4.1%) and SnO₂ films.

Film	<i>I</i> _{sc} /mA	<i>V</i> _{oc} /mV	<i>η</i> %	FF%
SnO ₂ /MgO(4.1%)	15.4	654	6.5	65
SnO ₂	12.5	330	1.3	31

higher I_{sc} , V_{oc} , η compared to SnO_2 cells? The explanations we offer are as follows. When electrons tunneled into SnO_2 , relax to the CB, the reverse tunneling probability is largely reduced. Thus, the MgO barrier suppresses recombinations of the electrons with the D^+ or the I_3^- at the electrolyte interface. Semiconductor nanocrystalites are densely populated with intra-band trap states distributed in the energy gap^{2,4,5,8}) and recombinations generally occur *via* mediation of a trapped state. Electrons injected into the CB during dye-sensitization return to shallow traps and also become thermally excited the CB.^{4,5}) An electron in a shallow trap, with energy E below the bottom of CB is described by a wave function of the form $\Psi \sim \exp(-r/a)$,¹¹) where r = the radial coordinate measured from the trapping site, $a = \hbar/(2m^*E)^{1/2}$, and m^* = electron effective mass. When $E \simeq kT$ (T = room temperature) and $m^* \sim 0.1m_e$ (for SnO_2 ,^{12,13}) the parameter ' a ' ($\simeq 4$ nm) has the same order of magnitude as the SnO_2 crystallite dimension. In this situation, the trapped electron would readily leak to the electrolyte (instead of returning back to the CB) and recombine with I_3^- or D^+ . The difference between the electron QFL in the semiconductor and the potential of the redox couple, determines the V_{oc} of a DS PEC. Although the QFL could rise to the bottom of the CB or above, most cells have V_{oc} below the theoretical limit, because of the recombinations. V_{oc} obtained from the DS SnO_2 cell is 350–400 mV. Upon coating MgO on SnO_2 , V_{oc} exceeding 700 mV was observed, suggesting that in this case QFL has risen even above the bottom of the CB. The increase in the FF in MgO-coated cells (Table I) again demonstrates the effectiveness of the MgO shell in reducing recombinations.

According to our own experience and other reports,¹⁴) DS PECs comparable in performance to those based on TiO_2 could not be prepared from ZnO. The CB position of ZnO is above that of TiO_2 and yet DS ZnO cells have lower V_{oc} s. Here again the reason seems to be the small electron effective mass ($\sim 0.2m_e$) in ZnO.¹⁵) Because of the large electron effective mass in TiO_2 (of the order $10m_e$ ¹⁶) or larger according to some reports¹⁷) an electron trapped (in a thermally excitable level) in the bulk of 10–30 nm thick TiO_2 crystallite

would not readily leak into the electrolyte interface. Although DS PECs made from SnO_2 or ZnO alone are inefficient, a composite DS SnO_2/ZnO PEC was found have an efficiency comparable to that of a TiO_2 cell.¹⁸) In this system, ZnO particles are more than one order of magnitude or larger compared to the SnO_2 particles and therefore, the electrons transferred to ZnO will not readily leak into the electrolyte interface. Obviously, films made from larger size (i.e., $\gg a$) SnO_2 or ZnO particles are unsuitable because of the low surface area. As the effective electron mass in TiO_2 is very large, efficient cells can be constructed from TiO_2 films composed of small crystallites.

- 1) B. O'Regan and M. Gratzel: *Nature* **335** (1991) 737.
- 2) D. Cahen, G. Hodes, M. Gratzel, J. F. Guillemoles and I. Reiss: *J. Phys. Chem. B* **104** (2000) 2053.
- 3) M. Gratzel: *Prog. Photovolt. Res. App.* **8** (2000) 171.
- 4) G. Franco, J. Gehring, L. M. Peter, E. A. Ponomarev and I. Ulendrof: *J. Phys. Chem. B* **103** (1999) 692.
- 5) P. E. de Jongh and D. Vanmaeklberg: *Phys. Rev. Lett.* **77** (1996) 3427.
- 6) J. Nelson: *Phys. Rev. B* **59** (1999) 15374.
- 7) R. Konenkamp, R. H. Henninger and P. Hoyer: *J. Phys. Chem. B* **97** (1993) 7328.
- 8) D. E. Skinner, D. P. Colombo, Jr., J. J. Cavaleri and R. M. Bowmann: *J. Phys. Chem.* **99** (1995) 7853.
- 9) Electrolyte composition was 0.6M dimethylpropyl imidazolium iodide + 0.1 M LiI + 0.05 M I_2 + 0.5 M t-butylpyridine in methoxyacetonitrile.
- 10) N. Sato: *Electrochemistry of Metal & Semiconductor Electrodes* (Elsevier, Amsterdam, 1998) p. 281.
- 11) For a simple derivation see R. P. Feynman, R. B. Leighton and M. Sands: *Lectures on Physics* (Narosa Publishing House, New Delhi, 1997) Vol. 3, pp. 1641–1643.
- 12) D. F. Morgan and D. A. Wright: *Br. J. Appl. Phys.* **17** (1966) 337.
- 13) R. Summitt and N. F. Borelli: *J. Phys. Chem. Solids* **26** (1965) 921.
- 14) H. Rensmo, K. Keis, H. Lindstrom, S. Sodergren, A. Solbrand, A. Hagfeldt, S. E. Linquist, L. N. Wang and M. Muhammed: *J. Phys. Chem. B* **101** (1997) 2598.
- 15) B. Enright and D. Fitzmaurice: *J. Phys. Chem.* **100** (1996) 1027.
- 16) C. Kormann, D. Bahnemann and M. Hoffmann: *J. Phys. Chem.* **92** (1988) 5196.
- 17) R. Breckenridge and W. Hosler: *Phys. Rev.* **91** (1953) 793.
- 18) K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda and V. P. S. Perera: *Chem. Commun.* **1999** (1999) 15.