

Dye-Sensitized Core–Shell Nanocrystals: Improved Efficiency of Mesoporous Tin Oxide Electrodes Coated with a Thin Layer of an Insulating Oxide

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Coating nanocrystalline SnO_2 electrodes for dye-sensitized solar cell applications with a thin layer of ZnO , TiO_2 , ZrO_2 , MgO , Al_2O_3 , Y_2O_3 , or other insulating oxides was found to improve dye adsorption and increase the sensitized photocurrent. The surface of the oxide coating is more basic than SnO_2 , which renders dye attachment by its carboxyl groups more favorable. At the same time, the photovoltage and fill factor are strongly enhanced, resulting in much better energy conversion efficiencies. This change is ascribed to inhibition of electron back transfer from SnO_2 to the redox electrolyte (I_3^-) by the insulating oxide. The optimum coating thickness is only a few angstroms, suggesting that electron transfer from the excited dye attached to the oxide surface to the underlying SnO_2 occurs by tunneling through the insulator layer. Different methods for coating SnO_2 nanocrystals with a thin layer of an insulating oxide were compared. The best results were obtained by adding a soluble metal salt to the SnO_2 colloid, which is converted to the oxide on firing of the electrode. Specific adsorption of the metal ions on the SnO_2 surface guarantees homogeneous coating at near-monolayer coverage. Although the energy conversion efficiency of such modified SnO_2 electrodes is still inferior to that of the usually employed TiO_2 electrodes, the larger band gap of SnO_2 offers the advantage of better long-term stability of the solar cell in the presence of UV light. Surface modification of nanocrystalline TiO_2 electrodes with very thin insulating oxide layers also improves the photovoltage but diminishes the current. Because of a blue shift in the photocurrent onset of insulator-coated TiO_2 , the solar cell stability in UV light is again enhanced.

Introduction

In the dye sensitization of large-band-gap semiconductors for photovoltaic solar cell applications, the highest energy conversion efficiencies have been achieved with titanium dioxide.¹ Other semiconductors, such as tin oxide,² zinc oxide,³ and niobium oxide,⁴ have been employed with less success. Therefore, it was surprising when Tennakone et al.⁵ reported recently that electrodes prepared from a mixture of tin dioxide colloid and zinc

oxide powder yield efficiencies superior to those of either of the oxides alone and comparable to those of titanium dioxide electrodes. The authors initially attributed the efficiency increase to ballistic electron motion through SnO_2 nanoparticles, which were thought to surround the larger ZnO grains. We achieved a similar enhancement by adding a small amount of zinc acetate to the tin dioxide colloid. Because the original recipe⁵ employed

(1) (a) Grätzel, M. *Prog. Photovoltaics Res. Appl.* **2000**, *8*, 171. (b) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613. (c) O'Regan, B.; Grätzel, M. *Nature* **1991**, *335*, 737. (d) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (e) Asbury, J. B.; Hao, E.; Wang, Y.; Ghosh, H. N.; Lian, T. *J. Phys. Chem. B* **2001**, *105*, 4545. (f) Hinsch, A.; Kroon, J. M.; Späth, M.; Roosmalen, J. A. M.; Bakker, N. J.; Sommeling, P.; van der Burg, N.; Kinderman, P.; Kern, R.; Ferber, J.; Schill, C.; Schubert, M.; Meyer, A.; Meyer, T.; Uhlendorf, I.; Holzbock, J.; Niepmann, R. In *Proceedings of the Sixteenth European Photovoltaic Solar Energy Conference*; James & James (Science Publishers) Ltd: London, 2000; p 32.

(2) (a) Bedja, I.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 4133. (b) Fungo, F.; Otero, L.; Durantini, E. N.; Silber, J. J.; Sereno, L. E. *J. Phys. Chem. B* **2000**, *104*, 7644. (c) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490.

(3) (a) O'Regan, B.; Schwartz, D. T.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Mater.* **2000**, *12*, 1263. (b) Bauer, C.; Boschloo, G.; Mukhtar, E.; Hagfeldt, A. *J. Phys. Chem. B* **2001**, *105*, 5585. (c) Keis, K.; Lindgren, J.; Lindquist, S. E.; Hagfeldt, A. *Langmuir* **2000**, *16*, 4688.

(4) (a) Lenzmann, F.; Krueger, J.; Burnside, S.; Brooks, K.; Grätzel, M.; Gal, D.; Rühle, S.; Cahen, D. *J. Phys. Chem. B* **2001**, *105*, 6347. (b) Eguchi, K.; Koga, H.; Sekizawa, K.; Sasaki, K. *J. Ceram. Soc. Jpn.* **2000**, *108*, 1067. (c) Barros, D. D.; Abreu, P. P.; Alves, O. L.; Franco, D. W. *J. Sol-Gel Sci. Technol.* **2000**, *18*, 259.

(5) (a) Tennakone, K.; Kumara, G. R. R. A.; Kottegoda, I. R. M.; Perera, V. P. S. *Chem. Commun.* **1999**, 15. (b) Bandara, J.; Tennakone, K. *J. Colloid Interface Sci.* **2001**, *236*, 375. (c) Kumara, G. R. A.; Konno, A.; Tennakone, K. *Chem. Lett.* **2001**, 180. (d) Kumara, G. R. R. A.; Tennakone, K.; Perera, V. P. S.; Konno, A.; Kaneko, S.; Okuya, M. *J. Phys. D: Appl. Phys.* **2001**, *34*, 868. (e) Tennakone, K.; Kottegoda, I. R. M.; De Silva, L. A. A.; Perera, V. P. S. *Semicond. Sci. Technol.* **1999**, *14*, 975. (f) One of the reviewers drew our attention to the more recent work of Tennakone et al. on MgO -coated nanocrystalline SnO_2 , which was published during the final stage of our manuscript preparation (Tennakone, K.; Bandara, J.; Bandaranayake, P. K. M.; Kumara, G. R. A.; Konno, A. *Jpn. J. Appl. Phys.* **2001**, *40*, L732 and presentations given at the International Workshop on Nanostructures in Photovoltaics, Dresden, Germany, Jul 28–Aug 4, 2001, as well as the 200th Meeting of the Electrochemical Society, San Francisco, CA, Sep 2–7, 2001). In that work, the authors concluded that MgO is first dissolved by acetic acid and then forms an insulating shell covering the SnO_2 particles that allows electron injection by tunneling but suppresses recombination.

acetic acid, which dissolves the zinc oxide to some extent, it appeared that the efficiency improvement was due, instead, to the formation of a thin zinc oxide layer covering the tin dioxide particles.^{5f} Because ZnO has a higher conduction band edge than SnO₂, the open-circuit photovoltage of the cell, given by the difference between the conduction band edge and the redox potential of the electrolyte, will thus be enhanced. Moreover, the coloration of the zinc-modified tin oxide electrode by the dye carrying carboxyl attachment groups is much stronger than that of the unmodified powder. This is expected from the higher isoelectric point (iep) of ZnO (iep at pH 9) compared to SnO₂ (iep at pH 4–5),⁷ resulting in better light absorption and, thus, a higher photocurrent.

Intrigued by these observations we investigated the surface modification of SnO₂ by other insulating oxides that might form a tunneling barrier between the dye sensitizer and the SnO₂ conduction band. It is well-established in solid-state metal–insulator–semiconductor (MIS) photovoltaics that such an insulating layer can enhance solar cell efficiency. In the case of dye-sensitized photoelectrochemical cells, the tunneling layer would suppress the dark current arising from the reduction of the redox electrolyte at the semiconductor surface, hence improving the photovoltage. In addition, the photocurrent can be enhanced, as already mentioned, by stronger dye adsorption on the modified semiconductor surface.

Experimental Section

SnO₂ Colloid Preparation. The results reported below were obtained with electrodes prepared from commercially available colloidal SnO₂ (Alfa Aesar, 15 wt % in H₂O, stabilized with NH₄OH at pH 9.5, BET surface area = 56 m²/g). To prevent cracking and peeling of thicker films (>1 μm) during sintering and also to enhance light absorption by scattering, we added SnO₂ powder (Ventron 99.9%, BET surface area = 6.3 m²/g), so that the nanoporous electrodes consisted of SnO₂ nanoparticles (diameter ≈ 15 nm) and larger particles (~140 nm). For example, 0.3 g of SnO₂ powder was ground in a small porcelain mortar with 0.1 mL of SnO₂ colloid and stepwise diluted under grinding with 0.9 mL of SnO₂ colloid (giving a total of 0.17 g of colloidal SnO₂). A drop of Triton X-100 was added to help spreading on the substrate. Electrodes prepared from other SnO₂ colloids or without the addition of SnO₂ powder gave similar results.

Surface Modification. For the surface modification of SnO₂, different procedures were compared (see Results and Discussion). The best efficiencies were obtained by dissolving magnesium, aluminum, or ytterbium nitrate; ZrOCl₂; TiCl₄; Zn(CH₃–COO)₂; or Sc(CF₃–SO₃)₃ in acetic acid and then adding the SnO₂ colloid/powder dispersion. Acidification of the basic SnO₂ colloid resulted in immediate gellation, but upon agitation and sonification, the colloid became more or less liquid again.

For example, 10 μL of 2.6 M Y(NO₃)₃ and 10 μL of acetic acid were mixed in a 1.5-mL Eppendorf cup with 0.2 mL of SnO₂ colloid/powder dispersion and sonicated for 1 min in an ultrasonic bath. In cases of Mg, Al, and Y, the pH was adjusted to 5 by the addition of ammonium hydroxide (25% NH₃ in water) to enhance cation adsorption (see Results and Discussion).

Photoelectrode Preparation and Characterization. Transparent conducting glass (SnO₂:F from Nippon Sheet Glass, sheet resistance = 10 Ω/square) was cut into 3 × 2.5

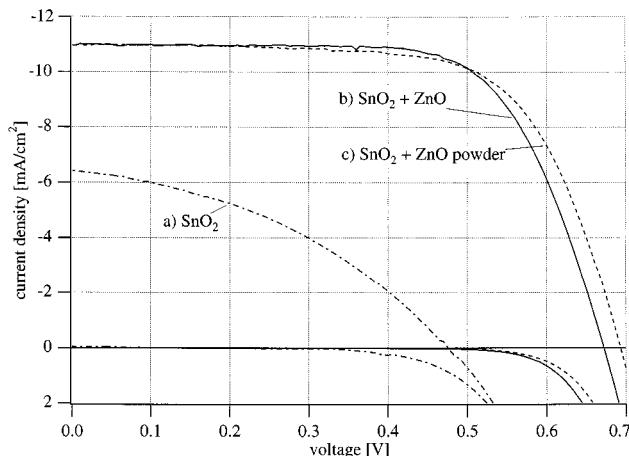


Figure 1. Photocurrent–voltage characteristics of dye-sensitized nanocrystalline photoelectrochemical cells with modified SnO₂ photoelectrodes at an irradiance of 1000 W/m², AM 1.5 (lower curves in darkness): (a) unmodified SnO₂, (b) SnO₂ coated with 40 μmol of ZnO/m² or 0.59 nm, (c) SnO₂ mixed with ZnO powder.

cm² pieces, cleaned by ultrasonification in 1% Triton X-100, and rinsed with distilled water. The longer edges were covered with scotch tape (40 μm thick), and 70 μL of the colloid was spread over the surface with a glass rod sliding on the scotch tape spacer. After drying at room temperature, the electrode was heated for 10 min on a hot plate at 500 °C. The film thickness determined with an Alpha-Step 200 apparatus (Tencor Instruments) was around 8 μm.

The electrode was cut into pieces of dimensions 1.25 × 1 cm², which were again heated for 10 min at 500 °C and transferred while still hot (~80 °C) into 0.5 mL each of 0.25 mM N719 dye [bis(tetrabutylammonium)-*cis*-bis(thiocyanato)-bis(2,2'-bipyridine-4,4'-dicarboxylato)ruthenium(II)]^{1d} in 50% acetonitrile/50% *tert*-butyl alcohol. After soaking for at least 1 day at room temperature, the colored electrode was dried in a stream of dry air and clamped against a counter electrode consisting of a thermally platinized⁸ 80-nm-thick sputtered platinum layer on ITO glass. Electrolyte (5 μL of 0.6 M dimethylpropylimidazolium iodide, 0.1 M iodine, 0.5 M 4-*tert*-butylpyridine, and 0.1 M lithium iodide in methoxy acetonitrile) was admitted by capillary action, and the electrode was illuminated perpendicularly with a parallel light beam directed through a mask of 0.44 cm² aperture.

Photocurrent/voltage characteristics and photoaction spectra were measured as described before.^{1b} For long-term stability tests,⁹ the solar cells were filled with 0.6 M dimethylpropylimidazolium iodide, 0.1 M iodine, and 0.5 M 4-*tert*-butylpyridine in γ-butyrolactone as the electrolyte, hermetically sealed, and irradiated at open circuit under a Suntest CPS plus lamp (ATLAS GmbH, 1000 W/m², AM 1.5, T = 55 °C).

Results and Discussion

Unmodified Dye-Sensitized Nanocrystalline SnO₂ Electrodes. Figure 1a shows the photocurrent/voltage characteristics of a dye-sensitized nanocrystalline SnO₂ electrode. Glass fibers of 10 μm diameter were inserted as a spacer between the photo- and counter electrodes in this case, because direct contact reduces the open-circuit photovoltage to less than 300 mV (depending on the contact pressure).

The coloration of the SnO₂ film was much weaker than that of a TiO₂ electrode of comparable active surface area. This is explained by the more acidic

(6) (a) Scaife, D. E. *Solar Energy* **1980**, *25*, 41. (b) Harris, L. A.; Wilson, R. H. *Annu. Rev. Mater. Sci.* **1978**, *99*.

(7) Parks, G. A. *Chem. Rev.* **1965**, *65*, 177.

(8) Papageorgiou, N.; Maier, W. F.; Grätzel, M. *J. Electrochem. Soc.* **1997**, *144*, 876.

(9) Solar cell stability was tested by Dr. P. Liska in our laboratory.

character of the SnO_2 surface, whose isoelectric point is at pH 4–5 as compared to pH 6.2 for TiO_2 (anatase),⁷ decreasing dye adsorption. Consequently, the short-circuit photocurrent is more than two times lower than the current with TiO_2 ($I_{sc} = 6.4 \text{ mA/cm}^2$ at 100 mW/cm²).

The open-circuit photovoltage ($V_{oc} = 475 \text{ mV}$) is also much lower than that obtained with TiO_2 (typically $V_{oc} \approx 700 \text{ mV}$). This is expected because the conduction band edge of SnO_2 is more positive than that of TiO_2 .⁶ Finally, the fill factor of the I – V curve is very poor ($ff = 0.4$, whereas TiO_2 typically gives $ff \approx 0.7$), resulting in an energy conversion efficiency of only $\eta = 1.2\%$ in full sun.

ZnO-Coated SnO_2 Electrodes. Zinc acetate was added to the SnO_2 colloid to deposit a thin layer of ZnO on the SnO_2 surface during firing (final relative composition = 0.22 g of ZnO + 1.0 g of SnO_2 colloid + 1.7 g of SnO_2 powder, corresponding to 40 μmol of ZnO per square meter of SnO_2), yielding a much more strongly colored electrode. The better dye adsorption on the ZnO -modified SnO_2 surface is easily explained by the basic character of ZnO (iep at pH 9),⁷ which favors attachment of the dyes carboxyl groups. Accordingly, the photocurrent (Figure 1b) is much higher with ZnO ($I_{sc} = 11.2 \text{ mA/cm}^2$) than without ZnO .

The open-circuit voltage ($V_{oc} = 670 \text{ mV}$) is also greatly improved, indicating that electrons are injected from the dye into the more negative conduction band of ZnO .⁶ The increased voltage and fill factor ($ff = 0.69$) show that back electron transfer from SnO_2 is efficiently suppressed by the ZnO layer, resulting in an energy conversion efficiency of $\eta = 5.1\%$ in full sun. Also, a spacer is no longer necessary to prevent a shunt between the photo- and counter electrodes.

A mixed SnO_2/ZnO electrode (relative composition = 1.15 g of ZnO powder + 1.0 g of SnO_2 colloid, thickness = 15 μm) prepared according to the method of Tennakone et al.⁵ shows very similar I – V characteristics (Figure 1c). Because the preparation involves acetic acid, which partially dissolves the ZnO powder, we assume that the improved efficiency is, in fact, due to the formation of a ZnO layer around the SnO_2 particles, as in the case of direct addition of zinc acetate. The optimum ZnO content is much higher in this case (53 wt %)^{5e} because only the most reactive part of the ZnO powder is dissolved by the weak acetic acid. In contrast, direct addition of zinc acetate yields equivalent cell performance only for 7.5 wt % ZnO , showing that a large amount of large ZnO particles is not required for efficient charge separation as claimed.^{5e}

Assuming a uniform coating^{5f} due to the specific adsorption of Zn^{2+} on SnO_2 ,¹¹ the thickness of the ZnO layer in Figure 1b estimated from the amount of zinc acetate added (giving 0.22 g of ZnO) and the surface area of the SnO_2 colloid (67 m^2) corresponds to 3.3 mg of ZnO/m^2 or 0.59 nm (taking the bulk density of ZnO as $\rho = 5.6 \text{ g/cm}^3$), which equals to only about two monolayers of ZnO on the $\varnothing 15\text{-nm}$ SnO_2 particles.

The impregnation of an already sintered colloidal SnO_2 electrode with zinc acetate solution followed by firing to deposit a ZnO coating around the SnO_2 particles also improved the I – V characteristics. However, the photovoltage and fill factor were always

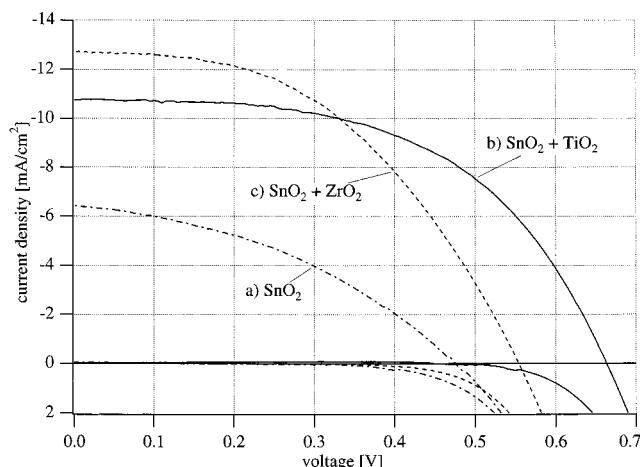


Figure 2. Photocurrent–voltage characteristics of dye-sensitized nanocrystalline photoelectrochemical cells with modified SnO_2 photoelectrodes at an irradiance of 1000 W/m^2 , AM 1.5 (lower curves in darkness): (a) unmodified SnO_2 , (b) SnO_2 coated with 18 μmol of TiO_2/m^2 or 0.35 nm, (c) SnO_2 coated with 25 μmol of ZrO_2/m^2 or 0.50 nm.

inferior to those obtained by the addition of zinc acetate to the SnO_2 colloid before sintering.

TiO₂- and ZrO₂-Modified SnO_2 . Coating the SnO_2 particles with TiO_2 by adding TiCl_4 to the colloid (resulting in 0.1 g of TiO_2 + 1.0 g of SnO_2 colloid + 1.7 g of SnO_2 powder or 18 μmol of TiO_2/m^2 of SnO_2) does not improve the dye adsorption as much as ZnO does, in accordance with the more acidic surface of TiO_2 (iep at pH 4.7 for rutile, pH 6.2 for anatase).⁷ Still, the I – V curve (Figure 2b) is strongly improved by the TiO_2 coating, which corresponds to 1.4 mg of TiO_2/m^2 or a thickness of 0.35 nm.

Interestingly, coating the SnO_2 with insulating ZrO_2 (band gap energy $E_g = 5.2 \text{ eV}$)^{6b} by adding ZrOCl_2 to the colloid (giving 0.19 g of ZrO_2 + 1 g of SnO_2 colloid + 1.7 g of SnO_2 powder or 25 μmol of ZrO_2/m^2 of SnO_2 or 0.5 nm) also improves the efficiency (Figure 2c). Because the conduction band level of ZrO_2 ($E_{cb} = -1.4 \text{ V}_{\text{NHE}}$ at pH 7)^{6b} lies above the excited-state level of the dye ($E_{S^*/S^+} = -1.3 \text{ V}_{\text{NHE}}$),^{1d} electron injection into the conduction band of ZrO_2 is not possible. Even though the band structure of a 0.5-nm-thick layer of ZrO_2 on SnO_2 might be different from that of a bulk ZrO_2 crystal, the experiment shows that the insulating ZrO_2 layer is thin enough to allow electron tunneling from the excited dye to the conduction band of the underlying SnO_2 . The increased photovoltage and fill factor are again explained by inhibition of the back electron transfer from SnO_2 to I_3^- through the ZrO_2 coating.

Suppression of the back current by a thin insulating tunneling layer is widely applied in solid-state photovoltaic cells of MIS (metal–insulator–semiconductor) structure and has also been observed in photoelectrochemical cells.¹⁰ To further exploit this approach with the dye-sensitized solar cell, we investigated insulating oxides other than ZrO_2 as the tunneling layer.

SnO_2 Electrodes with Insulating Oxide Coatings. Modifying the surface of the SnO_2 colloid with SiO_2 by adding $\text{Si}(\text{O}-\text{CH}_2-\text{CH}_3)_4$ along with HCl as a

(10) (a) Howe, A. T.; Fleisch, T. H. *J. Electrochem. Soc.* **1987**, 134, 72. (b) Howe, A. T. *J. Chem. Soc., Chem. Commun.* **1983**, 1407.

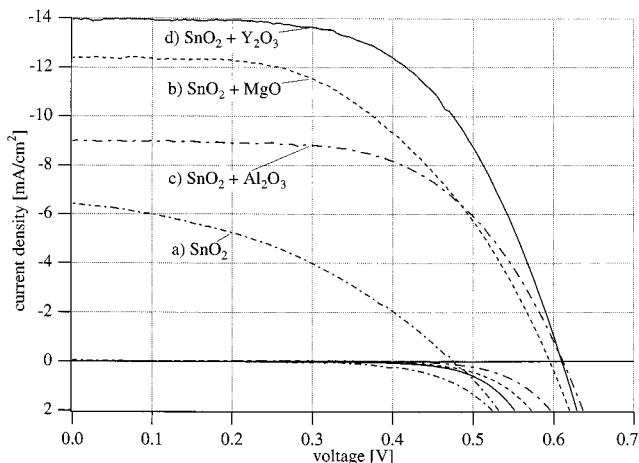


Figure 3. Photocurrent–voltage characteristics of dye-sensitized nanocrystalline photoelectrochemical cells with modified SnO_2 photoelectrodes at an irradiance of 1000 W/m^2 , AM 1.5 (lower curves in darkness): (a) unmodified SnO_2 , (b) SnO_2 coated with $12 \mu\text{mol}$ of MgO/m^2 or 0.13 nm , (c) SnO_2 coated with $6 \mu\text{mol}$ of $\text{Al}_2\text{O}_3/\text{m}^2$ or 0.16 nm , (d) SnO_2 coated with $6 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.27 nm .

catalyst resulted in very poor dye adsorption, because of the very acid character of the SiO_2 surface (iep at pH 2.0).⁷ Much better coloration and photocurrent/voltage characteristics (Figure 3) were obtained with the basic oxides MgO (iep at pH 12), Al_2O_3 (iep at pH 9), and Y_2O_3 (iep at pH 9).⁷

In fact, yttrium oxide, which is used as an insulating layer in semiconductor devices because of its high dielectric constant,¹⁷ gave the highest energy conversion efficiencies, and we therefore report the influence of different coating thicknesses of this oxide (Figure 4). At $3 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.13 nm (Figure 4b), the short-circuit photocurrent was already twice that of a pure SnO_2 electrode (Figure 4a), because of the much better dye adsorption. However, both the open-circuit photovoltage and the fill factor were still low, indicating back electron transfer from uncovered areas of SnO_2 . At $6 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.27 nm (Figure 4c), the short-circuit photocurrent remained about the same, but the photovoltage and fill factor were much improved. Further doubling of the coating thickness to $12 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.54 nm (Figure 4d) led to an additional gain in voltage, but the photocurrent was slightly suppressed by the tunneling barrier.

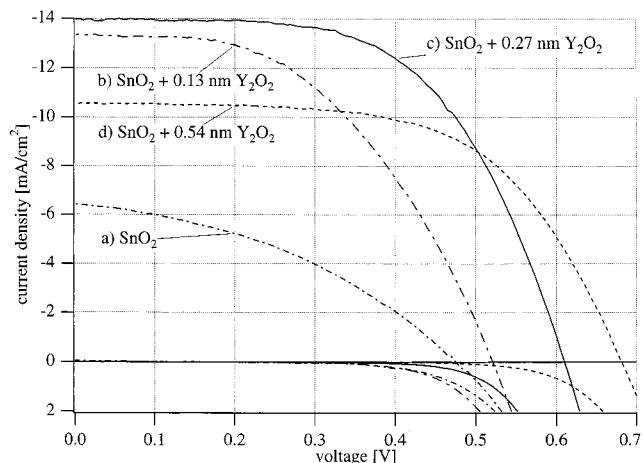


Figure 4. Photocurrent–voltage characteristics of dye-sensitized nanocrystalline photoelectrochemical cells with SnO_2 photoelectrodes coated with Y_2O_3 layers of different thicknesses at an irradiance of 1000 W/m^2 , AM 1.5 (lower curves in darkness): (a) unmodified SnO_2 , (b) SnO_2 coated with $3 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.13 nm , (c) SnO_2 coated with $6 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.27 nm , (d) SnO_2 coated with $12 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.54 nm .

The best results for different oxides are summarized in Table 1. As described in the Experimental Section, the oxide coatings were prepared by dissolving the magnesium, aluminum, or ytterbium nitrate; ZrOCl_2 ; TiCl_4 ; $\text{Zn}(\text{CH}_3\text{COO})_2$; or $\text{Sc}(\text{CF}_3\text{SO}_3)_3$ in acetic acid and then adding the SnO_2 colloid/powder dispersion. The SnO_2 colloid of Alfa Aesar is electrostatically stabilized by NH_4OH (pH 9.5), which imparts a negative charge to the SnO_2 particles (iep at pH 4–5).⁷ Mixing with acetic acid decreases the pH to about 3 and results in gelling of the SnO_2 colloid. However, in the presence of multivalent cations, such as Mg^{2+} , Al^{3+} , and Y^{3+} , the gel becomes liquid again upon agitation. This is a result of the specific adsorption of these cations,¹¹ which impart a positive charge to the SnO_2 particles and peptize the gel.

Subsequent increases of the pH to 5 and even 9 by the addition of NH_4OH to enhance cation adsorption or precipitate the hydroxides on the SnO_2 surface did not further improve the electrode efficiency. The addition of $\text{Y}(\text{NO}_3)_3$ alone (without acetic acid) to the basic SnO_2 colloid led to irreversible gelling. The presence of other acids, such as propionic, lactic, and nitric acids, and also of glycerol gave electrode efficiencies similar to those obtained in the presence of acetic acid. Comparable results were also obtained with a HNO_3 -stabilized (pH 1.5) SnO_2 colloid¹² upon addition of $\text{Al}(\text{NO}_3)_3$.

We conclude that acidic conditions or cation chelating molecules such as glycerol are required initially to ensure homogeneous cation adsorption on the SnO_2 surface to form a continuous oxide layer on firing.

As already mentioned for the ZnO -modified electrodes, the (repeated) impregnation of an already sintered colloidal SnO_2 electrode with a solution of magnesium, aluminum, or ytterbium nitrate or TiCl_4 , etc., followed by drying and firing to form an oxide coating on the SnO_2 particles also improved the I – V characteristics. However, the photovoltage and fill factor were always inferior to those obtained by cation adsorption on colloidal SnO_2 . The same is true for cathodic deposi-

(11) (a) James, R. O.; Healy, T. W. *J. Colloid Interface Sci.* **1972**, *40*, 65. (b) Wiese, G. R.; Healy, T. W. *J. Colloid Interface Sci.* **1975**, *51*, 435. (c) Fuerstenau, D. W.; Manmohan, D.; Raghavan, S. In *Adsorption from Aqueous Solution*; Tewari, P. H., Ed.; Plenum Press: New York 1981; p 93. (d) Jang, H. M.; Fuerstenau, D. W. *Colloids Surf.* **1986**, *21*, 235. (e) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, U.K., 1989; Vol. II, Chapter 12, p 709.

(12) The HNO_3 -stabilized SnO_2 colloid was prepared by F. Arendse in our laboratory by hydrolysis of SnCl_4 , dialysis, peptization with HNO_3 , and autoclaving at 230°C .

(13) Lee, J.; Tak, Y. *J. Ind. Eng. Chem.* **1999**, *5*, 139.

(14) Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V.; Grätzel, M. *J. Am. Ceram. Soc.* **1997**, *80*, 3157.

(15) Jarzebski, Z. M.; Marton, J. P. *J. Electrochem. Soc.* **1976**, *123*, 333C.

(16) Hawn, D. D.; Armstrong, N. R. *J. Phys. Chem.* **1978**, *82*, 1288.

(17) (a) Sharma, R. N.; Rastogi, A. C. *J. Appl. Phys.* **1993**, *74*, 6691. (b) Zhang, S. Q.; Xiao, R. F. *J. Appl. Phys.* **1998**, *83*, 3842. (c) Araiza, J. J.; Cardenas, M.; Falcony, C.; Mendez-Garcia, V. H.; Lopez, M.; Contreras-Puente, G. *J. Vac. Sci. Technol. A* **1998**, *16*, 3305. (d) Hunter, M. E.; Reed, M. J.; El-Masry, N. A.; Roberts, J. C.; Bedair, S. M. *Appl. Phys. Lett.* **2000**, *76*, 1935.

Table 1. Photoelectric Parameters of Dye-Sensitized Nanocrystalline Solar Cells with SnO_2 or TiO_2 Photoelectrodes Coated by Different Oxides at Indicated Coverage^a

colloid	modified with	resulting oxide coating	oxide coverage ($\mu\text{mol}/\text{m}^2$)	equivalent coating thickness (nm)	short-circuit photocurrent I_{sc} (mA/cm^2)	open-circuit photovoltage V_{oc} (mV)	fill factor ff (%)	energy conversion efficiency η (%)
SnO_2	—	—	0	0	6.4	480	40	1.2
SnO_2	ZnO powder	ZnO	?	?	11.2	690	67	5.2
SnO_2	$\text{Zn}(\text{CH}_3\text{COO})_2$	ZnO	40	0.59	11.2	670	69	5.1
SnO_2	TiCl_4	TiO_2	18	0.35	10.9	660	54	3.9
SnO_2	ZrOCl_2	ZrO_2	25	0.50	12.9	550	47	3.4
SnO_2	$\text{Mg}(\text{NO}_3)_2$	MgO	12	0.13	12.6	600	51	3.8
SnO_2	$\text{Al}(\text{NO}_3)_3$	Al_2O_3	6	0.16	9.7	610	61	3.6
SnO_2	$\text{Y}(\text{NO}_3)_3$	Y_2O_3	3	0.13	13.6	530	49	3.7
SnO_2	$\text{Y}(\text{NO}_3)_3$	Y_2O_3	6	0.27	13.8	610	59	4.9
SnO_2	$\text{Y}(\text{NO}_3)_3$	Y_2O_3	12	0.54	10.7	680	60	4.4
SnO_2	$\text{Sc}(\text{CF}_3\text{SO}_3)_3$	Sc_2O_3	10	0.35	11.0	610	61	4.2
SnO_2	$\text{La}(\text{NO}_3)_3$	La_2O_3	8	0.40	14.0	510	46	3.3
SnO_2	$\text{Sm}(\text{NO}_3)_3$	Sm_2O_3	8	0.40	14.0	530	49	3.6
SnO_2	$\text{Nd}(\text{NO}_3)_3$	Nd_2O_3	8	0.40	13.1	520	48	3.2
SnO_2	$\text{Ga}(\text{NO}_3)_3$	Ga_2O_3	9	0.28	11.3	580	49	3.3
SnO_2	$\text{In}(\text{NO}_3)_3$	In_2O_3	5	0.20	8.2	500	—	1.8
TiO_2	—	—	0	0	12.9	700	66	5.9
TiO_2	$\text{Mg}(\text{NO}_3)_2$	MgO	4.6	0.05	7.0	800	72	4.0
TiO_2	$\text{Al}(\text{NO}_3)_3$	Al_2O_3	2.3	0.06	10.0	740	70	5.2
TiO_2	$\text{Y}(\text{NO}_3)_3$	Y_2O_3	2.3	0.10	6.8	770	75	3.9

^a Irradiance = 1000 W/m^2 , AM 1.5.

tion of Y(OH)_3 on a colloidal SnO_2 electrode from $\text{Y}(\text{NO}_3)_3$ solution.¹³ This indicates the presence of uncovered SnO_2 areas resulting from a less homogeneous oxide coating.

Insulating Coatings on TiO_2 Electrodes. Colloidal TiO_2 (anatase) prepared by hydrolysis of titanium isopropoxide, peptization with HNO_3 , and autoclaving at 230 °C (surface area = 100 m^2/g , pH 1.0)¹⁴ was surface-modified by the addition of magnesium, aluminum, or ytterbium nitrate. On addition of NH_4OH to pH 5, no gelling occurred, as would have been the case in the absence of these cations, indicating their specific adsorption on TiO_2 .

The adsorption of multivalent cations on TiO_2 has been extensively studied.¹¹ TiO_2 is a special case because of its very high dielectric constant ($\epsilon = 80$ –180), which favors the specific adsorption of multivalent cations by electrostatic shielding. According to the cited studies, the formation of a homogeneous layer of adsorbed cations is expected under our experimental conditions, which is then converted into a continuous insulating oxide layer by firing.

The I – V characteristics of transparent thin layer electrodes prepared from such modified TiO_2 colloids are shown in Figure 5. An increase in the open-circuit voltage with respect to that of the unmodified TiO_2 electrode is observed, despite the very low insulator coverage, but the photocurrent diminishes, resulting in an overall loss of energy conversion efficiency (Table 1). The decrease in the photocurrent probably results from poor electrical contact between the particles caused by their insulating shell reducing the charge collection efficiency. Coating the titania nanoparticles after they have been sintered to give the mesoporous film may overcome this problem.

UV Action Spectra and Cell Stability. None of the modified SnO_2 or TiO_2 electrodes is as efficient in solar energy conversion as the pure TiO_2 electrode (Table 1). However, TiO_2 (anatase), with a band gap of $E_g = 3.2$ eV, absorbs UV light below $\lambda_g = 400$ nm, which leads to the formation of strongly oxidizing valence band holes

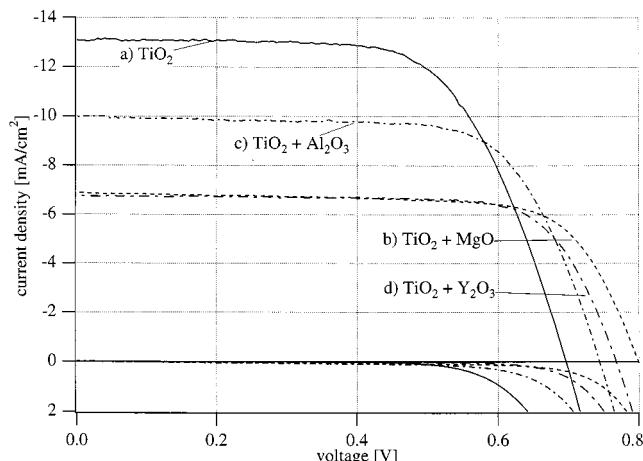


Figure 5. Photocurrent–voltage characteristics of dye-sensitized nanocrystalline photoelectrochemical cells with modified TiO_2 photoelectrodes at an irradiance of 1000 W/m^2 , AM 1.5 (lower curves in darkness): (a) unmodified TiO_2 , (b) TiO_2 coated with 4.6 μmol of MgO/m^2 or 0.05 nm, (c) TiO_2 coated with 2.3 μmol of $\text{Al}_2\text{O}_3/\text{m}^2$ or 0.06 nm, (d) TiO_2 coated with 2.3 μmol of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.10 nm.

($E_{\text{vb}} = 3 \text{ V}_{\text{NHE}}$ at pH 7) that can attack the electrolyte solvent of the solar cell.

Most of the valence band holes will oxidize I^- to I_3^- in the same way as the oxidized dye, while the corresponding conduction band electron created by UV excitation will contribute to the photocurrent and reduce I_3^- back to I^- at the counter electrode. On the other hand, any holes that oxidize the solvent irreversibly rather than regenerating I_3^- will result in an unrecoverable loss of I_3^- , which is required as an electron acceptor at the counter electrode.

Stable solar cell performance under several months of UV illumination has been obtained with very inert solvents such as propio- or valeronitrile.^{1f} Yet, cells with more reactive solvents such as γ -butyrolactone, which is preferred to acetonitrile because of its higher boiling point, can degrade within a few days of illumination through the loss of I_3^- . From this point of view, SnO_2 is an interesting alternative to TiO_2 , because its larger

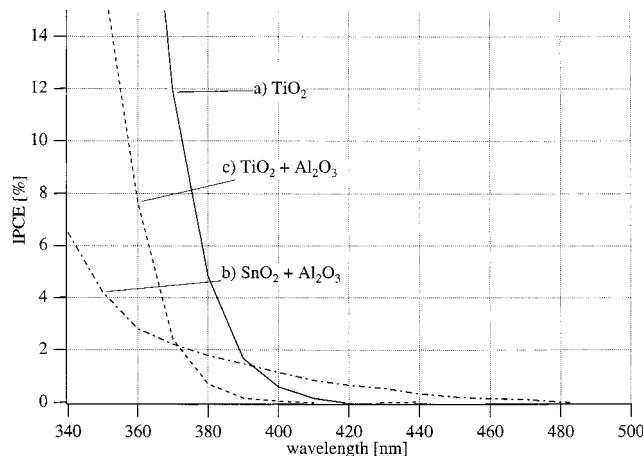


Figure 6. UV action spectra of unsensitized nanocrystalline photoelectrochemical cells. The incident photon-to-current conversion efficiency (IPCE) is plotted as a function of excitation wavelength: (a) unmodified TiO_2 , (b) SnO_2 coated with 6 $\mu\text{mol of Al}_2\text{O}_3/\text{m}^2$ or 0.16 nm, (c) TiO_2 coated with 2.3 $\mu\text{mol of Al}_2\text{O}_3/\text{m}^2$ or 0.06 nm.

band gap ($E_g = 3.5$ eV)¹⁵ corresponds to an absorption edge of $\lambda_g = 360$ nm, so that fewer valence band holes will be created under illumination.

A comparison of the photocurrent action spectra of TiO_2 and $\text{SnO}_2/\text{Al}_2\text{O}_3$ electrodes without dye sensitizer (Figure 6) indeed shows a blue-shifted absorption edge for $\text{SnO}_2/\text{Al}_2\text{O}_3$. Unfortunately, the $\text{SnO}_2/\text{Al}_2\text{O}_3$ electrode exhibits a weak tail extending up to 480 nm, which might be due to the indirect absorption edge at 2.5 eV.¹⁵ Still, solar cells with dye-sensitized $\text{SnO}_2/\text{Al}_2\text{O}_3$ electrodes and γ -butyrolactone as the electrolyte solvent were stable for 10 weeks under continuous illumination with simulated sunlight (AM 1.5) including ultraviolet photons,⁹ whereas an unmodified TiO_2 electrode showed I_3^- consumption within a few days. Cells with MgO - and Y_2O_3 -coated SnO_2 electrodes were less stable, despite the fact that their UV action spectra were similar to those of Al_2O_3 -coated SnO_2 electrodes. Presumably, MgO and Y_2O_3 , which, in contrast to Al_2O_3 , are both slightly water soluble, are slowly desorbed by the electrolyte from the SnO_2 surface.

Interestingly, coating a TiO_2 electrode with a thin layer of Al_2O_3 (cf. Figure 5c), or with a thin layer of Y_2O_3 or MgO , also results in a blue shift of the photoaction spectrum (Figure 6c). Again, solar cells with dye-sensitized $\text{TiO}_2/\text{Al}_2\text{O}_3$ photoelectrodes and γ -butyrolactone as the electrolyte solvent were much more stable than cells with unmodified TiO_2 or $\text{TiO}_2/\text{Y}_2\text{O}_3$ photoelectrodes.

It is well-known in pigment applications of TiO_2 that coating the paint with an insulator such as Al_2O_3 or SiO_2 prevents chalking, which occurs as a result of photodegradation of the organic binder at the TiO_2 surface. In the case of dye-sensitized photoelectrochemical cells, the insulator coating has to be very thin so that electron injection from the excited dye into the conduction band of TiO_2 is still possible. Further studies will be necessary to optimize the efficiency and long-term stability of this new type of solar cell.

Conclusion

Surface modification of nanocrystalline SnO_2 electrodes with a thin layer of ZnO , TiO_2 , ZrO_2 , MgO , Al_2O_3 , Y_2O_3 , or other insulating oxides was found to improve

dye adsorption and thus increase the sensitized photocurrent. This difference is ascribed to the more basic surface of the oxide coating as compared to SnO_2 , favoring dye attachment through its carboxylic acid groups. At the same time, the photovoltage and fill factor of the cell are strongly enhanced, resulting in much better energy conversion efficiencies. This is explained by the suppression of electron back transfer from SnO_2 to the redox electrolyte (I_3^-) in the presence of the insulating oxide.

The optimum coating thickness is only a few angstroms, suggesting that electron transfer from the excited dye attached to the oxide surface to the underlying SnO_2 occurs by tunneling through the insulator layer. Thicker layers yield a higher open-circuit photovoltage but result in a decreased photocurrent.

The best results were obtained by adding a soluble metal salt to the SnO_2 colloid, which was converted to the oxide upon firing of the electrode. Posttreatment of nanocrystalline SnO_2 electrodes with a metal salt solution always gave poor fill factors, indicating incomplete coverage of the SnO_2 surface. The more homogeneous oxide coating in the case of metal salt addition to the colloid is explained by specific adsorption of the metal ions on the SnO_2 surface. Although this should also result in a thin insulating oxide layer in the contact area between SnO_2 particles, the electron transfer at these grain boundaries seems not to be impaired if the coating is sufficiently thin. Probably, sintering at 500 °C allows sufficient interdiffusion of SnO_2 to yield good electrical contact.

The energy conversion efficiency of such modified SnO_2 electrodes is still inferior to that of pure TiO_2 electrodes. However, the larger band gap of SnO_2 makes the solar cell less sensitive to UV degradation when solvents are employed that react with the valence band holes generated by band gap excitation.

Surface modification of nanocrystalline TiO_2 electrodes with very thin layers of MgO , Al_2O_3 , or Y_2O_3 also improves the photovoltage but diminishes the current. Interestingly, the insulating oxide coating results in a blue shift in the photocurrent onset of TiO_2 . The suppression of the UV photocurrent through band gap excitation of TiO_2 can be explained either by inhibition of hole transfer to the electrolyte by the insulator or by trapping of charge carriers in surface states followed by electron/hole recombination. This observation might be useful for improving the long-term stability under UV irradiation of dye-sensitized solar cells.

As an alternative to the oxide coatings on SnO_2 investigated here, surface modification with organometallic compounds such as functionalized silanes (e.g., γ -aminopropyltrimethoxysilane)¹⁶ can be envisaged to improve dye attachment and suppress back electron transfer. However, the long-term stability of such coatings might be inferior to that of simple oxide coatings.

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