An efficient dye-sensitized photoelectrochemical solar cell made from oxides of tin and zinc

K. Tennakone,* G. R. R. A. Kumara, I. R. M. Kottegoda and V. P. S. Perera

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka. E-mail: ifs@ifs.ac.lk

Received (in Cambridge, UK) 1st September 1998, Accepted 19th November 1998

A photoelectrochemical solar cell made from a porous film consisting of a mixture of tin (IV) and zinc oxides sensitized with a ruthenium bipyridyl complex suppresses recombination of the photogenerated electrons and dye cations, generating a short-circuit photocurrent of *ca.* 22.8 mA cm^{-2} and an open-circuit voltage of *ca.* 670 mV in direct sunlight (900 W m^{-2}) with an efficiency *ca.* 8 %.

Dye-sensitized (DS) photoelectrochemical cells (PECs) based on nanoporous films of TiO_2 are gaining much attention as promising solar energy conversion devices.[1–6] Although dye-sensitization can be achieved with porous films of high band-gap semiconductors other than TiO_2, DS PECs as efficient as the Gratzel's cell have not been fabricated earlier using other materials. We have succeeded in constructing a DS PEC from porous films of tin(IV) oxide containing *ca.* 53% zinc oxide. The cell generates an I_{sc} of *ca.* 22.8 mA cm^{-2} and V_{oc} of *ca.* 670 mV at 900 W m^{-2} in direct sunlight. The energy conversion efficiency of *ca.* 8% at this intensity is increased to *ca.* 15 % in diffuse daylight (100 W m^{-2}) as a consequence of the increase of the fill factor from 0.5 to 0.6. Both oxides (Sn and Zn) are essential for functioning of the cell. The enhanced values of I_{sc} and V_{oc} are explained as resulting from the high probability of transfer of an electron by an excited dye molecule adsorbed at a SnO_2 crystallite to a ZnO crystallite and subsequent relaxation to the conduction band (CB) of another SnO_2 crystallite attached to the original ZnO crystallite. This process leads to efficient spatial separation of photogenerated charges (D^+ and e^-), suppressing recombinations.

Porous films consisting of SnO_2 and ZnO were prepared by the following method. A colloidal 15% aqueous solution of SnO_2 of crystallite size of *ca.* 0.015 μm. (1.5 ml), acetic acid (0.1 ml) and ZnO of crystallite size of *ca.* 2 μm (0.3 g, prepared by thermal decomposition of zinc oxalate) were ground in an agate mortar, mixed with 20 ml of methanol and agitated ultrasonically for 30 min. The solution was sprayed onto a fluorine doped conducting tin oxide (CTO) glass plate (1.25 × 1.5 cm, sheet resistance *ca.* 10 Ω □$^{-1}$) heated to 150 °C until a layer of thickness *ca.* 8–10 μm was deposited and sintered at 500 °C in air for 35 min (sintering completely removes organic compounds in the solution). The sintered film was coated with the dye {*cis*-dithiocyanato [*N*-bis(2,2′-bipyridyl-4-4′-dicarboxylic acid)]ruthenium(II)} by boiling the plate in the dye solution (2 × 10^{-4} M in ethanol) for 3 min. A lightly platinized CTO glass plate, used as the counter electrode was kept in contact with the dyed film and the edges are sealed after introducing the electrolyte (0.5 M KI + 0.03 M I_2 in acetonitrile containing 10% ethylene glycol). The construction of the cell is schematically depicted in the inset of Fig. 1.

The *I–V* characteristics of the cell in direct sunlight (900 W m^{-2}) and diffuse daylight presented in Fig. 1 correspond to efficiencies of 8 and 15%, respectively. In direct sunlight, the efficiency is comparable to that of the Gratzel's cell based on TiO_2. However, at lower intensities (diffuse daylight) the efficiency of the present system appears to exceed that of Gratzel's cell. When the film is 100 % SnO_2, the maximum values of I_{sc} and V_{oc} obtained are *ca.* 2.5 mA cm^{-2} and *ca.* 335 mV respectively. Introduction of even a small quantity of ZnO increases both I_{sc} and V_{oc} significantly. The optimum values of I_{sc} and V_{oc} are reached when ZnO% is *ca.* 53%, a further increase of ZnO decreases I_{sc} and V_{oc} and for a cell made from 100% ZnO, I_{sc} = *ca.* 4 mA cm^2 and V_{oc} = *ca.* 540 mV. As SnO_2 particles have much smaller dimensions compared to ZnO (r_{ZnO}/r_{SnO_2} = *ca.* 133). The surface area of SnO_2 film ($S = 3w/\rho r$, where w = weight of the oxide, ρ = density, r = radius of the particle) is *ca.* 107 times the ZnO surface when the ZnO% corresponds to the optimum. Consequently, the light absorption occurs mostly at the dye coated SnO_2. The above observation is also supported by the photocurrent action spectra of cells made with composite SnO_2/ZnO films and those of SnO_2 and ZnO. The peaks of the action spectra of SnO_2 and SnO_2/ZnO systems were observed at almost the same position (*ca.* 539 nm), whereas a pure ZnO cell showed a peak at *ca.* 528 nm, indicating that in the composite system photocurrent originates mostly *via* sensitization of SnO_2. Furthermore ZnO adsorbs the Ru-complex, very feebly compared to SnO_2.

The mechanism of photocurrent generation which can explain the observations is as follows: in the composite film the larger ZnO particles are surrounded by SnO_2 particles (Fig. 2). An excited dye molecule on a SnO_2 particle could inject an electron to the CB of SnO_2 as in normal dye-sensitization of a semiconductor. However, as the excited level of the dye is above the CB of ZnO (Fig. 2) the energetic electron (*i.e.* the 'hot carrier' which has not relaxed to the CB of the SnO_2 particle) could also be driven to the CB of a ZnO particle in its vicinity, traversing across several SnO_2 particles. This enables a significant number of dye coated SnO_2 particles to participate in

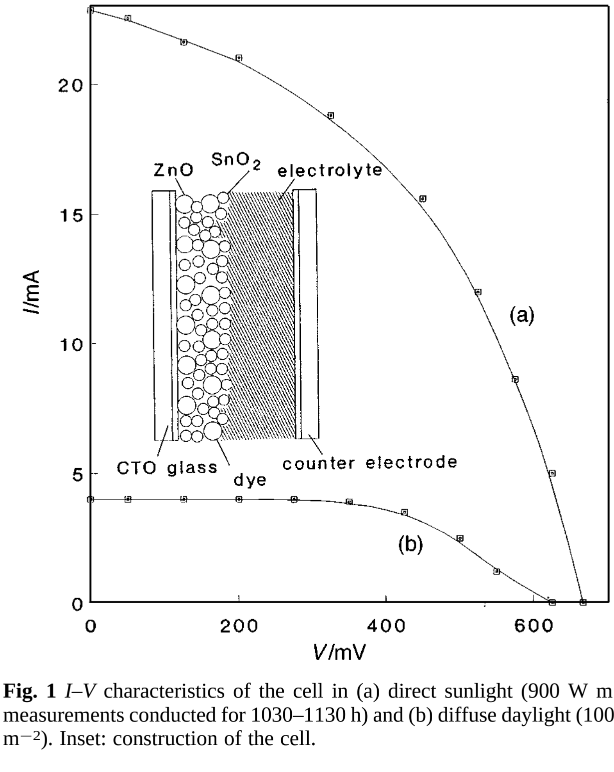

Fig. 1 *I–V* characteristics of the cell in (a) direct sunlight (900 W m^{-2}, measurements conducted for 1030–1130 h) and (b) diffuse daylight (100 W m^{-2}). Inset: construction of the cell.

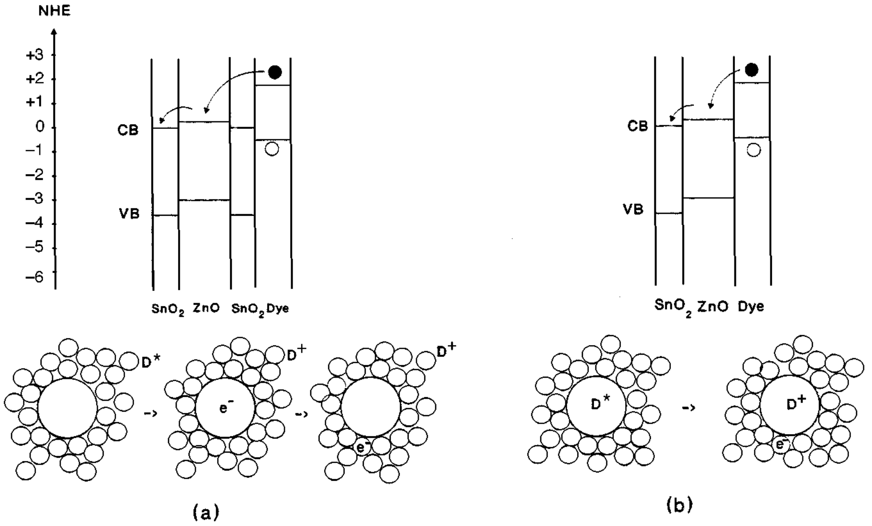

Fig. 2 An energy level diagram (NHE = normal hydrogen electrode) and a schematic diagram illustrating the transfer of an electron by an excited dye molecule (a) adsorbed at the surface of a SnO_2 particle to the CB of a ZnO particle in the vicinity and to the CB of another SnO_2 particle and (b) adsorbed at the surface of a ZnO particle to the CB of the ZnO particle and then to the CB of a SnO_2 particle.

the above electron injection process. The transfer of the electron into the CB of ZnO which is at a higher level in comparison to the CB of SnO_2 generates a V_{oc} greater than that of a cell comprising of 100% SnO_2. Subsequently the electron excited to the CB of ZnO is transferred to the CB of a SnO_2 particle in contact with the ZnO particle. As a result photogenerated negative and positive charges (D^+ and e^-) are widely separated by a ZnO barrier and the recombination is suppressed. An energy level diagram and a schematic diagram illustrating interparticle charge transfer are presented in the Fig. 2(a). The electrons separated from the dye cations are taken to CTO back contact *via* interconnection of SnO_2 particles. In DS PECs of the Gratzel type, the recombination of the photogenerated electron with the dye cation is one of the principal factors that limits the photocurrent quantum efficiency[7–10] and to some extent the V_{oc}. In the present system recombinations of this nature are largely suppressed due to rapid movement of the electron to a distance comparable to the size of the ZnO particle. This is supported by the observation that if ZnO particles of size comparable to that of SnO_2 particles are used the enhancement of I_{sc} and V_{oc} is not significant. As explained earlier, the contribution to the photocurrent from sensitization of ZnO is less effective compared to that from SnO_2. However, even this process suppresses recombinations, because the electron injected to the CB of ZnO from the excited dye molecule is immediately transferred to a SnO_2 particle in contact with ZnO [Fig. 2(b)]. Although the I_{sc} and V_{oc} of the cell are quite high, the efficiency at higher intensities are low because of the lower fill factor at higher intensities (*i.e.* 0.6 at 100 W m^{-2} and 0.5 at 900 W m^{-2}). This is the general behavior of DS PECs based on nanoporous semiconductor films. A possible cause is recombination (D^+ and e^-) across voids (where CTO surface is exposed to the electrolyte) in the film. When the surface density of voids is high, the fill factor is found to decrease. The cell remained stable during the few days of operation. Apart from fluctuations, I_{sc} and V_{oc} did not show any signs of decay.

Notes and references

1 A. J. McEvoy and M. Gratzel, *Sol. Energy Mater. Sol. Cells*, 1994, **32**, 221.
2 B. O. Regan and M. Gratzel, *Nature*, 1991, **353**, 737.
3 A. Mills and S. L. Hunte, *J. Photochem. Photobiol.*, 1997, **108**, 1.
4 G. Smestad, C. Bignozi and R. Argazzi, *Sol. Energy Mater. Sol. Cells*, 1994, **32**, 259.
5 M. K. Nazeerudin, A. Kay, I. Rodicio, R. Humphry Baker, E. Miller, P. Liska, N. Vlachopoulus and M. Gratzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
6 A. Hagfeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 45.
7 H. Lu, J. N. Prieskorn and J. T. Hupp, *J. Am. Chem. Soc.*, 1993, **115**, 4927.
8 B. O. Regan, B. Moser, M. Anderson and M. Gratzel, *J. Phys. Chem.*, 1990, **94**, 8720.
9 G. Hodes, I. D. J. Howell and L. McPeter, *J. Electrochem. Soc.*, 1992, **139**, 3136.
10 P. V. Kamat and B. Patrick, in *Electrochemistry in Colloids and Dispersions*, ed. R. A. Mackay and J. Teseter, VCH Publishers, New York, 1992.

Communication 8/06801A