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The Effect of MgO on the Enhancement of the Efficiency in Solid-State Dye Sensitized Photocells Fabricated with SnO_2 and CuI

Susira Perera, Rohan Senadeera,* Kirthi Tennakone, Seigo Ito,† Takayuki Kitamura,†† Yuji Wada,†† and Shozo Yanagida*,††

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

†Venture Business Laboratory, Osaka University, Suita, Osaka 565-0871

††Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

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Solid-state dye-sensitized photo cells were fabricated with nanocrystalline SnO_2 covered with a thin layer of MgO as the anode and the hole conductor CuI as the cathode. While the cell fabricated with SnO_2/Ruthenium bipyridyl dye/CuI delivered almost no photocurrent with very low photovoltage, the cell SnO_2 (MgO)/Ruthenium bipyridyl dye/CuI delivered a short circuit photocurrent of $\sim$2.5 mA cm^{-2} with an open circuit voltage of $\sim$500 mV. Enhancement in the photocurrent and the voltages was found when the percentage of MgO to SnO_2 was around 4 wt%. This is due to the formation of a thin energy barrier, which suppresses the recombination of photoelectrons.

During the last decade, a great deal of attention has been focused on the development of the dye-sensitized photoelectrochemical solar cells based on nanoporous oxide semiconductors. A major breakthrough occurred when the impressive solar to electrical energy conversion of a photoelectrochemical cell (PEC) was reported by Grätzel and coworkers.[1–5] Besides PECs, fully solid-state dye-sensitized solar cells have also been fabricated by replacing liquid electrolyte with suitable hole conductors.[6–12] In these solid cells, electrons are injected from the excited dye molecules into the conduction band of the n-type semiconductor followed by holes transfer to the p-type semiconductor. The injected electrons must cross the n-type semiconductor matrix and reach the conducting substrate where the semiconductor is deposited. However, at the semiconductor interface (as in conventional p/n junctions) these injected electrons could migrate across the dye layer and undergo recombination with the holes.[13,14] For the cell to work efficiently, p-type material and the conducting substrate where the n-type semiconductor is deposited must not contact each other. Any contact between these two surfaces would short-circuit the cell, which reduces the overall performances. In this context, it has been observed that a barrier on the surface of the n-type semiconductor can improve the performances of the dye-sensitized solar cells.[15–17]

In the process of these investigations, here we report a method of construction of a solid state dye sensitized solar cell with SnO_2 film covered by a dye-adsorbed thin layer of MgO sandwiched with p-CuI as the hole collector.

Experimental

Nanoporous films of SnO_2 coated with MgO were deposited on fluorine doped conducting tin oxide (CTO) glass (1.0 $\times$ 1.5 cm^2, sheet resistance $\sim$10 Ω square^{-1}) by the following method. Appropriate amounts of MgO (Fluka) were added to tin(IV) oxide powder (0.25 g, average particle size $\sim$100 nm, Aldrich) and $SnCl_2$ (0.75 g, Aldrich). The mixtures were ground thoroughly in an agate mortar, adding 1 mL of deionized water and few drops of non-ionic surfactant Triton X-100. The mixture was diluted to 15 mL with propan-2-ol and sonicated for 10 minutes. The addition of $SnCl_2$ to the mixture improves the adherence of oxide particles to the CTO surface. The solution was then diluted with ethanol and sprayed onto the CTO glass plates, placed on a hot plate (120 °C). The plates were then sintered at 500 °C for 30 minutes. The particle size of the above compositions was estimated by X-ray diffractometry (XRD) (Rigaku) and gradient centrifuging particle size analysis (Horiba, CAPA 7000). The average size of the SnO_2 particles was 70–100 nm; this was also confirmed by scanning electron micrographic (SEM) measurements (JEOL, JEM-2010). Since MgO crystallites on SnO_2 are ultra fine, it was difficult to give an accurate estimate of their size from either XRD or SEM techniques. Oxide films (SnO_2 and SnO_2(MgO)) were then washed with ethanol and dried in a stream of hot N_2. The cleaned plates were immersed in ethanolic solutions of the dye "N3", which is: $RuL_2(SCN)_2$ where L = 4,4′-dicarboxy-2,2′-bipyridine (2×10^{-4}M) for 24 hours for dye adsorption. The dyed plates were then rinsed with ethanol and dried. CuI deposition on the dyed plates was carried out as follows. A solution of CuI was prepared by dissolving 0.6 g of CuI in 50 mL of moisture free acetonitrile. The dye-coated plates were placed on a hot surface (80–100 °C) and the CuI solution was lightly spread over the dyed film using a dropper allowing acetonitrile to evaporate. This process was repeated until all the pores are filled and the thickness of CuI extended up to $\sim$6 μm (Film thickness was measured by SEM). The electrical contact to the CuI was made by pressing a gold-coated CTO glass plate onto the CuI surface. A schematic diagram illustrating the construction of SnO_2(MgO)/Dye/CuI cell is shown in Fig. 1.

The photocurrent action spectrum of the cell was recorded with

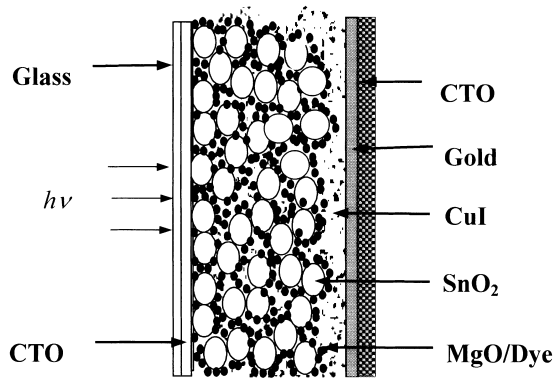

Fig. 1. Schematic diagram of the construction of the cell n-SnO_2(MgO)/Dye/CuI.

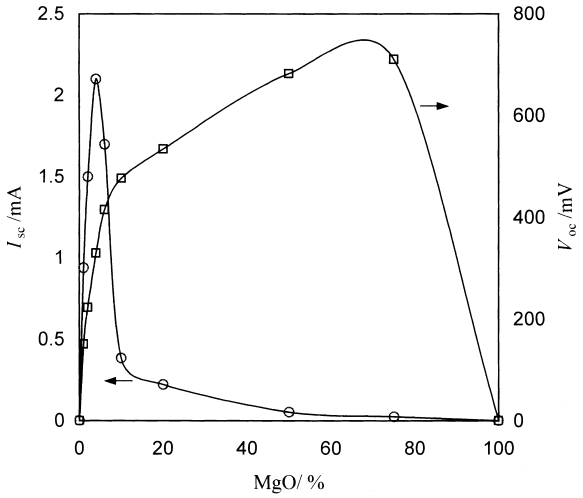

Fig. 2. Composition dependence of short circuit current (I_{sc}) and the open circuit voltage (V_{oc}).

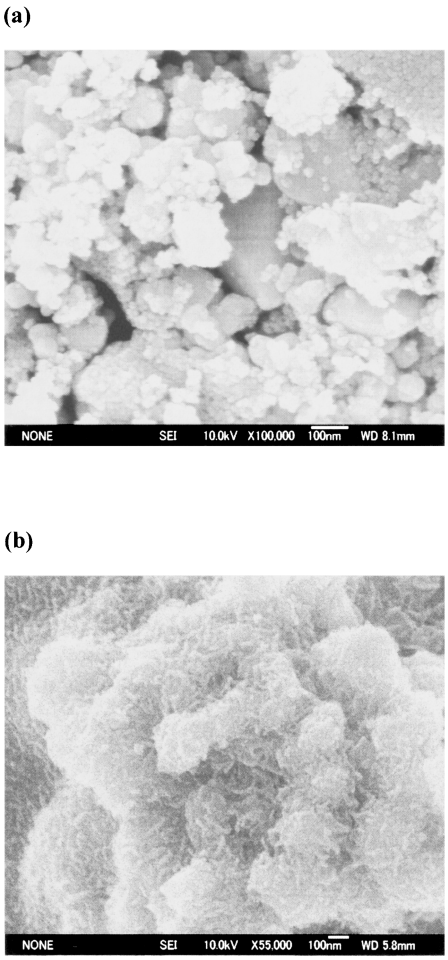

Fig. 3. SEM images of (a) SnO_2 Film (b) SnO_2/MgO composite film (MgO 4%).

a Nikon monochromator auto-scanner ASC-1101 coupled to a light chopper and a lock-in-amplifier (Stanford). I–V characteristics of the cell were examined with a standard solar irradiation of 100 mW cm^{-2} (Xe-lamp with an Orial AM 1.5 filter) as the light source. An Eko pyranometer was used to measure light intensities and a Keithley 2420 source meter coupled to a computer was used for data acquisition. The optical absorption measurements were carried out with a Shimadzu dual wavelength/double beam spectrophotometer (Model UV-3000).

Results and Discussion

Figure 2 shows the variation of the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}) of the SnO_2(MgO)/dye/CuI cell as a function of the percentage of MgO. As can be seen from the figure, I_{sc} rapidly increases with the concentration of MgO, reaches a maximum when the MgO percentage is 4%, and then decreases exponentially with the MgO percentage. The V_{oc} of the above system reaches a peak value at ~70% of MgO, and decreases rapidly when the percentage of MgO is further increased. However, the maximum value of efficiency of the above cells corresponds to the position of the maximum I_{sc}. The atomic absorption spectroscopy measurements revealed that the amount of Mg present in the film is almost the same as the amount used in the preparation. The surface area of SnO_2(MgO) (4 wt%) and SnO_2 determined by desorption of adsorbed dye is found to be ~750 and 800 times larger than the geometrical surface area. XRD measurements showed no separate MgO peaks or other phases, excluding the possibility of Mg^{2+} substitution at the lattice positions of Sn^{4+}; otherwise the XRD peaks for SnO_2 would be shifted to some extent. We have observed similar results in some of our reported investigations where the SnO_2 is covered with Al_2O_3 and also with the liquid cells with MgO covering.[13–17] Therefore, by considering all these observations, we concluded that Mg^{2+} ions were adsorbed on to the SnO_2 and turned to the oxide form during the sintering.

Figures 3a and b show the SEM images of pure SnO_2 films (without MgO) and films with MgO respectively. It should be mentioned that films of pure SnO_2 were prepared by following the procedure explained in the experimental section without adding MgO. As can be seen in the Fig. 3b, the haziness of the SnO_2 crystallites could be an indication for the existence of the MgO coating around the SnO_2 crystallites.

Figure 4a illustrates the current voltage characteristics of the cell SnO_2(MgO)/dye/CuI under the illumination of 100 mW cm^{-2} (1.5 Air Mass). The cell delivered ~2.5 mA cm^{-2} photo current with ~500 mV photovoltage at an efficiency of

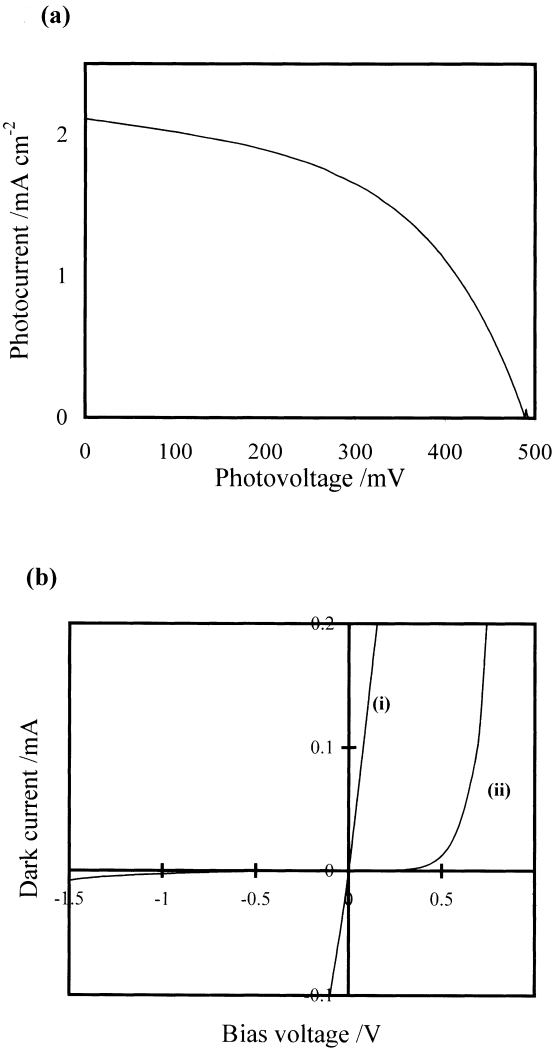

Fig. 4. (a) I–V characteristics of the cell SnO_2(MgO)/Dye/CuI under the illumination of 1000 W m^{-2} at 1.5 Air Mass (cell area 1.0 cm^2). (b) Dark I–V characteristics for the cells (i) SnO_2/Dye/CuI and (ii) SnO_2(MgO)/Dye/CuI.

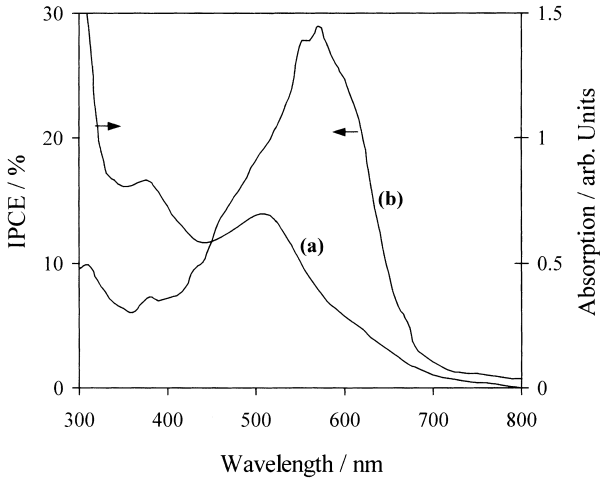

Fig. 5. (a) Optical absorption spectrum of Ruthenium dye and (b) Photocurrent action spectra (incident photon conversion efficiency, IPCE) of the cell SnO_2(MgO)/Dye/CuI.

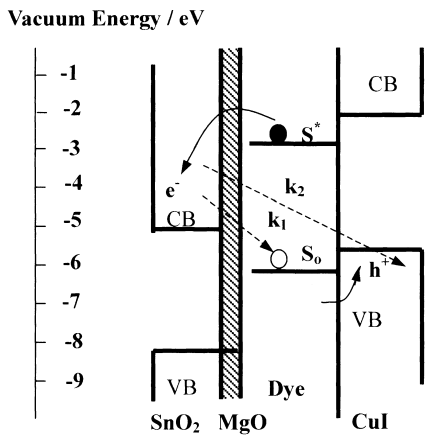

Fig. 6. Energy band diagram of the semiconductors and the energy levels of the ground and the excited levels of the dye.

0.5% (fill factor = 0.39). The cell with no MgO, i.e., SnO_2/dye/CuI delivers almost no current with photovoltage in micro region. Direct contacts of the CuI with CTO glass and fast recombination might be some reasons for this lower value. The dark current rectification characteristics under forward and reverse bias of the above cell with respect to the gold electrode are shown in Fig. 4b. No or very poor rectification was observed when the cell is prepared without MgO and drastic improvement in rectification was observed when MgO was coated on SnO_2.

The absorption changes of the SnO_2(MgO)/Ru dye films in the range of 300 to 800 nm are shown in Fig. 5a. An intense absorption band was observed peaking at ~530 nm. In order to identify the surface to which the dye is attached, another dye, Hemotoxylene (H), was used to obtain the absorptions of the films of SnO_2, MgO and composites of SnO_2(MgO)[16] (not shown). In this context, different spectral responses were observed for the films of SnO_2 and MgO. However, the SnO_2 films including MgO showed the same spectral responses as in the case of MgO, further confirming that the SnO_2 crystallites in SnO_2(MgO) composites include the outer shell of MgO. The calculated incident photon to current efficiencies (IPCE) of the cell SnO_2(MgO)/Dye/CuI are shown in Fig. 5b. The peak in the action spectrum is slightly red-shifted with respect to that in the absorption spectrum shown in the figure. Although the exact reason for this shifting is not clear, we believe that this shifting might be attributed to the acidicity of the interface between MgO(dye) and CuI or to the overall pH conditions of the interfaces. Besides this small shifting, the close correspondence between the absorption and the action spectra suggests that the photosensitization mechanism is directly associated with the photo excitements of the dye molecules.

In order to understand the charge transfer mechanism, relative levels of energies of these materials are considered as shown in Fig. 6. Upon the illumination, the energetic hot electrons expeled from the excited dye molecules tunnel through the thin layer of MgO to the conduction band (CB) of the SnO_2. The presence of this thin layer might reduce the recombination processes of these electrons with the dye cations (k1

process in Fig. 6) as well as the hole transport material CuI (k2 process in Fig. 6). Further, this thin layer also avoids penetration of CuI crystallites to make direct contacts with the conducting glass where the films were deposited. Therefore, due to these effects the overall performances of the cell are enhanced.

Conclusion

The results presented in this work clearly demonstrate that the performances of solid-state photocells consisting of SnO_2 and CuI could be enhanced by covering the SnO_2 crystallites with a thin layer of MgO. The improved cell performances achieved by this method may be attributed to the formation of an energy barrier at the n-type semiconductor and the p-type semiconductors which apparently increases the overall cell performances by decreasing the rates of recombination processes between either the injected electrons and the dye cations or the holes in the p-type material or both processes. Even though this cell is not a suitable choice for a practical device due to its low conversion efficiency, preliminary study revealed that the overall performances could be enhanced by introducing some additives such as imidazolium thiocyanates[18] and derivatives of arylamines. Further investigations are underway to study the effect of additives on the properties of the above cell.

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