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Dye-sensitized solid-state solar cells made from magnesiumoxide-coated nanocrystalline titanium dioxide films: enhancement of the efficiency

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Abstract

Dye-sensitized solid-state solar cells have low energy and quantum-conversion efficiencies because of the high recombination rate at the n-type semiconductor/dye/p-type semiconductor interfaces. It is found that the efficiency of dye-sensitized solid-state solar cells with nanocrystalline TiO_2 as the n-type material and CuI as the p-type material can be greatly enhanced by the deposition of an ultrathin layer of MgO on the TiO_2 crystallites. Mechanism involved is explained.

Keywords: Dye-sensitization; Photoelectrochemical solar cell; Solid-state cell; Recombination; Nanocrystalline titanium dioxide film

1. Introduction

After nearly a decade of extensive work on dye-sensitized photoelectrochemical solar cells [1–4] (DPSCs) based on nanostructured semiconductor films, the dye-sensitized solid-state solar cells [5–9] (DSSCs) have begun to receive considerable attention as the most promising system for conversion of solar energy. The avoidance of the technical problem of confining a liquid and the absence of ionic discharge that could lead to chemical irreversibility are the merits of DSSCs. Unfortunately the DSSCs reported so far have energy conversion efficiencies well below the optimized DPSCs [5–9]. The reasons seem to be the higher rate of recombinations in a DSSCs and the difficulty of filling the pores of the dye-coated nanocrystalline n-type film with a suitable p-type material (hole collector) to form secure contacts. The choice of the hole collecting material is highly restrictive and needs to satisfy several criteria. Of the hole collectors tested, p-CuI gives the highest efficiency and the problem of filling the pores of the n-type film with CuI has also been resolved by incorporation of a crystal growth inhibitor into the coating solution [10]. Our earlier experiments indicated that the deposition of ultra-thin outer shells of insulators (or high band gap semiconductors) is a successful strategy of suppressing recombinations in DPSCs [11] as well as DSSCs [12]. Here, we report that the efficiency of the CuI-based DSSCs can be increased up to ∼4.7% by coating an ultra thin shell of MgO on the TiO_2 particles. This is the highest recorded efficiency of DSSCs.

2. Experimental

Nanocrystalline films of TiO_2 adoptable for the fabrication of DSSCs (i.e., largely free of interconnected pores going up to the back contact) were prepared by the procedure described below. Titanium tetra-isopropoxide (5 ml) mixed with propan-2-ol (15 ml) and acetic acid (5.5 ml) was hydrolyzed by drop wise addition of water to a total volume 30 ml and agitated ultrasonically after mixing with 0.65 g of P25 Degussa TiO_2 powder. A few drops of the suspension were lightly spread onto transparent conducting glass sheets (fluorine-doped SnO_2 glass with a sheet resistance of 10 Ω/□) heated at 150 °C and sintered at 450 °C for 10 min in air. After allowing the plate to cool, the loose crust on the surface was wiped off and then this process was repeated until a film of ∼10–13 μm was formed. Particles in the film were coated with an ultra-thin shell of MgO

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as described below. The plate (deposited with the TiO_2 film) was boiled in a 2×10^{-3} M solution of magnesium acetate in 85% ethanol for 1 min, washed with ethanol to remove magnesium acetate inside the pores and sintered again at 450 °C. Hydrolysis of magnesium acetate covers the TiO_2 particle surface with a layer of MgO (or hydrous MgO). Sintering removed moisture, resulting a firmly adhered outer shell of MgO on the TiO_2 particles. The MgO shell on TiO_2 particles was not readily observed by SEM or TEM. However, EDX shows presence of MgO and the MgO content of the film was estimated by the extraction of MgO with HCl and atomic adsorption spectrophotometric estimation. The thickness t of the MgO shell was calculated as $t = (\text{weight of MgO})/S\rho$, where S = surface area of TiO_2 film (S determined by the desorption of the dye into an alcoholic alkaline solution and spectrophotometric estimation = 560 times geometrical cross-section of the film = 1 cm^2) and ρ = density of MgO. Prolongation of the duration of boiling or increase in concentration of magnesium acetate enabled variation of the thickness of the MgO shell. The film was dyed by keeping it immersed in a 3×10^{-4} M ethanolic solution of *cis*-dithiocyanato [*N*-bis(2,2′-bipyridyl-4,4′–dicarboxylic acid]Ru(II) at 40 °C for 8 h. CuI solution was prepared by dissolving 0.6 g of CuI and 8 mg of triethylamine hydrothiocyanate in 20 ml of moisture free acetonitrile (triethylamine hydrothiocyanate and related molten salt thiocyanates inhibit CuI crystal growth [10,13]. Solution was spread on the dye-coated TiO_2 surface (heated to ∼110 °C) allowing acetonitrile to evaporate, until CuI gets deposited to a level slightly above the TiO_2 surface. The thickness of the CuI film was ∼5 μm above the TiO_2 surface. Gold sputtered conducting tin oxide glass plate pressed onto the CuI surface was served as the back contact. *I–V* characteristics at AM 1.5 1000 W m^{-2} and incident photons-to-current conversion efficiencies (IPCE) at constant intensity (50 μW cm^{-2}) were determined using a solar cell evaluation system (Bunko Keiki CEP-25BX).

3. Results and discussion

In the absence of a MgO shell on the TiO_2 particles, the cell (i.e., a cell prepared in same manner as described above but omitting the procedure for deposition of MgO) delivered a short-circuit photocurrent $I_{sc} = 13.2\,\text{mA cm}^{-2}$, open-circuit voltage $V_{oc} = 520$ mV at an efficiency $\eta = 3.2\%$ and a fill factor FF = 0.46. On increasing the MgO shell thickness, V_{oc} and η gradually increased with slow decrease in I_{sc} and η reached an optimum when the MgO shell thickness is ∼0.5 nm (Fig. 1). An increase of the thickness of the shell beyond the optimum gave rapid decreased of I_{sc} and η, while V_{oc} continues to increase up to a maximum of ∼750 mV and again decreased on further increase of the shell thickness. Fig. 2 shows the *I–V* characteristics of the cell at the optimum thickness corresponding to the cell parameters being $\eta = 4.7\%$, $I_{sc} = 13.0\,\text{mA cm}^{-2}$, $V_{oc} = 620$ mV and FF = 0.58. The inset of the same figure shows the photocurrent action spectrum indicating an IPCE of 60% (not corrected for the reflection losses) at the peak of the spectrum (535 nm). IPCE remained nearly at the same value (∼60%) in the absence of the MgO shell (IPCE measured at low intensities (50 μW cm^{-2}) does not, in general, commensurate with the I_{sc} measured at high intensities. IPCE is not influenced by cell resistance as I_{sc}. Therefore, the decrease in IPCE with shell thickness becomes less significant compared to I_{sc}). It is clear that the MgO shell has a profound effect on η, V_{oc} and FF of the cell. The MgO shell suppresses recombinations enabling raising of the quasi-Fermi level which determines the V_{oc} of the cell.

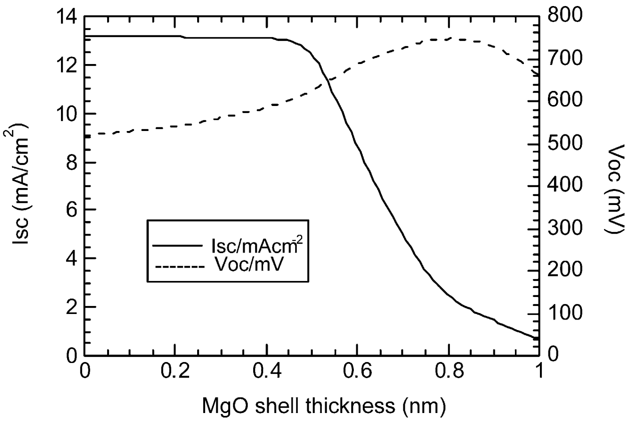

Fig. 1. Variation of the short-circuit photocurrent (I_{sc}) and the open-circuit voltage (V_{oc}) with MgO shell thickness.

Fig. 3 represents schematically, the conduction and valence band (CB and VB) positions of TiO_2, CuI and energy levels of the dye [6]. A photoexcited dye molecules anchored to the MgO surface injects an electrons to TiO_2 via tunneling across the MgO barrier, concomitantly injecting a hole to CuI. Because of the location of band positions as illustrated in Fig. 3, the transfer of electrons in the CB of TiO_2 to CB of (CuI) or holes in the VB of CuI to VB of TiO_2 are energetically forbidden. However, the recombinations could

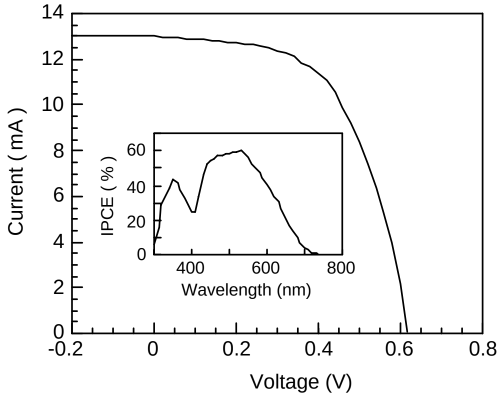

Fig. 2. *I–V* characteristics of the dye-sensitized solid-state solar cell made from MgO-coated TiO_2. Inset: photocurrent action spectrum of the cell (the peak at ∼350 nm originate from carrier injection via band gap excitation of TiO_2, Illumination cell area; 0.25 cm^2).

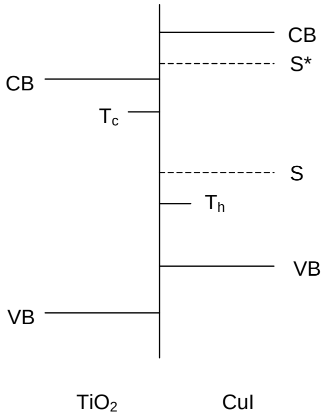

Fig. 3. Schematic energy level diagram showing the positions of TiO_2 and CuI, ground and excited levels of the dye (S, S^*), electron and hole trap levels at the interface (T_e, T_h).

occur via the following two processes. (1) Electrons in the CB of TiO_2 could enter the VB of CuI or the holes in the VB of CuI could enter the CB of TiO_2. (2) Electrons in TiO_2 or holes in CuI could enter into traps located at the interfaces of the respective materials (i.e., T_e and T_h) which mediate the recombinations (Fig. 3). The barrier of MgO on TiO_2 particles reduces the probability of these recombinations. A factor limiting the V_{oc} of dye-sensitized solid-state cells is the short-circuiting across the voids in the TiO_2, which admits direct contact between the hole collector and the conducting surface of glass. In an earlier work [6], open-circuit voltages (largely insensitive to light intensity) of the order 600 mV were obtained in the absence of a MgO barrier. Here, CuI was deposited without incorporating a crystal growth inhibitor. Large CuI crystals formed reduces the density of points where short-circuiting contacts are formed favoring an increase of the V_{oc}. Better penetration of CuI into the TiO_2 porous matrix in presence of the crystal growth inhibitor also fills more finer short-circuiting paths reducing the V_{oc}. This short-circuiting would predominantly affect the V_{oc} rather than the I_{sc}. A more severe drawback of the earlier version dye-sensitized solid-state solar cell based on CuI [6] is the rapid decay of the I_{sc} and the V_{oc} is attributed to formation of large CuI crystals [10]. Incorporation of the crystal growth inhibitor greatly improved the stability [10] of the cell and when a MgO shell was present, the efficiency is also increased. Furthermore, the reproducibility of the earlier method was poor and the experiment had to conducted in a glove box as moisture interferes with the CuI coating process. On incorporation of the crystal growth inhibitor CuI coating can be conducted in open air.

4. Conclusion

We have demonstrated that a significant increase in the efficiency of dye-sensitized solid-state can be achieved by deposition of an ultra-thin shell of MgO on the TiO_2 nanocrystallites before the deposition of the dye. Shell thickness becomes crucial because too thick film of MgO would slow down the electron injection rate. A problem encountered was the difficulty of depositing ultra-thin MgO on TiO_2 nanocrystallites to cover the entire crystal surface area. EDX measurements revealed that about 15–20% of the remain bare or very lightly covered with MgO. We believe that the development of better techniques for the deposition of MgO enable further improvements of dye-sensitized solid-state solar cells. Improvement of the TiO_2 film morphology to minimize formation of short-circuiting paths would remedy the problem of open-circuit voltage. We have tested deposition of outer shells of other materials (e.g., Al_2O_3), although an improvement is noticeable the highest efficiency was obtained with MgO.

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