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TiO_2 compact layer for dye-sensitized SnO_2 nanocrystalline thin film

Hui Yang [a], Pan Li [a], Jingbo Zhang [a,*], Yuan Lin [b]

[a] Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, China
[b] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

A TiO_2 compact layer was coated on fluorine-doped tin oxide (FTO) glass substrate prior to deposition of SnO_2 nanocrystalline thin film to suppress backflow of electrons from FTO to the SnO_2 nanocrystalline thin film. The resultant thin film was used as a photoelectrode to fabricate dye-sensitized solar cell. For comparison, a SnO_2 compact layer was also prepared to discuss the effect of the TiO_2 compact layer on the electron backflow process. Compared with the dye-sensitized SnO_2 nanocrystalline thin film solar cell without the compact layer, light-to-electric conversion efficiency for the solar cell with the TiO_2 compact layer was improved by 82.1% and it was even improved by 41.7% compared with the cell with the SnO_2 compact layer. Electrochemical impedance spectroscopy and open-circuit voltage decay of dye-sensitized solar cells were measured to demonstrate the improvement mechanism due to the TiO_2 compact layer. Both recombination resistance at the photoelectrode/electrolyte interface and lifetime of electrons on the SnO_2 nanocrystalline thin film were increased due to introduction of the TiO_2 compact layer. Because the conduction band of TiO_2 is higher than that of SnO_2, the TiO_2 compact layer acts as not only a physical barrier to separate FTO substrate from electrolyte, thus suppressing recombination of electrons on FTO with the electrolyte, but also a potential barrier to effectively block the backflow of electrons from FTO substrate to the SnO_2 thin film.

1. Introduction

Dye-sensitized solar cell (DSSC) inaugurated a new era in solar cells and has been considered as a potential alternative to the conventional silicon solar cell due to its low production cost, simple fabrication process and high energy conversion efficiency [1–3]. Typically, the conventional liquid-state DSSC consists of a working electrode usually made up of a porous semiconductor nanocrystalline thin film sensitized with organic dye molecules on fluorine doped tin oxide (FTO) substrate, a counter electrode (CE) and liquid electrolyte containing a redox couple. The interfaces in DSSC include FTO/nanocrystalline thin film, working electrode/electrolyte, electrolyte/CE and so on, which play a significant role in improving the energy conversion efficiency of DSSCs [4]. Recently, intensive efforts have been made to modify each interface to improve the photoelectrochemical performance of DSSCs. And the charge recombination at the FTO/electrolyte interface cannot be also neglected to some extent. Because FTO substrate cannot be covered by the porous nanocrystalline thin film completely, which leads to direct contact of FTO substrate with the electrolyte, resulting in a recombination process of electrons transferred to FTO with the electrolyte, it is essential to introduce an efficient compact layer as a physical barrier to reduce this charge recombination [5]. The compact layers of ZnO [6], Nb_2O_5 [7], HfO_2 [8], $SrCO_3$ [9], Cr_2O_3 [10] and TiO_2 [11–13], have been studied to improve the conversion efficiency of DSSCs, among which the TiO_2 compact layer has drawn much attention in recent years. However, much research has been devoted to the discussion about the compact layer playing a role to suppress recombination of electrons from FTO substrate to the electrolyte [14–16].

SnO_2 nanocrystals are known to have higher electron mobility than TiO_2 nanocrystals [17]. It is an interesting candidate of photoanode material owing to its higher recombination resistance, faster charge transport and more efficient charge separation. Especially, it has lower conduction band than TiO_2 and ZnO, which makes it more suitable for some inorganic sensitizers with lower conduction band such as PbS and PbSe quantum dots. Since the conduction band of FTO is almost same as that of the SnO_2 nanocrystals, it will be necessary to introduce a compact layer to hinder the backflow of electrons from FTO substrate to the SnO_2

* Corresponding author. Tel.: +86 10 8261 5031; fax: +86 10 8261 7315.
E-mail address: hxxyzjb@mail.tjnu.edu.cn (J. Zhang).

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nanocrystalline thin film. Because the conduction band of TiO_2 is higher than that of SnO_2, the TiO_2 compact layer may be used as a potential barrier layer to block the backflow of electrons from FTO to SnO_2 nanocrystals.

In this study, the TiO_2 compact layer prepared by the hydrolysis of $TiCl_4$ solution with a facile spin-coating method was applied in dye-sensitized SnO_2 nanocrystalline thin film. The thickness of the TiO_2 compact layer was first optimized by changing the concentration of $TiCl_4$ solution. The highest energy conversion efficiency was obtained for DSSC with the TiO_2 compact layer. It is higher than that of the cell without the compact layer, and even higher than that of the cell with the SnO_2 compact layer. The enhancement mechanism due to the TiO_2 compact layer was analyzed by measuring electrochemical impedance spectroscopy (EIS) and open-circuit voltage decay (OCVD) of DSSCs. The TiO_2 compact layer plays a double role at the same time as mentioned above in enhancing energy conversion efficiency of DSSCs based on the SnO_2 nanocrystalline thin film.

2. Experiment

2.1. Materials

Titanium chloride (99%), stannous chloride (99%), 3-methoxypropionitrile (99%), iodine (99.8%), potassium iodide (99%) and two kinds of SnO_2 nanoparticle powders with the mean size of about 50 nm and 13-19 nm were purchased from Alfa Aesar Inc. China. Fluorine-doped tin oxide conducting glass (FTO, 10 $\Omega \cdot sq^{-1}$, Nippon Sheet Glass Co., Ltd. Japan) was ultrasonically cleaned sequentially in deionized water, acetone and isopropanol and finally soaked in isopropanol. The well-cleaned FTO was used as a substrate for deposition of the nanocrystalline SnO_2 thin film.

2.2. Preparation of TiO_2 compact layer by hydrolysis of $TiCl_4$ solution

The TiO_2 compact layer was prepared according to the method reported previously [18]. In short, $TiCl_4$ was added dropwise into the mixture of deionized water and ice. $TiCl_4$ solutions of 0.05 M, 0.2 M and 0.5 M were prepared for formation of different thickness TiO_2 compact layer by the hydrolysis of $TiCl_4$ solution. The resultant solution was then used to coat a TiO_2 compact layer on the FTO surface by spin-coating under two speed steps of 400 r·min^{-1} for 6 s and 3000 r·min^{-1} for 30 s. The coating layer was dried in air, and then sintered at 450 °C for 60 min to form the TiO_2 compact blocking layer. The compact SnO_2 layer was also prepared to demonstrate the double roles of the TiO_2 compact layer. $SnCl_2$ was added into 20 ml n-butanol to prepare 0.2 M $SnCl_2$ solution. The preparation process of the SnO_2 compact layer is same as that of the TiO_2 compact layer.

2.3. Preparation of SnO_2 nanocrystalline thin film electrodes

The SnO_2 paste was prepared by adding 0.25 g of SnO_2 nanoparticle powders with mean size of 13-19 nm and 0.75 g of SnO_2 nanoparticle powders with mean size of 50 nm into a mixture solvent of triton x-100 and n-butanol, followed by vigorously milling for 2 h at room temperature to form SnO_2 slurry. The SnO_2 nanocrystalline thin film was prepared by coating with the SnO_2 slurry on FTO with and without the compact layer through the doctor-blade method. After drying, the thin films were sintered in air at 450 °C for 30 min. The resulting nanoporous SnO_2 electrodes were semi-transparent. Surface morphologies of the nanocrystalline thin film were observed with a scanning electron microscopy (SEM, FEI Nova Nano SEM 230, 15 kV). Then the electrodes were immersed into 0.2 M $TiCl_4$ aqueous solution at 70 °C for 30 min followed by washing them with deionized water and sintering at 450 °C for 30 min. The porous SnO_2 thin films with and without the compact layer were immersed into a 5×10^{-4} M anhydrous ethanol solution of Ru(dcbpy)$_2$(NCS)$_2$ (dcbpy: 2,2-bipyridine 4,4-dicarboxylic acid) (N3, Solaronix) for 12 h to sensitize SnO_2 nanocrystalline thin films with the dye. The dye-anchored thin films were washed with anhydrous ethanol, and then dried in air before measurements.

2.4. Assembly and characterization of DSSCs

DSSC with a sandwich cell configuration was assembled using a N3 dye-sensitized photoanode, a Pt counter electrode and I^-/I_3^- electrolyte. A 3-methoxypropionitrile solution containing 0.5 M KI and 0.05 M I_2 was used as the redox electrolyte. The photocurrent-voltage (*J-V*) curve and OCVD of the assembled dye-sensitized solar cells were measured with a computerized voltammetry system (Hokuto Denko HSV-100) under light intensity of 100 mW·cm^{-2} at AM 1.5 supplied by a solar simulator. The active area was 0.20 cm^2. EIS was measured in the darkness at a bias voltage of -0.23 V with a frequency response tracer (Solartron 1255B) and a potentiostat (Solartron SI 1287). The frequency range of EIS is 10^5 to 10^{-1} Hz [19].

3. Results and discussion

3.1. Morphology and crystalline structure of SnO_2 nanocrystalline thin film

Two kinds of SnO_2 nanoparticle powders with the mean particle size of 13-19 nm and 50 nm were used to prepare the SnO_2 nanocrystalline thin film. Only one kind of nanoparticle powders cannot form the satisfied nanocrystalline thin film. The thin film made by the particles with the size of 13-19 nm shows smaller pores, and the film with only 50 nm particles shows poor mechanical stability. Two kinds of SnO_2 nanoparticles mixed according to an appropriate ratio (here it is 1:3 for particles with the size of 13-19 nm and 50 nm) can form the stable thin film with a desirable porous structure. Fig. 1 showed SEM surface morphology of the SnO_2 nanocrystalline thin film on FTO substrate. SEM image showed the SnO_2 thin film has a crack-free and uniform structure. It is a typical porous structure, and the thickness of the SnO_2 thin film was determined by SEM cross section image to be about 3 μm. Powder XRD pattern of the nanocrystalline SnO_2 thin film (Fig. 1S)

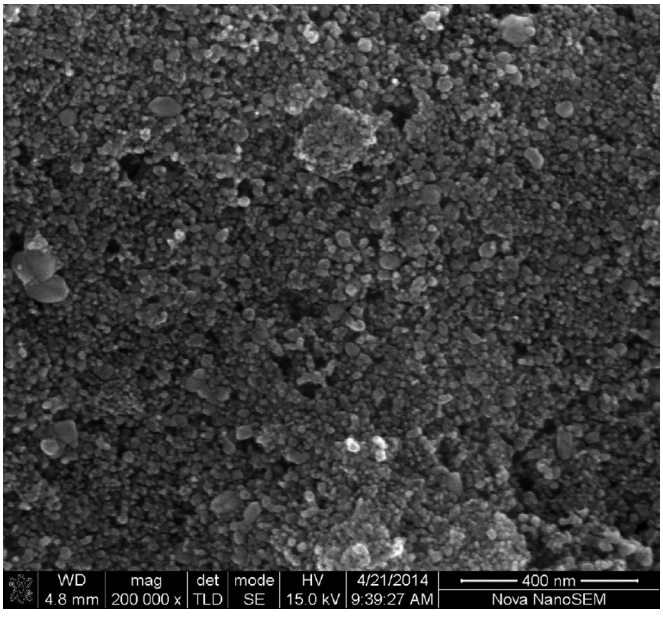

Fig. 1. SEM morphologies of the SnO_2 nanocrystalline thin film.