

ZnO-treated TiO₂ inverse opal electrodes for dye-sensitized solar cells



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ABSTRACT

We report that the photovoltaic properties of inverse opal TiO₂ (io-TiO₂) electrodes in dye-sensitized solar cells can be enhanced by ZnO treatment of the inverse opal structures. ZnO was coated on the surface of io-TiO₂ via the sol–gel reaction of ZnO precursors. Energy dispersive X-ray spectroscopy (EDX) measurements showed that the amount of ZnO on the io-TiO₂ surface was measured to be 0.12–0.50 wt% of zinc, depending on the number of coatings. Compared to bare inverse opal electrodes, the energy conversion efficiency of cells increased for the 0.35 wt% ZnO-coated electrodes, and then decreased for the 0.50 wt% ZnO-coated electrodes. The maximum efficiency of 5.3% was achieved, corresponding to a 23% increase in efficiency compared with bare io-TiO₂ electrodes. The enhanced efficiency was mainly attributed to the improvement of the open-circuit voltage (V_{OC}). EIS and dark current measurements confirmed that this enhancement in V_{OC} was due to the movement of the conduction band edge in a negative direction after ZnO treatment, rather than the formation of a barrier layer for electron recombination.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been developed based on nanocrystalline TiO₂ electrodes, which are sensitized by ruthenium dye and soaked in an iodine/iodide electrolyte solution. They are attractive as next-generation photovoltaic devices, due to their low cost, the simplicity of their fabrication, and, most of all, their potential to allow the construction of transparent devices, which would enable their application in building materials [1]. In DSSCs, TiO₂ electrodes are one of the key components, in that the TiO₂ electrode is involved in the lifetime of the photo-generated electrons, encompassing injection, transport and recombination. Specifically, in DSSCs, the electrons are generated by the dye coated on the TiO₂ electrodes, and are injected into the electrodes. The TiO₂ electrodes also allow the transport of electrons to a collecting electrode (i.e., the FTO substrate), and provide an interface where the electrons are recombined with a redox couple in the electrolyte solution.

Randomly packed TiO₂ nanoparticles have been widely applied; results have suggested that the efficiency of DSSCs can be further enhanced by providing a more efficient electron transport path through the TiO₂ electrodes. In this regards, recent researches have focused on applying microstructured electrodes (i.e., more ordered

structures compared to the randomly packed TiO₂ nanoparticle structure). For example, the use of nanotubes or nanowires produced a much improved electron lifetime [2]; in the case of nanotubes, the lifetimes measured were approximately 10 times longer than those measured for conventional nanocrystalline TiO₂ electrodes, due to the more direct electron pathways [2,3]. An inverted structure of monodisperse colloidal crystals (or inverse opal structure) was applied as an alternative microstructured electrode. These electrodes showed improved electron transport compared with conventional electrodes, due to their fully three-dimensionally connected structure [4,5]. Most significantly, the pore size could be easily controlled over a range of several hundreds of nanometers, via the use of different sizes of colloidal particles in the colloidal crystal template [6]. This facile control over the macroscale pores has been advantageous for the application of solid-state electrolytes such as polymer electrolytes containing mesoscale polymer molecules [5].

In this work, we extended our previous work on the bilayer inverse opal electrodes to examine the improvement of efficiency of DSSCs by introducing ZnO treatment [14]. Metal oxide shell coatings such as Nb₂O₅, Al₂O₃ and ZnO have been applied to nanocrystalline TiO₂ electrodes [7–9]. Since the individual particle size of these electrodes is small enough not to generate the space charge layer, the formation of such an energy barrier layer have been applied to decrease electron recombination losses; this results in the increase of the photocurrent density (J_{SC}), or/and the open-circuit voltage (V_{OC}) [8]. ZnO has been widely applied, since it has

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an energy band gap similar to that of TiO₂ (~3.2–3.3 eV at room temperature), and additionally various morphologies can be formed [10]. However, it should be noted that previous studies have shown different effects of ZnO treatment depending on the coating method and thickness, and electrode structures [9,11,12]. For example, in the case of thin-layer ZnO coating below a few nm thickness, the shift of conduction band edge of TiO₂ was observed rather than the formation of an energy barrier, resulting in the enhancement of V_{OC}. As the thickness of ZnO layer increased, the formation of dye-Zn ion complexes led to increased electron injection resistance, which rather reduces the J_{SC} [13]. Here, we applied a facile multiple coating method to coat ZnO layer on TiO₂ inverse opal with controlled coating quantity, and observed the photovoltaic parameters to evaluate the effect of ZnO treatment. Briefly, the ZnO treatment induced the increase of V_{OC}, and thereby the enhancement of photon-to-electric conversion efficiency by 23%. Based on the electrochemical spectroscopy analysis and dark current measurement, we also showed that the ZnO treatment enhanced V_{OC} by shifting the conduction band edge of TiO₂.

2. Experimental details

2.1. Preparation of io-TiO₂ electrodes

The FTO substrate was pretreated via immersion in an aqueous 0.04 M TiCl₄ solution for 30 min, to deposit a blocking layer on the FTO. The polystyrene particles (which were 900 nm in diameter) were then synthesized in a dispersion polymerization of styrene, and were subsequently cast on the FTO substrate and assembled during the evaporation of water [5]. TiO₂ nanoparticles (average size 15 nm, dispersed in water, Nanoamor Inc.) were infiltrated into the PS particle film via spin coating. The substrate was heat-treated in air at 500 °C for 2 h, leaving behind the inverse opal structure. The sample was immersed in an aqueous 0.3 M TiCl₄ solution, followed by calcination in air at 450 °C for 30 min (as a post-treatment). In this work, the post-treated inverse opal will be referred to as io-TiO₂. The thickness of the io-TiO₂ film was around 10 μm.

2.2. Multiple coating of ZnO

The ZnO precursor solution was prepared using 0.006 M Zn(NO₃)₂ (Alfa Aesar), titrated with NH₄OH (Junsei) to pH 11.0–11.5. A ZnO-treated io-TiO₂ structure was obtained via a sol-gel reaction, where the io-TiO₂ electrode was immersed in the aqueous ZnO precursor solution. The io-TiO₂ structure was soaked in the solution for 15 s and then dipped in water at 90–95 °C for 30 s. We controlled the deposition of ZnO by performing the treatment two, four, or six times. Finally, the substrate was sintered at 350 °C for 2 h, to remove the water and complete the conversion into ZnO.

2.3. Assembly of DSSCs

The io-TiO₂ layer was immersed for 20 h in a dye solution containing 0.5 mM N719 dye (Dyesol) in anhydrous 2-propyl alcohol (99.5%, Sigma–Aldrich). Subsequently, an active area of the TiO₂ electrode was formed by scraping. The surface areas were around 8 mm². The counter electrode was prepared by coating a 0.7 mM H₂PtCl₆ solution in anhydrous ethanol on the FTO substrate. The TiO₂ electrode was assembled with the counter electrode, and the gap size between electrodes was controlled using a 60 μm-thick polymeric film (Surlyn, DuPont). The electrolyte solution was then injected into the gap between the two electrodes. The redox couple/electrolyte solution contained 0.05 M LiI (Sigma–Aldrich), 0.03 M I₂ (Yakuri), 0.7 M 1-butyl-3-methylimidazolium iodide (BMII) (TCI), 0.5 M 4-tert-butylpyridine (Aldrich), and 0.1 M guanidine thiocyanate (GSCN) (Wako), in a solution of acetonitrile (Aldrich) and valeronitrile (85:15 v/v).

2.4. Characterization

The surface morphology of the inverse opals and the ZnO-treated inverse opals was investigated using scanning electron microscopy (SEM, Carl Zeiss). The atomic concentration of ZnO was measured using energy dispersive X-ray spectroscopy (EDX), which was performed using instrumentation attached to the SEM. The photocurrent and voltage of the DSSCs were measured using a Source Meter (Keithley Instruments) without masking; this was performed under simulated solar light, which was produced using a 150 W Xe lamp (Oriel) and AM 1.5G filters. The intensity was adjusted using a Si reference cell (BS-520, Bunko-Keiki) to a power density of 100 mW cm⁻². The electrochemical impedance spectra were measured using a potentiostat (Versastat, AMETEK). The frequency range explored in the impedance measurements was 10⁵–0.1 Hz.

3. Results and discussion

The TiO₂ inverse opals were prepared using PS colloidal templates and TiO₂ nanoparticle dispersion, as reported elsewhere [14]. The inverse opals were post-treated with TiO₂ precursors in order to increase the surface roughness (the resulting electrodes will be referred to as io-TiO₂; see Fig. 1b). ZnO was then coated on the io-TiO₂ via a sol-gel reaction, using a dilute ZnO precursor (Zn(NO₃)₂). Fig. 1 shows SEM images of the PS colloid template (Fig. 1a), the io-TiO₂ without ZnO treatment (Fig. 1b) and the io-TiO₂ with the ZnO treatment (Fig. 1c). In the case of the io-TiO₂ structure, a TiCl₄ post-treatment was applied for 60 min, which grows TiO₂ nanoparticles (average size 40 nm) on the surface, as shown in Fig. 1b. X-ray diffraction measurements disclosed that the io-TiO₂ had a rutile crystalline polymorph structure (data not shown here).

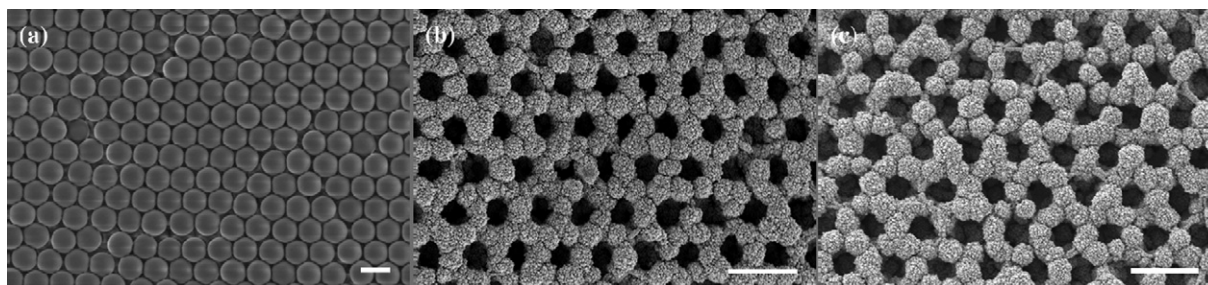


Fig. 1. (a) SEM image of the colloidal crystal templates, made using 900 nm PS particles, (b) io-TiO₂ structure without ZnO treatment, and (c) 0.35 wt% ZnO-treated io-TiO₂ structure (scale bar, 1 μm).

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