TiO$_2$@MgO Core-Shell Film: Fabrication and Application to Dye-Sensitized Solar Cells

LI Bihui, LÜ Gang, LUO Lijuan, TANG Yiwen†
Institute of Nano-Science and Technology, Huazhong Normal University, Wuhan 430079, Hubei, China

Abstract: In this study, TiO$_2$@MgO core-shell film was obtained by using a simple chemical bath deposition method to coat a thin MgO film around TiO$_2$ nanoparticles. The core-shell configuration was characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and high-resolution transmission electron microscopy (HRTEM). Lattice fringes were observed for the TiO$_2$ particles, and the MgO shell showed an amorphous structure, revealing a clear distinction between the core and shell materials. Applying the core-shell film as photoanode to the dye-sensitized solar cells (DSSCs), it shows a superior performance compared to the pure TiO$_2$ electrode. Under the illumination of simulated sunlight (75 mW·cm$^{-2}$), the short circuit photocurrent ($J_{sc}$), the open circuit photovoltage ($V_{oc}$), and the fill factor ($F_{f}$) are 8.80 mA·cm$^{-2}$, 646 mV, and 0.69, respectively, and the conversion efficiency ($\eta$) increased by 21.8% (from 4.32% to 5.26%) when dipping for optimum condition.

Key words: TiO$_2$@MgO; core-shell; electrode; dye-sensitized solar cell (DSSC)

CLC number: O 47

0 Introduction

The dye-sensitized solar cells (DSSCs) have a significant potential as a low-cost solar cell as compared to the traditional silicon batteries. The DSSCs are typically constructed from thick films of semiconductor nanoparticles that are sintered into mesoporous network with a large internal surface area for the adsorption of light harvesting dye molecules, such as TiO$_2$, SnO$_2$, and ZnO films[1-3]. The semiconductor is deposited onto a transparent conducting optical (TCO) glass, a redox electrolyte ($I^-/I^-$) that acts as a conductor, and a TCO glass that is deposited by Pt as a counter electrode. Under illumination, electrons are injected from the photoexcited dye into the nanocrystalline film and holes, leaving the opposite side of the device by means of redox mediator[4]. Since the electrolyte penetrates throughout the nanoporous structure, a large surface area is available for a reaction between the photoinjected electrons in the semiconductor and the oxidized ions in the redox mediator or oxidized dye at the semiconductor surface[5, 6]. The photoinjected electrons are prone to recombination with the oxidized ions or oxidized dye.

Coating another semiconductor (e.g., SrTiO$_3$[7], Al$_2$O$_3$[8], Nb$_2$O$_5$[9], and In$_2$O$_3$[10]) around the TiO$_2$ particle as a barrier layer is an effective way to retard the electron-hole pair from recombining. The Nb$_2$O$_5$ barrier layer restricts the electrons to the TiO$_2$ particles, therefore, reduces the recombination rate. Consequently, all parameters of the DSSC improved resulting in a 35% increase of the cell efficiency[9]. In common, the core-shell nanoporous elec-
trode consists of a nanoporous inorganic semiconductor matrix that is covered with a shell of other metal oxide. The thicknesses of the shell films are often determined by X-ray photoelectron spectroscopy by calculating the relative concentrations of the core and shell materials. However, the problem with the use of this method is the requirement for a large scan area over the nanostructure. Menzies et al. first introduced high-resolution transmission electron microscopy (HRTEM) technique to illustrate the In$_2$O$_3$ shell on TiO$_2$ core, and the thickness of the shell was observed directly from the HRTEM images.

MgO is a typical wide band gap oxide (6.0-7.8 eV). Kumara et al. and Taguchi et al. reported that a thin layer of MgO coated TiO$_2$ retarded recombination of the holes and back transferred electrons in the solid-state DSSCs. Jung et al. blended magnesium methoxide with TiO$_2$ powder first rather than coating the TiO$_2$ electrode with a chemical bath deposition method. Recently, Grinis et al. reported a sol-gel electrophoretic deposition method that coated amorphous TiO$_2$ or MgO shell onto photoanodes for DSSC based on plastic substrate in low temperature.

In this paper, a thin layer MgO film was coated on the TiO$_2$ nanoparticles by using a simple chemical bath deposition method. We demonstrate that the MgO layer on TiO$_2$ electrode can form a core-shell configuration by energy dispersive X-ray (EDX) and HRTEM characterizations. The influence of the MgO layer thickness on the parameters of the DSSCs is also investigated.

1 Experimental

1.1 Fabrication of Working Electrodes

A 120 g/L TiO$_2$ colloid was prepared by the procedure reported in Ref. [1], except that autoclaving was performed at 220 °C instead of 200 °C. The TiO$_2$ colloid was dropped on the TCO glasses (10-15 Ω/square, Asahi Company) and spread uniformly. Then, the films were annealed at 450 °C in atmosphere. The 5 μm-thick TiO$_2$ were obtained after repeating above procedure several times. The TiO$_2$ films were dipped in anhydrous ethanol solution of magnesium acetate (0.05 mol/L) at a constant temperature of 40 °C, and then, the films were calcined in the oven. Both uncoated and coated TiO$_2$ films were put into 0.5 mmol/L anhydrous ethanol solution of a ruthenium complex, cis-bis (isothiocyanato)-bis (2, 2′-bipyridyl-4, 4′-dicarboxylato) ruthenium (II) (abbreviated as N3) for 12 h.

1.2 Characterization of the Electrodes

X-ray diffraction (XRD) measurement was carried out by a Bruker D8 advance X-ray diffractometer with monochromatized Cu Kα radiation (λ = 0.154 18 nm). Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectra were obtained by using JSM-6700F microscope. The morphology and structure of the products were characterized using a JEOL JEM-2010 transmission electron microscope (TEM) operating at 200 kV further. Optical absorption of films was studied by employing a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer.

1.3 Fabrication and Characterization of the Cell

The counter electrode was TCO glass on which Pt was deposited by sputtering. The electrolyte was an acetonitrile-based solution containing 0.05 mol/L iodine, 0.1 mol/L lithium iodide, 0.6 mol/L 1-methyl-3-propylimidazolium iodide (MPII), and 0.5 mol/L 4-tert-butylpyridine. The N3-coated film was illuminated through the conducting glass support with an Oriel 69920 solar simulator as light source. A series of current density-voltage (J-V) curves were monitored and recorded using a computerized Keithley Model 2400 source measure unit. The active electrode area was typically 0.15 cm$^2$.

2 Results and Discussion

2.1 Characterization of Electrodes

The phase structure of the films was examined by XRD. Figure 1 shows the XRD pattern of the pure TiO$_2$ film. The peaks denoted by asterisks attribute to the TCO glass, and the peaks at 25.8°, 47.3°, 53.3°, and 54.4° are corresponding to the planes (101), (200), (105), and (211), which is body-centered cubic and anatase TiO$_2$.