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Performance enhancement of dye-sensitized solar cells using nanostructural TiO_2 films prepared by a graft polymerization and sol–gel process

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ABSTRACT

Nanostructural TiO_2 films with large surface areas were prepared by the combined process of graft polymerization and sol–gel for use in dye-sensitized solar cells (DSSCs). The surface of the TiO_2 nanoparticles was first graft polymerized with photodegradable poly(methyl methacrylate) (PMMA) via atom transfer radical polymerization (ATRP), after which the particles were deposited onto a conducting glass. The PMMA chains were removed from the TiO_2 films by UV irradiation to generate secondary pores, into which titanium isopropoxide (TTIP) was infiltrated. The TTIP was then converted into small TiO_2 particles by calcination at 450 °C, as characterized by energy-filtering transmission electron microscopy (EF-TEM) and field emission scanning electron microscopy (FE-SEM). The nanostructural TiO_2 films were used as a photoelectrode in solid-state DSSCs; the energy conversion efficiency was 5.1% at 100 mW/cm^2, which was higher than the values achieved by the pristine TiO_2 (3.8%) and nongrafted TiO_2/TTIP photoelectrodes (3.3%). This performance enhancement is primarily due to the increased surface area and pore volume of TiO_2 films, as revealed by the N_2 adsorption–desorption isotherm.

1. Introduction

Since the first report of dye-sensitized solar cells (DSSCs) by O'Regan and Gratzel in 1991 [1], DSSCs have received much attention in science and technology owing to favorable characteristics, including high efficiency, low cost, ease of fabrication, low manufacture toxicity, amenability to scale-up, and use of flexible cell design [2–4]. A DSSC consists of a transparent conducting oxide (TCO) glass, a ruthenium complex-based dye, a porous TiO_2 photoelectrode, a redox $I^-/I_3{}^-$ electrolyte, and a platinized counter electrode. To enhance the performance of DSSCs, extensive investigations have been performed on each component: the sensitizing dye [5,6], the TiO_2 photoelectrode [7–12], the redox electrolyte [13–16], and the counter electrode [17,18]. The TiO_2 photoelectrode in particular plays an essential role in converting photons to electrical energy because it serves as a pathway for photoinjected electrons. For example, the efficiency of charge transport is strongly dependent on the surface area, phase, porosity, and connectivity of the TiO_2 photoelectrode [7–12].

DSSC photoelectrodes are often prepared by doctor-blade casting of a TiO_2 paste formed by mixing a binder and commercial TiO_2 powder (e.g., Degussa P25) in an appropriate solvent. This method yields low conversion efficiency, however, owing to small the surface area, recombination of injected electrons with triiodides, or direct contact between triiodides and the photoelectrode substrate [19,20]. Sol–gel processing for TiO_2 has been also extensively investigated with the goal of refining TiO_2 films and controlling their stability and structure. Films prepared by the sol–gel process have larger surface area, smaller particle size, and greater stability than those obtained by other methods. However, there is still the problem that the thickness of the TiO_2 films is constrained to less than approximately 1 μm. Such thin TiO_2 photoelectrodes provide insufficient surface area, leading to low light harvesting by the adsorbed dye on the photoelectrode [21].

In this study, to fabricate nanostructural TiO_2 photoelectrodes with larger surface area and greater thickness, we have implemented the combined process of graft polymerization and sol–gel. The surfaces of TiO_2 nanoparticles were chemically modified via atom transfer radical polymerization (ATRP) using poly(methyl methacrylate) (PMMA) chains that are photodegradable under UV irradiation [22]. After the removal of the PMMA chains, a titanium precursor consisting of titanium(IV) isopropoxide (TTIP) was infiltrated into the pores, followed by a sol–gel process and calcination at 450 °C. Graft copolymerization from the TiO_2 nanoparticles was characterized in detail by thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, UV–visible spectroscopy, and wide angle X-ray scattering (WAXS). Morphological changes in the TiO_2 nanoparticles were investigated using energy filtering transmission electron microscopy (EF-TEM), field emission

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scanning electron microscopy (FE-SEM), Brunauer–Emmett–Teller analysis (BET), and Barrett–Joyner–Halenda analysis (BJH). DSSCs with a solid polymer electrolyte consisting of poly(ethylene glycol dimethyl ether) (PEGDME), fumed silica nanoparticles (SiO_2), ionic liquid (methyl-3-propyl imidazolium iodide, MPII), and I_2 were fabricated using the nanostructural TiO_2 photoelectrodes. The interfacial properties of the DSSC were also characterized in detail by electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, 99%), 2-chloropropionyl chloride (CPC), triethylamine (TEA), 4-(dimethylamino) pyridine (DMAP), methylenedichloride (MC), copper(I) chloride (CuCl), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), titanium(IV) isopropoxide (TTIP, 97%), hydrogen chloride solution (HCl, 35 wt%), acetic acid (CH_3CO_2H, 99.7%), sodium hydroxide solution (NaOH, 0.1 N), fumed silica nanoparticles (SiO_2, 14 nm), poly(ethylene glycol dimethyl ether) (PEGDME, $M_n = 500$ g/mol), iodine (I_2), titanium(IV) bis(ethyl acetoacetato) diisopropoxide, and chloroplatinic acid hexahydrate (H_2PtCl_6) were purchased from Aldrich. Distilled water was obtained from a water purification system made by Millipore Corporation. Commercial TiO_2 powder (P25) was provided by Degussa, Germany. 1-Methyl-3-propyl imidazolium iodide (MPII, $C_7H_{13}N_2I$) and ruthenium dye (535-bisTBA, N719) were purchased from Solaronix, Switzerland. Acetonitrile (CH_3CN, 99.9%), butanol ($C_4H_{10}O$, 99.9%), isopropanol (C_3H_7OH, 99.9%), chloroform ($CHCl_3$, 99.9%), ethanol (C_2H_6O, 99.9%), tetrahydrofuran (THF, C_4H_8O), and dimethyl sulfoxide (DMSO, $(CH_3)_2SO$) were purchased from J.T. Baker. Fluorine-doped tin oxide (FTO) conducting glass substrate (TEC8, 8 Ω/sq, thickness 2.3 mm) was purchased from Pilkington, France. All solvents and chemicals were reagent grade and were used as received without further purification.

2.2. Synthesis of TiO_2–PMMA nanoparticles

TiO_2 nanoparticles grafted with PMMA (TiO_2–PMMA) were synthesized according to the two-step synthetic method [23], as shown in Scheme 1. In the first step, 3.68 g of DMAP was mixed with 20 mL of MC and 2.8 mL of TEA at 0 °C with ice. Next, 4.8 mL of CPC in 20 mL of MC was added to the solution. Then, 20.0 g of TiO_2 in 100 mL of MC was added dropwise to the solution, which was subsequently purged with nitrogen for 30 min. The mixture was stirred at room temperature for 18 h. After the reaction, the resulting solution was precipitated into methanol, and the product was separated by centrifugation. Finally, TiO_2–Cl nanoparticles were obtained and dried in a vacuum oven overnight at room temperature.

In the second step, 8 mL of MMA was dissolved in 10 mL of DMSO. Then, 0.0264 g of CuCl and 0.072 mL of HMTETA were added to the solution, followed by the addition of 2 g of TiO_2–Cl nanoparticles. The solutions were purged with nitrogen for 30 min. The mixture was placed in a 90 °C oil bath for 18 h. After polymerization, the resulting solution was precipitated into methanol, and the polymer was separated by centrifugation. The product was washed with THF and methanol several times to remove impurities. Finally, TiO_2–PMMA nanoparticles were obtained and dried in a vacuum oven overnight at room temperature.

2.3. Preparation of polymer electrolytes

A polymer electrolyte solution was prepared by dissolving fumed silica nanoparticles (SiO_2), PEGDME, MPII, and I_2 in acetonitrile [24]. The mole ratio of ether oxygen to iodide salt was fixed at 20, and the iodine content was fixed at 10 wt% with respect to the salt.

2.4. Preparation of photoelectrodes

Transparent glass, coated with conductive FTO, was used for the photoelectrode. The neat glass was cleaned by sonication in isopropanol and then in chloroform. The clean conducting surface of the FTO glass was blocked by spin coating with a layer of titanium(IV) bis(ethyl acetoacetato) diisopropoxide, followed by heating to 450 °C for 2 h, holding for 30 min, and cooling to 30 °C over 4 h. The pristine TiO_2 (P25) solution was prepared by dispersing 0.039 g of P25 powder in 1.08 mL of 2-propanol, followed by sonication for 1 h to ensure homogeneous dispersion of the solution. After casting the TiO_2 solution onto FTO glass using a doctor-blade technique, the electrode was aged at room temperature at 80% relative humidity for 30 h [11]. The nanocrystalline TiO_2-coated FTO glass, 10 μm thick, was sintered at 450 °C for 30 min.

The fabrication steps for the nanostructural TiO_2 photoelectrode are shown in Scheme 2. The nanocrystalline TiO_2–PMMA layer was deposited onto the FTO glass using the same method used for the pristine TiO_2 (P25). The photoelectrode was aged at room temperature and 80% relative humidity for 30 h and then irradiated with UV radiation at room temperature and washed with acetic acid. UV irradiation was performed using a UV hand lamp (UVllite®, UVitec) with a wavelength of 254 nm from a distance of 1 mm for 60 min, resulting in the photodegradation of the PMMA [22]. Next, to prepare the sol–gel precursor, 0.18 mL of TTIP was dissolved and stabilized in a solution consisting of 0.2 mL of HCl and 0.04 mL of H_2O while being vigorously stirred. After aging for 15 min, the TTIP solution was added to 0.039 g of a solution of triblock copolymer consisting of ethylene oxide and propylene oxide (Pluronic P123), which was dissolved in 1.08 mL of 1-butanol. The sol was aged under mild stirring at room temperature for 3 h. The resulting TiO_2 sol was deposited onto the TiO_2 photoelectrode (with PMMA removed) using a drop coating method. The TiO_2-coated FTO glasses were sintered at 450 °C for 30 min. The nanocrystalline TiO_2 layers were then sensitized with a 10^{-4} mol/dm^3 alcoholic ruthenium solution at 50 °C for 2 h in darkness. The dye-sensitized photoelectrodes were rinsed with absolute ethanol and dried in a vacuum oven.

2.5. Preparation of counter electrode

Transparent glasses coated with a conductive FTO were used as counter electrodes. These glasses were cleaned by sonication in isopropanol and then in chloroform. The counter electrodes were prepared by spin coating in a 4 wt% H_2PtCl_6 isopropanol solution onto the conductive FTO glass and sintering at 450 °C for 30 min.

2.6. Fabrication of DSSC

DSSCs with an active area of 0.4 cm^2 were constructed by drop-casting the electrolyte solution onto the photoelectrode and covering with the counter electrode, using a previously reported procedure [11,24–26]. The thickness of the TiO_2 films was fixed at approximately 10 μm for comparison. The cells were placed in a vacuum oven for one day to permit complete evaporation of the solvent and then sealed with an epoxy resin. The photoelectrochemical performance characteristics, including short-circuit current (J_{sc}, mA/cm^2), open-circuit voltage (V_{oc}, V), fill factor (FF), and overall energy conversion efficiency (η), were measured using a Keithley Model 2400 and a 1000-W Xenon lamp (Oriel, 91193). The light was homogeneous over an 8 in. × 8 in. area, and it was calibrated with a Si solar cell (Fraunhofer Institute for Solar