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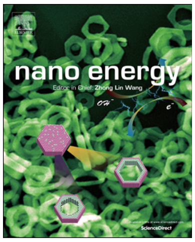

RAPID COMMUNICATION

Highly efficient dye-sensitized solar cells composed of TiO_2@SnO_2 core-shell microspheres

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Abstract

Hierarchical microspheres constructed from a TiO_2 core and a SnO_2 shell have been successfully fabricated using a one-step solvothermal method. The synthesized products were characterized by XRD, SEM, TEM and FT-IR measurements. It was found that the concentration of precursor Sn^{4+} in the reaction system plays a key role in the formation of the hierarchical microspheres. The core-shell microspheres of TiO_2@SnO_2 were formed by a self-assembly process, accompanied by the Kirkendall effect. These core-shell microspheres of TiO_2@SnO_2 have been used for the first time as the electrode for C106 dye-sensitized solar cells; they exhibited an efficiency of 6.24%. This might be attributed to large surface area and hierarchical structure of the microspheres, leading to light scattering, an increase of dye adsorption, a suppression of charge recombination and prolonging the electron lifetime.

Introduction

Dye-sensitized solar cells (DSCs) present a promising third generation photovoltaic device, which have recently exhibited an efficiency of 12.3% [1]. In general, DSCs are composed of a nanocrystalline wide band-gap semiconducting oxide on a transparent conducting substrate, a sensitizing dye, a redox shuttle for regeneration of the dye and a catalytic counter

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electrode [2-5]. Various metal oxides, such as TiO_2, ZnO, SnO_2, Nb_2O_5, etc., have been used as the electrode film for dye attachment and carrier transport [3-11]. Of these materials, TiO_2 has been the most successful oxide so far because of the charge separation and transport resulting from a number of factors, including (i) ease of preparing nanoparticles, (ii) band alignment with various organic and inorganic dyes and (iii) stability. However, low electron mobility through TiO_2 (0.1-1.0 $cm^2\,V^{-1}\,S^{-1}$) is a crucial issue and imposes severe limitations for enhancement of the efficiency of the DSC, closer to its theoretical limit [12,13]. One of the main hurdles that give rise to the inferior electron mobility is the electron recombination with the electrolyte if the thickness of the electrode film is larger than the diffusion length of the electron [14]. By comparison, tin oxide (SnO_2) nanostructures are a well-known transparent conducting oxide for nanoelectronics due to two advantageous features: (i) high electron mobility (100-200 $cm^2\,V^{-1}\,S^{-1}$), suggesting a faster diffusion transport of photoinduced electrons in the SnO_2 film compared with TiO_2 one [15]; (ii) a larger band gap (3.6 eV), which creates fewer oxidative holes in the valence band, leading to long-term stability of the DSC. However, the efficiency of the dye-sensitized SnO_2 solar cell has still to be improved. This is because the more positive shift of its conductive band results in faster interfacial electron recombination [16] and lower isoelectric point leads to poorer dyes adsorption [17]. To increase the efficiency of SnO_2-based DSCs, various methods have been considered. Vilaca et al. modified the electrode surface of SnO_2 with trialkynylorganotins to improve dye adsorption [18,19]. The SnO_2 electrode has been combined with TiO_2, ZnO, MgO or Al_2O_3 in order to suppress charge recombination in the DSC [20-23]. Also, when the surface of the SnO_2 crystallite is coated with a thin layer of other oxides, it results in an enhancement of the electron conduction [24-27]. As reported by the Grätzel group, the highest efficiency, 5.1%, was achieved using ZnO-coated SnO_2 as the electrode [17]. Qian et al. reported an efficiency of 5.65% for a cell made of TiO_2 coated SnO_2 hollow microspheres [28]. Bandara et al. fabricated cells made of SnO_2 coated with a ZnO layer and observed that the electron transfer could occur from the high band semiconductor to the low band semiconductor or vice versa, depending on which surface adsorbs the dye more strongly [21]. These results clearly indicate that the photovoltaic properties of SnO_2-based DSCs can be efficiently enhanced if the electrode films are first modified by other oxides. This also encourages us to extend our studies to an investigation of hierarchical nanostructures for DSCs. To the best of our knowledge, however, dye-sensitized solar cells composed of hierarchical microspheres with a TiO_2 core and a SnO_2 shell (TiO_2@SnO_2) have not previously been fabricated. In the present work, the TiO_2@SnO_2 microspheres were used as an electrode material in DSCs for the first time. The highest efficiency achieved was 6.24%. Furthermore, the relationships between the intrinsic structure of the electrode materials and the photovoltaic properties were also investigated in detail.

Experimental

Materials preparation

In a typical synthesis, tin chloride pentahydrate ($SnCl_4\cdot 5H_2O$) with different amounts (0, 0.1, 0.4, 0.7, 1.0 and 1.3 g) was added to 42 mL of isopropyl alcohol (IPA) and stirred for 5 min to obtain a clear solution. After 1.5 mL of titanium isopropoxide (TIP) was dropped to the solution, 30 μL of diethylenetriamine (DETA) was added under strongly stirring. With increasing ratio of Sn/Ti for the precursor, the white precipitation appeared. The obtained mixture solutions were transferred to a 60 mL Teflon-lined autoclave and kept in an oven at 200 °C for 6-36 h. After cooled to room temperature, the white precipitate was collected by centrifugation, and washed with ethanol, and then dried at 60 °C overnight. As a reference sample, SnO_2 nanoparticles were also synthesized according to the previous report [29,30].

Materials characterization

X-Ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert spectrometer using Co-Kα radiation (λ=1.78897 Å) and the data were converted to Cu-Kα data. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM, FEI F20) were taken on a Hitachi S4800 instrument and a FEI F20 instrument, respectively. Fourier-transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum 2000.

DSCs assembly

FTO glass (8-10 Ω/□, Nippon sheet glass) was first spin-coated with a compact TiO_2 blocking layer (ca. 300 nm in thick) which was prepared according to the reports [8,9]. The paste of TiO_2@SnO_2 core-shell microspheres and SnO_2 nanoparticles for the screen printing was prepared according to our previous works [29,30]. Typically the paste was composed of powder of TiO_2@SnO_2 microspheres/SnO_2 nanoparticles, ethyl cellulose (10 wt%, Kanto Chemical Co.) as a binder, α-terpineol (5 wt%) as a solvent, and ethanol. The mixture of these components was dispersed sufficiently with homogenizers (Ultra-turrax T18 and Ultrasonic Crusher JY98-3D) to obtain a homogeneous paste. The paste was concentrated by an evaporator (EYELA N-1100S, Tokyo rikakikai) to a final concentration of 20 wt%. The paste was printed on FTO glass using a screen printer (Mitani MEC 2400) with a suitable screen mesh and then calcined at 525 °C for 2 h in air. After cooling to the room temperature, a 50 mM aqueous solution $TiCl_4$ was dropped onto the film and kept at 70 °C for more than 30 min. After $TiCl_4$ treatment, the films were calcined at 450 °C for 30 min in air. The thickness of the electrode films was measured by an instrument (Surfcom130A) and the active area of the electrode films was 0.25 cm^2.

Dye C106 (NaRu(4,4′-bis(5-(hexylthio) thiophen-2-yl)-2,2′-bipyridine)(4-carb-oxylicacid-4′-carboxylate-2,2′-bi-pyridine) $(NCS)_2$) (0.3 mM) was dissolved in a solution of tert-butyl alcohol and acetonitrile (volume ratio=1). The prepared films were immersed into the dye solution overnight at room temperature, and the color of the films was changed. The dye-sensitized electrode films were incorporated into a thin-layer, sandwiched solar cell. The counter electrode was Pt sputtered on a transparent conducting glass using an ion coater (Eiko engineering, IB-5). A polyethylene spacer (30 and 60 μm thickness) was used to prevent the cell from short-circuiting when the counter- and working electrodes were clamped together. The electrolyte consisted of 0.6 M 1,