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TiO_2–Au plasmonic nanocomposite for enhanced dye-sensitized solar cell (DSSC) performance

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Abstract

Anatase TiO_2 nanoparticles dressed with gold nanoparticles were synthesized by hydrothermal process by using mixed precursor and controlled conditions. Diffused Reflectance Spectra (DRS) reveal that in addition to the expected TiO_2 interband absorption below 360 nm gold surface plasmon feature occurs near 564 nm. It is shown that the dye sensitized solar cells made using TiO_2–Au plasmonic nanocomposite yield superior performance with conversion efficiency (CE) of ~6% (no light harvesting), current density (J_{SC}) of ~13.2 mA/cm^2, open circuit voltage (V_{oc}) of ~0.74 V and fill factor (FF) 0.61; considerably better than that with only TiO_2 nanoparticles (CE ~ 5%, J_{SC} ~ 12.6 mA/cm^2, V_{oc} ~ 0.70 V, FF ~ 0.56).

Keywords: Hydrothermal; Dye-sensitized solar cells; Hybrid composite; Au; Anatase TiO_2

1. Introduction

Semiconducting metal oxides have gained prominence in recent years in view of their several interesting and application-worthy properties in the arena of optoelectronic applications (Hochbaum and Yang, 2010; Nowotny, 2008; Arakawa and Sayama, 2000). An application of particular interest based on nano-meso-porous metal oxide photoanodes is dye sensitized solar cells (DSSCs) discovered by O'regan and Gratzel (1991). Since then several research efforts have been expended on manipulating the corresponding architecture involving inorganic and organic systems as well as various interfaces so as to enhance the cell performance (Hagfeldt et al., 2010; Zhang et al., 2009; Dhas et al., 2011, 2008; Muduli et al., 2009). Although the concept of using functional nanocomposites involving metals (or semiconductors) with metal oxides has been attempted in this context, the metal based composites do not appear to have been fully explored. Kamat et al. have shown that electron transfer occurs from semiconductor to Au in colloidal solutions (Kamat and Shanghavi, 1997). Noble metals deposited on semiconductor particles have been shown to improve photocatalytic electron transfer processes at the semiconductor interface (Subramanian et al., 2001). Wood et al. (2001) examined the photoinduced interaction between a semiconductor and Au, and concluded that the role of Au is primarily to accept electrons from the photo-excited semiconductors. They explored the behavior of Au and Pt with ZnO and concluded that Pt establishes Ohmic type contact while Au–ZnO is a Schottky type contact. Chen et al. have carried out a systematic investigation of the photoluminescence of ZnO nanowire-Au nanoparticle hybrid nanostructure

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synthesized by attaching Au nanoparticles onto ZnO nanowires (Chen et al., 2008). Dhas et al. have also reported that ZnO nanoflowers loaded with Au NPs yield solar energy conversion efficiency of ~2.5%, considerably higher than the unloaded nanoflowers (Dhas et al., 2008). Snaith and coworkers have recently outlined a strategy for incorporating metal nanoparticles with strong surface plasmon resonance into dye-sensitized solar cells that overcomes four main issues related to the introduction of metal nanoparticles into the bulk of a solar cell, namely (a) charge recombination within the metal, (b) thermal stability during processing, (c) chemical stability, and (d) control of metal nanoparticle dye chromophore separation to inhibit non-radiative quenching (Brown et al., 2011). This new plasmonic photovoltaic system has thus led to enhanced light absorption and photocurrent generation in dye-sensitized solar cells.

In this work, we have hydrothermally synthesized anatase TiO_2 nanoparticles as well as TiO_2–Au nanocomposites and have examined DSSCs made using these. The DSSCs made with TiO_2–Au nanocomposite are found to yield a much superior performance than the cells made with only TiO_2 nanoparticles. Various processes such as interfacial charge transfer and stability of interfaces can greatly influence the ability of a semiconductor–metal composite to sustain charge separation. We present results of different measurements and outline the possible origin of this effect.

2. Experimental section

2.1. Materials

The $RuL_2(NCS)_2$:$(TBA)_2$ (L = 2,2′-bipyridine-4,4′-dicarboxylicacid, TBA = tetrabutylammonium) (N719) and Fluorine-doped SnO_2 (FTO) electrode (sheet resistance 15 Ω^{-2}) were purchased from Solaronix Co. High purity water (Milli-Q, Millipore) was used in all experiments. The FTO electrodes were washed with acetone, ethanol and deionized (18.2 MΩ cm) water in an ultrasonication bath for 15 min with a final wash in isopropanol.

2.2. Preparation of a TiO_2–Au nanocomposite

The TiO_2 nanoparticles attached with Au NPs were synthesized by hydrothermal route using high purity Titanium tetra isopropoxide (TIP) and $HAuCl_4$. For obtaining TiO_2–Au nanocomposite 1 ml of TIP was hydrolyzed in a mixed solvent of 10 ml of ethanol and 10 ml of deionized water under stirring. Then, 10 ml of 0.6 M urea aqueous solution was added drop wise to the stirred solution. 1 ml of 0.1 M $HAuCl_4$ aqueous solution was introduced, and the resulting solution mixture was transferred into a Teflon lined stainless steel autoclave. It was then sealed and maintained at 180 °C for 18 h. After the reaction a pink colored solid powder was recovered by centrifugation followed by washing with distilled water and ethanol to remove the residual ions in the final product. Thereafter the powder was finally dried at 60 °C in air for 10 h. The same protocol was followed to prepare TiO_2 nanoparticles without the addition of $HAuCl_4$ solution. The TiO_2 and TiO_2–Au nanocomposite films were made by the doctor blade method and the films were then annealed at 450 °C for 30 min. The thickness of TiO_2–Au nanocomposite films was ~12 μm. For sensitization, the TiO_2 and TiO_2–Au nanocomposite films were impregnated with 0.5 mM N719 dye in ethanol for 24 h at room temperature. The sensitizer-coated TiO_2 films were washed with ethanol. The electrolytes were used with 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, and 0.5 M 4-tert-butylpyridine in methoxyacetonitrile.

2.3. Characterization

Various techniques such as X-ray diffraction (XRD, Philips X'Pert PRO), Diffused Reflectance Spectra (DRS, Jasco V-570 spectrophotometer), Raman (Horiba Jobin Yvon LabRAM HR System), Transmission Electron Microscopy (TEM) and Electrochemical Impedance Spectroscopy (EIS, Autolab PGSTAT30 (Eco-Chemie)) were used to characterize the samples. The impedance measurements were performed at a room temperature.

2.4. Measurements

I–V characteristics were measured using a solar simulator (Newport) at 100 mW/cm^2 (1 sun AM 1.5). Standard Silicon solar cell (SER NO. 189/PVM351) from Newport, USA was used as a reference cell. The measurements of incident-photon-to-current conversion efficiency (IPCE) were done using Quantum Efficiency Setup (Newport Instruments).

3. Results and discussion

Fig. 1 compares the XRD patterns for TiO_2 NPs with TiO_2–Au nanocomposite. The peaks in Fig. 1 at 25.4 (101), 38.1 (004), 48.1 (200), 54.2 (105), 55.0 (211), 62.8 (204), 69.1 (116), 70.3 (220) and 75.4 (215) (PCPDF-WIN #211 272) clearly represent the anatase TiO_2 phase. The tiny peaks at 38.1 (111) (overlapping with the TiO_2 (004)), 44.4 (200), 64.6 (220) and 77.6 (311) in the full red[1] curve of Fig. 1 are attributed to metallic gold (PCPDFWIN #040784) in the TiO_2–Au nanocomposite. Presence of gold nanoparticles can also be clearly elucidated by Diffused Reflectance Spectra (DRS).

Fig. 2 shows the diffused reflectance spectrum (DRS) for TiO_2–Au nanocomposite. In addition to the strong interband absorption feature for anatase titania at 358 nm, a peak at ~564 nm corresponding to the surface plasmon absorption due to Au nanoparticles testifies to the formation of the

[1] For interpretation of color in Figs. 1–9, the reader is referred to the web version of this article.