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Dye-sensitized solar cells enhanced by optical absorption, mediated by TiO_2 nanofibers and plasmonics Ag nanoparticles

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ABSTRACT

Light harvesting in dye-sensitized solar cells (DSSCs) mediated by plasmonic metallic nanoparticles and sub-micron light-scattering metal oxides is a facile and cost-effective approach to achieving high device performance. Ag nanoparticles, protected by thin shells of TiO_2, were incorporated in TiO_2 photoanode. The large plasmonic near-field intensity generated by these nanoparticles caused an 18.3% rise in photocurrent, which resulted in an enhanced efficiency of 6.23% as compared to 5.29% efficiency of DSSC based on unmodified TiO_2 photoanode. In addition, DSSC with TiO_2 nanofibers (NFs) embedded in TiO_2 photoanode was also constructed, which because of the efficient light scattering ability of the nanofibers, attained an efficiency of 7.14% as a result of a current rise of 36.9%. Another DSSC was assembled with Ag NPs added to the photoanode of the NFs-based DSSC to further boost cell performance. The addition of Ag NPs, however, did not produce an appreciable change in the cell performance. The reason for this unexpected outcome was probably due to the low internal resistance associated with charge recombination and large resistance to electron transport in the cell as determined by electrochemical impedance analysis computed in this work.

1. Introduction

Though recently DSSCs have attained a record high efficiency of 12.3% [1,2], they still lag behind their silicon counterpart in power conversion efficiency [3,4]. Nevertheless, DSSCs have some merits over silicon cells because of their low cost, simple manufacturing processes, simplicity of large-scale production, and their capability for mechanically flexible applications [5–7]. Several methods have been employed to enhance DSSCs performance, including $TiCl_4$ post-treatment [8], incorporation of hole-blocking layers [9], use of a mixture of dyes with different spectral responses [10], doping of TiO_2 with non-metals [11] and transition metals [12], and application of photoanode with various structures and morphologies.

Two approaches that have gained considerable attention for DSSC enhancement are the scattering of incident light and plasmonic near-field effect in the photoanode to promote increased optical absorption in the dye monolayer covering the internal surface of TiO_2 photoanode. The essence of scattering light in the photoanode is to increase its path length, thus keeping it longer in the electrode in order to increasing its probability of exciting dye molecules. The increased absorption in the dye will cause more electrons to be injected into TiO_2 nanocrystalline conduction band, and consequently produce large device photocurrent. Typical anatase TiO_2 films of particles size 20 nm have high internal surface area allowing for large dye adsorption, but these films are highly transparent and poor light scatterers, resulting in the transmittance of long wavelength (near-infrared) part of the solar spectrum and poor light harvesting [13–15]. Many studies have focused on the use of large TiO_2 structures such as submicron TiO_2 beads and nanofibers (NFs), of dimensions greater than 100 nm to effectively scatter light in the film [15]. These structures are either embedded in the film or placed on the surface as a scattering layer to reflect transmitted light back into the film. Nanobeads are porous spherical structures composed of nano-crystallites that cluster together to form larger secondary particles, thereby functioning as light scatterers without sacrificing the internal surface area needed for effective dye-uptake [16]. However, large voids between beads exist in the photoelectrode films, compared to TiO_2 nanocrystallites films, due to the large sizes of beads, which would result in low connectivity for effective charge transport between beads [17,18]. NFs, unlike nanobeads, are not so porous because of their fused nanocrystallites. This makes them an efficient medium for electrons transport [19], but due to their large sizes, their presence in the film reduces the internal surface area, which results in low dye loading.

DSSCs enhancement by plasmonic near-field can be achieved by local surface plasmon (LSP) supported by metallic

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nanoparticles (NPs) that are considerably smaller than the wavelength of light. LSP are collective oscillations of the conduction electrons in metal particles upon excitation with incident light. LSP resonance depends on the geometry, size, shape, and dielectric environment of the metallic particles. At resonance, LSP can generate pronounced field enhancements which are in close proximity (~10 nm) to the metals [20–23]. These large near-field enhancements can effectively excite nearby dye molecules.

In this paper we report the plasmonic and light scattering enhancement of DSSCs by incorporating silver-TiO_2 core-shell nanoparticles (Ag@TiO_2 NPs), and TiO_2 NFs, respectively, in the TiO_2 photoanode. Ag@TiO_2 NPs and TiO_2 NFs nanostructures were synthesized and applied separately and in combination in DSSCs. Charge transport properties in the cells are investigated and the measurements obtained are used to study the outcome of the cells parameters. The cell enhancement due to optical scattering of TiO_2 NFs is compared to that due to plasmonic Ag@TiO_2 NPs and an explanation is suggested to justify why the TiO_2 NFs are more effective in cells enhancement than the Ag@TiO_2 NPs.

2. Experimental

2.1. Materials

Ammonia (25–28 wt% NH_3 in water), ethylene glycol (99.9%), Titanium isopropoxide (TTIP 98+%), silver nitrate, ethanol (99.7%), acetone (99.5%), acetic acid (HAc, glacial, >99.5%), isopropanol (IPA, anhydrous, >99.7%), *N*,*N*-dimethylformamide (DMF, anhydrous, >99.5%), titanium (IV) *n*-butoxide (TNBT, >98%), were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Polyvinylpyrrolidone (PVP, Mw = 1,300,000; and PVP-10, Mw = 10,000, >99%) was acquired from Aladdin Chemistry Co., Ltd (China). Ru dye, cis-di(thiocyanato)-bis(2,20-bipyridyl-4,40-dicarboxylate) ruthenium (II) (N719), was purchased from Solaronix (Switzerland). Iodine (I_2, 99.8%) was obtained from Beijing Yili Chemicals (China). Fluorine-doped SnO_2 conductive glass (FTO, sheet resistance 10–15 $\Omega\ sq^{-1}$, Asahi Glass, Japan) was cleaned prior to use by washing with acetone and ethanol, and subsequently drying in air. All chemicals, except ammonia, were used as purchased without any modification.

2.2. Synthesis of Ag NPs

Ag NPs were synthesized using a modified polyol method [24,25]. Ethylene glycol served as the solvent, $AgNO_3$ as the precursor, and PVP-10 as the stabilizing agent. In a typical synthesis, 0.5 g of PVP-10 and 0.1 mmol (0.17 g) of $AgNO_3$ were added to 25 ml of ethylene glycol and the mixture stirred vigorously until $AgNO_3$ dissolved. Then the mixture was heated to 120 °C at a constant rate of 1–7.5 $^{\circ}C\ min^{-1}$. The temperature was kept at 120 °C for 1 h under vigorous stirring and then cooled to room temperature.

2.3. Preparation of Ag@TiO_2

To separate Ag NPs from ethylene glycol, 200 ml of acetone was added to the reaction mixture and then centrifuged at 3000 rpm for 7 min. The supernatant was removed, and the NPs were washed with ethanol and centrifuged at 7000 rpm for 15 min. After removing the supernatant, the NPs were dispersed in 18 ml of ethanol and 2 ml of 4% ammonia in ethanol. Subsequently, this solution was stirred and sonicated for at least 45 min. To coat with TiO_2 shell, 6 μl of TTIP in 1 ml of ethanol was added into the solution under vigorous stirring. The mixture was kept stirring for 24 h at room temperature in the dark.

2.4. Preparation of TiO_2 NFs by electrospinning

To prepare TiO_2 NFs, 1.08 g of TNBT, 1.08 g PVP (Mw = 1,300,000), 5 ml of IPA, 5 ml of DMF, and 1.0 ml of acetic acid were mixed at room temperature [26]. The resultant transparent mixture was loaded into a syringe having a 21-gauge blunt end needle. During the electrospinning, a positive high voltage of 15 kV was applied to the needle, and the feed rate of 1.0 ml/h was maintained using a syringe pump (TS2-60 dual syringe pump, LongerPump, China). The precursor nanofibers jet was collected on an electrically grounded aluminum foil that covered a plat support perpendicular to the needle axis. The distance between the tip of the needle and the collector (aluminum foil) was kept at 13 cm. The as-prepared nanofibers were kept in open air at room temperature for 12 h to allow the TNBT in the nanofibers to hydrolyze. The as-spun nanofibers were peeled off from the aluminum foil and placed in a furnace, which was heated from room temperature to 500 °C at the heating rate of 10 °C. The temperature was maintained at 500 °C for 6 h in constant flow of air to completely burn off and remove the organic contents, and then allowed to cool to room temperature.

2.5. Preparation of photoanodes

Four films containing different weight percents (wt%) of TiO_2, Ag@TiO_2 NPs, and TiO_2 NFs listed in Table 1 below in were prepared. Pastes containing NFs were prepared by first dispersing NFs in ethanol by sonication for 30 min and then mixing with TiO_2 colloids for at least 30 min. Thereafter, the mixture was concentrated to remove ethanol and reduce the water content by rotary evaporation. Similar process was carried out for pastes containing Ag@TiO_2 NPs, except that the NPs did not need to be dissolved in ethanol because it was already dispersed in ethanol. Photoanode of each paste was prepared by doctor-blading on a clean FTO glass, followed by sintering at 500 °C for 30 min. After sintering, the process was repeated to prepare a second layer, bringing the film thickness to about 11 μm.

2.6. Assembly of DSSCs

The prepared photoanodes were immersed in a 0.5 mM solution of N719 dye in acetonitrile and tert-butyl alcohol (volume ratio of 1:1) and kept at room temperature for 48 h. Then the TiO_2 electrodes were washed with acetonitrile to remove the accumulated dye molecules to ensure that the nanocrystalline TiO_2 was covered with a monolayer of dye molecules, followed by drying at 60 °C in air. The Pt-coated FTO, used as the counter electrode, was prepared by a sputtering method. The electrolyte consisted of 0.1 M 1-propyl-3-methylimidazoliumiodide (PMII), 0.05 M LiI, 0.1 M guanidinium thiocyanate (GNCS), 0.03 M I2 and 0.5 M 4-tert-butylpridine (TBP) in a mixed solvent of acetonitrile and propylene carbonate (PC) (volume ratio of 1:1). Finally, the electrolyte was sandwiched between the photoanode and counter electrode. The active area of the dye-coated TiO_2 film was 0.25 cm^2.

Table 1
Contents of photoanodes of four DSSCs tested. The contents comprising of TiO_2, Ag NPs, and NFs, were evaluated by weight percent (wt%).

Contents (wt%)	Pure TiO_2	TiO_2 + Ag NP	TiO_2 + NF	TiO_2 + Ag NP + NF
TiO_2	100	99.8	88.8	88.6
Ag NPs	–	0.2	–	0.2
NFs	–	–	11.2	11.2