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Silver-loaded anatase nanotubes dispersed plasmonic composite photoanode for dye-sensitized solar cells

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ABSTRACT

In this article, a typical silver-loaded anatase TiO_2 nanotube (Ag-TNTs) was developed and assembled in DSSCs. By blending the Ag-TNTs and TiO_2 nanoparticles as the composite photoanode, this hybrid nanostructure exhibits a promising architecture for accelerating electron transport as well as enhancing dye adsorption. These nanotubes could provide direct charge transfer pathways and increase electrolyte penetration in comparison with the TiO_2 nanoparticles alone network. Moreover, the presence of the Ag nanoparticles could enhance the light harvesting efficiency and promote the charge separation, which further improves the performance of the DSSCs. The DSSC with metal-modified hybrid nanostructures has achieved an efficiency of 8.19% which is about 56% higher than DSSCs based on TiO_2 nanoparticles photoanode with 5.26%.

1. Introduction

In recent years, Dye-sensitized solar cells (DSSC) have attracted much attention and scientific research since 1991 [1]. With the advantages of being inexpensive, light weight, easy-fabrication and flexible, this type of solar cells has become available and considerable for reducing the cost of electricity generation [2]. Today, DSSCs has reached a power conversion efficiency as high as 12.3% [3]. A number of factors influence the performance of DSSCs. In particular, enhancing light-harvesting efficiency (LHE) and promoting the carrier transfer in film are the most desired factors to improve the performance of the DSSCs [4]. Developing one-dimensional (1D) architecture instead of random nanocrystalline structures as photoanode is a potential way for the better performance of DSSCs. Such as nanotubes, [5] nanowires [6] and other array structures, [7] can act as the single crystal and be beneficial of rapid electron transport. However, the major problems of 1D nanostructures are their poor adhesion with substrates, which leads to an insufficient surface area. Consequently, hybrid nanostructures, TiO_2 nanoparticles/1D nanostructures composite electrode have recently been expected as a more effective architecture for electron transport as well as dye adsorption [8,9]. The existence of the 1D structure is beneficial in electrolyte penetration and light scattering, and leads to the rapid electron transport in photoanode [10,11]. Also the hybrid structures without losing high surface area promise the enough absorbed dyes.

Besides the development of the hybrid nanostructure, surface plasmon resonance (SPR) of metal nanostructures has been regarded as another promising way to improve the performance of photovoltaic devices [12]. SPR effect is a light-induced collective oscillation of conduction band

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electrons on the surface of metal nanostructures [13]. A lot of related nanostructures have been designed and assembled in DSSCs to increase the light absorption and accelerate the charge separation. In this case, combining the hybrid architecture and SPR effect in DSSCs is expected to further improve the performance of photovoltaic devices by exploiting metal-modified hybrid photoanode.

Guided by this principle, we designed a kind of unique Ag-loaded titania nanotubes (Ag-TNTs) and prepared the Ag-TNTs/TiO_2 nanoparticles (NPs) composite photoanode in DSSCs. A dramatic increase in efficiency (8.19%) is achieved in device of Ag-TNTs/TiO_2 NPs in compared with that of TiO_2 NPs (5.26%). Our study shows that beyond the advantage of TNTs, the presence of Ag nanoparticles also delivers superior performance on photoelectric and photocatalytic properties. SPR effect stimulated by the Ag could enhance the light absorption of dye and the generation of the photoelectrons [14]. As to the electrical aspect, Ag nanoparticles could play a role as the electrons transport-separation center, which accelerated the electron to move through the photoanode network and reduced the charge recombination [15]. Furthermore, this type of photoanode can be fabricated by an ordinary paste coating technique. The high-efficiency, cost-effective and widely applicable electrodes have good prospects for developing the performance of the DSSCs.

2. Experiment details

2.1. Synthesis of Ag-loaded anatase TiO_2 nanotube

The anatase titanium dioxide nanotubes were prepared by the hydrothermal method [16]. Anatase titania powder 1 g and an aqueous solution of NaOH (50 ml, 10 M) were placed into the Teflon-lined autoclave. The mixture was kept stirred to form a colloidal suspension, then the mixture was sealed and hydrothermally treated at 160 °C for 20 h. The precipitate was separated by filtration and washed with deionized water until a pH value near 7 was reached. The precipitate was then ground in alcohol followed by ultrasonic-assisted dispersion and oven-dried at 60 °C until the sample was fully dried into powder. After that, the initial titanate nanotubes were obtained. The products were annealed at 600 °C for 2 h to crystallize into the anatase phase.

Ag-loaded TNTs were prepared as following: Adding a small amount NaOH to 20 ml ethylene glycol to adjust the PH of solution to 8; Adding 0.2 g anatase TNTs to the solution, then put the mixed solution under ultrasonic dispersion 30 min to form a colloidal suspension, adding 5 ml of the saturated solution of $AgNO_3$ (anhydrous ethanol as the solvent). Put the final mixed solution under magnetic stirring at 50 °C for 9 h, after cooled at room temperature, the mixed solution was centrifugal washing with anhydrous ethanol three times, then the precipitate was fully dried at 50 °C, at last we will get dark brown powder signed as the Ag-TNTs.

0.1 g original Ag-TNTs was added into 30 ml deionized water, then 0.02 g titanium tetraisopropoxide (TTIP) as the TiO_2 precursor was added in the solution, and stirring was continued for an additional 30 min at 60 °C to ensure completion of the reaction. Ag-TNTs with thin TiO_2 shell layer around the Ag nanoparticles were then obtained. The solution was washed several times and centrifuged at 3000 rpm to remove TTIP.

2.2. Fabrication of photoanodes and DSSCs

Glass substrates coated FTO (Nippon Sheet Glass, Japan, 2.2 mm thickness, 14 $\Omega\,\square^{-1}$) were cleaned in a detergent solution for 30 min in an ultrasonic bath, rinsed with deionized water, isopropanol and ethanol for 30 min successively. The pure TiO_2 pastes were prepared by TiO_2 powder (Degussa, P25), devices with different photoanodes were synthesized by stirring various pure nanotubes and Ag-loaded nanotubes and into the TiO_2 pastes according to a series of mass ratios (TiO_2 NPs = 100%; TNTs = 5%, 10%, 20%, 30%, 50%, 100%; Ag-TNTs = 5%, 10%, 20%, 30%). Then these kinds of transparent TiO_2 pastes were screen-printed onto the FTO as the transparent layer, then the coated films were dried at temperature of 125 °C for 6 min. This screen-printing procedure with the paste was repeated to obtain an appropriate thickness of 8 μm of TiO_2 for the working electrode. The coated substrates were thermally treated under an air flow at 325 °C for 5 min, 375 °C for 10 min, 450 °C for 15 min and 500 °C for 15 min, respectively. After cooling down to 80 °C, the TiO_2 electrode was stained by immersing it into a dye solution containing N719 sensitizer (300 μM) in a mixture of acetonitrile and tert-butyl alcohol (volume ratio: 1:1) overnight. The TiO_2 photoanodes absorbed dye and 2 nm Pt counter electrodes were assembled into a sealed sandwich-type cell by a 60 μm hot-melt ionomer film Bynel (DuPont) as a spacer between the electrodes. A drop of the electrolyte solution, 0.6 M 1-butyl-3-methyl imidazolium iodide (BMII), 0.03 MI_2, 0.02 M LiI, 0.10 M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15), was injected into the cell.

2.3. Characterization

The morphology of the AgNW@TiO_2 was investigated by scanning electron microscopy (SEM) (Quanta 250, FEI) and transmission electron microscope (TEM) (2100, JEOL). The chemical species were analyzed by Energy-dispersive X-ray spectroscopy (EDX) (EDAX, Quanta 250, FEI). The crystalline structure of the various TiO_2 films was determined by X-ray diffraction (XRD) (D/MAX-2400, Rigaku, Japan). The UV–Vis absorption spectra were obtained on a UV–Vis spectrophotometer (Fluoromax 4, HORIBA Jobin Yvon, USA). The Incident Photon-to-current Conversion Efficiency (IPCE) was evaluated by the solar cell quantum efficiency measurement system (SolarCellScan 100, Zolix instruments. Co. Ltd). The photocurrent density-voltage characteristics were evaluated by an AAA solar simulator (XES-301S, SAN-EI Electric. Co. Ltd.), AM 1.5G illumination (100 mW cm^{-2} in intensity), and a Keithley digital source meter (Model 2602). Electrochemical impedance spectra (EIS) of the cells were evaluated using CHI-660D over the frequency range of 1 Hz ~ 100 KHz under the conditions