Journal of Alloys and Compounds 773 (2019) 743–751

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Bilayer films using broadband nanoparticles and mesoporous TiO_2 for high efficient dye sensitized solar cells

Haoran Li [a, b], Yurong He [a, b, *], Xinzhi Wang [a, b], Dan Liu [a, b], Ziyu Liu [a, b]

[a] *School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, People's Republic of China*
[b] *Heilongjiang Key Laboratory of New Energy Storage Materials and Processes, Harbin Institute of Technology, Harbin 150001, People's Republic of China*

ARTICLE INFO

Article history:
Received 24 June 2018
Received in revised form
20 September 2018
Accepted 23 September 2018
Available online 24 September 2018

Keywords:
Dye-sensitized solar cells
Broadband absorption
Core–shell plasmon harvesting
Mesoporous particle scattering
Metal/semiconductor interface

ABSTRACT

The improvement of the power-conversion efficiency of dye-sensitized solar cells (DSCs) has slowed down in recent years due to limited light absorption of the dyes in the near-infrared region. In this study, we present a novel strategy that uses ultra-broadband core–shell Ag@TiO_2 nanoparticles and mesoporous TiO_2 particles to improve light absorption and reduce charge recombination in DSCs. The effect of the concentration of nanoparticles on both photovoltaic performance and charge recombination is studied. The results show that Ag@TiO_2 nanoparticles can significantly improve the short-circuit current of DSCs and reduce the charge-transfer resistance at the TiO_2-dye/electrolyte interface. These are key factors to achieve high power-conversion efficiency. A power-conversion efficiency of 8.34% is achieved by integrating core–shell NPs (0.6 wt%) with pure P25 TiO_2 particles. This efficiency can be improved further (to 10.02%) by depositing a layer of mesoporous TiO_2 particles, which increases the propagation distance of incoming light. The good interconnection between the TiO_2 crystals of mesoporous particles and the faceted nanocrystal surface enhance electron transport. This work shows a new route to speed-up the transfer of photo-generated carriers, and to split electron-hole pairs more efficiently.

1. Introduction

Dye-sensitized solar cells (DSCs) continue to attract attention by researchers and industries due to their potential advantages with regard to low cost, simple fabrication, and flexible solar applications [1,2]. Recently, a power-conversion efficiency (η) of 28.9% under indoor light irradiation, which represents an η of ~11.3% under air mass 1.5 global sunlight, has been achieved by Grätzel's group [3]. The cell performance depends strongly on the quality of each device component, which includes the nanocrystalline TiO_2 photo-anode film, dye sensitizer, redox electrolyte, and counter electrode. The dye molecules determine the efficiency of the photon collection and electron excitation, which is a key factor for the overall efficiency of DSCs [4]. In highly efficient DSCs, the dye should absorb a large part of the solar spectrum, especially wavelengths ranging from visible to near-infrared [5]. Although some methods were found to improve the molecular structure of dyes to increase some aspects of light absorption, the overall efficiency of DSCs did not improve sufficiently because the light absorption at the absorption peak of the dyes decreased [6].

Some materials have show excellent absorption in near-infrared spectral region, which also improve both separation and transport of photo-generated electron-hole pairs [7]. An attractive method is the use of surface plasmon resonance (SPR) effect in noble metal nanoparticles (NPs) such as Au and Ag [8–10]. Saravanan et al. [11] mixed green synthesized bare Ag NPs with P25 powder, which yielded a modest η of ~3.6%. When plasmons are utilized, a higher photocurrent and/or photovoltage can be obtained via SPR effect, absorption, and scattered light, which produces a strong electric field and alters the density of states of vicinal materials [12,13]. After optimizing the Au NPs concentration, improvements of the photocurrent density (by 26.42%) and the η (by 66.85%) were reported [6]. The η increased by about 24% after coating spherical Ag NPs (with a diameter of 28 mm) onto a TiO_2 photo-electrode [14]. However, both charge recombination and a back reaction of photo-induced charge-carriers occur owing to the erosion of the NP surfaces when the bare NPs are in direct contact with both dye and electrolyte [15,16]. Moreover, the NPs can also serve as electron traps, which reduces the electron collection efficiency [17]. To address these problems, the NPs are usually coated with a thin layer

---

* Corresponding author. School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, People's Republic of China.
E-mail address: rong@hit.edu.cn (Y. He).

https://doi.org/10.1016/j.jallcom.2018.09.279

of semiconductor materials, e.g., SiO_2 [15,18], and TiO_2 [19,20]. Due to the synergetic effect between electron transport and plasmonic enhancement, devices with Ag@TiO_2 NPs show a significant increase in photocurrent density (from 12.46 to 16.46 mA/cm^2) compared to DSCs with TiO_2 NPs film only [21]. Service as a typical semiconductor, TiO_2 can charge the metal core, which enhances both short-circuit current and open-circuit voltage [22]. Furthermore, the SPR bandwidths of Au and Ag NPs concentrate around 400–550 nm. Compared to Au NP, nano-sized Ag may be more suitable for photon collection and electron excitation because of the stronger near-field enhancement effect and lower price. One of the drawbacks of Ag NPs is that their absorption bandwidth is rather narrow [23]. For this reason, nanocomposite photoanodes with tunable plasmonic properties, which were assembled from multi-shaped Ag NPs, were applied [5,24]. It is noteworthy that excessive light absorption should be avoided because some electrons may recombine with the holes of the dye or be backward transferred [25], which decreases η. Nbelayim et al. [26] prepared DSCs using Ag@TiO_2 NPs-doped TiO_2 photoanodes with a wide range of doping concentrations. Unfortunately, their devices showed a modest η due to the charge recombination at a high charge-density.

A photoanode made of small TiO_2 NPs is too transparent to scatter visible light [27]. Furthermore, a considerable amount of incoming light passes directly through the NPs and cannot be absorbed efficiently. Thanks to the discovery that the mesoporous (MS) TiO_2 particles in DSCs harvest light more effectively, they are expected to be good candidates as scattering layers and yield a higher η [28,29]. The mesoporous TiO_2 structures in DSCs provide high surface-areas, which results in the efficient adsorption of dye molecules [30]. Moreover, they shorten the diffusion path of guest molecules within the substrates [29].

In our previous work [31], core–shell Ag@TiO_2 nanoparticles (CS NPs, with a 19.7 nm core diameter and 2.2 nm shell thickness), which showed a sunlight-matched plasmon peak (located at 474 nm) as well as absorption for visible wavelengths, were synthesized. Inspired by the excellent absorbance, in this work, we introduced the CS NPs to enhance light harvesting and reduce charge recombination in DSCs. The main contributions of this paper include: (1) the effect of CS NP concentration (0.0–1.0%, w/w) on photovoltaic conversion and charge transfer-recombination was studied; (2) to further improve the photocurrent conversion, a bilayer device consisting of a CS NPs/TiO_2 layer for light harvesting and a MS TiO_2 layer to scatter light back was fabricated and optimized. Each of the two approaches to improve the performance of DSC have been considered previously, but we fancifully combined them in one DSC to obtain higher efficiency. To the best of our knowledge, this is a novel report of a double-layer structured DSC that combines the advantages of SPR harvesting with MS particle scattering.

2. Materials and methods

2.1. Chemicals

Titanium tetrachloride ($TiCl_4$), ethanol, α-terpineol, acetonitrile, isopropanol, tertiary butanol, hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), polyethylene glycol, OP-10 emulsifier, sodium hydroxide, acetylacetone, and titanium butoxide were purchased from Aladdin Industrial Corporation, China. TiO_2 powder (P25) was purchased from Degussa, Germany. Fluorine-doped tin oxide (FTO) glass plates with a square resistance of 15Ω/□ and a thickness of 2.3 mm were purchased from Nippon Sheet Glass, Japan. The dye (N719) was purchased from Dyesol, Australia. Ethyl cellulose and the iodide-ion electrolyte (AN-I) were purchased from OPV Tech New Energy Co., Ltd., China. The surlyn film with a thickness of 60 μm was purchased from Solaronix, Switzerland.

2.2. Synthesis of the particles

Ag NPs with a diameter of about 20 nm and CS NPs with the same core diameter and 2.2-nm thickness were synthesized using the solvothermal method described in Section S1, Supporting Information. To synthesize MS TiO_2 particles, the aldol condensation reaction of acetylacetone in isopropanol was employed. Typically, 30 mL acetylacetone was mixed with 20 mL isopropyl alcohol under vigorous stirring for 10 min. Subsequently, 1.5 mL titanium butoxide was rapidly added to the solution. After stirring for another 20 min, the transparent yellowish mixture was transferred to a 100-ml Teflon-lined stainless steel autoclave. After annealing at 200 °C for 6 h, the yellowish-brown precipitate was collected via centrifugation, washed with ethanol for several times, and then dried at 60 °C.

2.3. Preparation of TiO_2 and CS/TiO_2 paste

Pure TiO_2 paste (named CS 0.0) was prepared as described in Ref. [32]. Two types of pure ethyl cellulose powder, EC-10 (0.113 g) and EC-45 (0.113 g), were dissolved in 10 mL ethanol. Subsequently, 0.5 g P25 powder and 1.667 g α-terpineol were mixed with the ethyl cellulose solution to yield a wet cake. This mixture was then stirred for 60 min and sonicated for 30 min. The solvent was removed through evaporation at 60 °C. The CS NPs/TiO_2 and MS TiO_2 pastes were prepared in the same manner as CS 0.0. CS NPs were mixed with the TiO_2 power in ratios ranging from 0.2 to 1.0% (w/w, named CS 0.2–1.0) before adding them to ethyl cellulose solutions.

2.4. Fabrication of the DSCs

FTO glass plates were used as substrates for both working and counter electrodes. The FTO glass-substrates were cleaned with ethanol in a 500 W ultrasonic wave cleaner (JekenPS-100A) for 30 min, then sonicated and washed with water. Subsequently, the working-electrode glass was immersed in a 0.1 M $TiCl_4$ solution at 70 °C for 30 min, washed with water and ethanol, and annealed at 450 °C for another 30 min. The working electrode was fabricated by doctor-blade depositing the paste onto the $TiCl_4$ pretreated FTO glass plate. Adhesive tape was used as the isolated window. The film thickness was controlled by adjusting the particle concentration in the paste or the number of wipes. The TiO_2 electrode was heated stepwise at 325, 375, 450, and 500 °C for 5, 5, 15, and 15 min, respectively [33–35], with a heating rate of 2 °C/min. After cooling, it was treated with $TiCl_4$ solution and sintered again, as described above. After cooling to 120 °C, the electrode was collected and immersed in 0.5 mM N719 dye solution, in a mixture of acetonitrile and tertiary butanol (v/v, 1:1), for 24 h. The counter electrode was fabricated by spin-coating one drop of H_2PtCl_6 solution (0.3 g $H_2PtCl_6 \cdot 6H_2O$, 0.1 g polyethylene glycol, and 40 μL OP-10 emulsifier in 4 mL isopropanol) onto the FTO glass plate at 1000 rpm, followed by annealing at 500 °C for 5 min using a heat gun, and another 30 min in a muffle furnace. The TiO_2 anode and the counter electrode were assembled into a sandwich-type cell and sealed with surlyn film via hot-pressing at 125 °C and 0.38 mPa for 15 s. A drop of iodide-ion based electrolyte was injected through a 1-mm-diameter hole into the counter electrode. The injection hole was subsequently sealed using thermoplastic film and cover glass.