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Comparison of two ways using Ag nanoparticles to improve the performance of dye-sensitized solar cells

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ABSTRACT

The photoanode plays an important role in the dye-sensitized solar cells (DSSCs). Herein, two ways adding Ag nanoparticles into the photoanode successfully improved the performance of DSSCs. One is that Ag nanoparticles were mixed with P25 powders (named mixture with Ag), the other is that a thin layer of Ag nanoparticles was added between FTO and P25 (named Ag layer). As a result, the best DSSCs based on the two ways achieved a power conversion efficiency (PCE) of 7.09% (mixture) and 6.97% (layer) respectively, indicating a ~19% enhancement compared with that of the pure P25 DSSC (5.94%). By comparing, the mixture with Ag DSSCs was found to show better dye adsorption, catalytic effect and optical absorption by the local surface plasma resonance (LSPR) effect, and the Ag layer DSSCs was mainly attributed to the Mie scattering effect and improved interfacial charge transfer. However, no matter what kind of ways, the excess and concentrated Ag nanoparticles were found to become the recombination centers to boost the interfacial recombination of photo-excited charges.

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1. Introduction

As a kind of environmental friendly and renewable energy production, solar cells have been paid more and more attention by global researchers [1]. Dye-sensitized solar cells (DSSCs), a potential candidate for next generation solar cells has been studied extensively for their many irreplaceable advantages such as low-cost materials and simple fabrication procedures [2,3]. A typical DSSC consists of the photoanode, dye, electrolyte and cathode [4]. Among them, the photoanode plays a major role since the factors such as the adsorption of dye molecules [5] and the transmission of electrons [6]. Hence, in order to improve the power conversion efficiency (PCE), many studies have been conducted to improve the photoanode material of the DSSCs.

It is well known that one promising strategy is to incorporate some noble metallic nanoparticles such as Au, Ag or Pt nanoparticles into the TiO_2 photoanode of DSSCs to improve chemical and electronic properties of the photoanode material by the localized surface plasmon resonance (LSPR) effect or other effects [7–10]. LSPR is generated by collective electron charge oscillations in metallic nanoparticles that are excited by light [11]. They exhibit enhanced near-field amplitude at the resonance wavelength so that the noble metal nanoparticles decorated on TiO_2 photoanode of DSSCs exhibit stronger optical behavior in the ultraviolet–visible light region [12,13]. Moreover, it has been also reported that the noble metallic nanoparticles can exhibit a strong scattering effect to enhance light harvesting [14–16] or improve interfacial charge transfer to retard charge recombination [17] in the DSSCs. Consequently, this strategy has been proved to be a very effective method to optimize performance of DSSCs.

So far, most of the researchers using this strategy have focused on loading Ag nanoparticles onto various morphologies [18–21], or making different morphologies of Ag nanoparticles to enhance DSSCs conversion efficiency [22–24]. Only Kim et al. have researched the effects of the quasi-monolayer of Ag nanoparticles between the layer of TiO_2 nanoparticles and the scattering layer [25], and only a few people such as Guo et al. and Qi et al. have discussed the effects of photoanodes made by Ag@TiO_2 nanoparticles in the DSSCs [7,26]. However, there are few studies on the comparison of the different effects of Ag nanoparticles at different locations of the photoanodes. These differences are worthy investigating.

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Herein, two different ways of adding Ag nanoparticles into the photoanode were explored and compared. One is that Ag nanoparticles were mixed with P25 powders (named mixture with Ag), the other is that a thin layer of Ag nanoparticles was added between FTO and P25 (named Ag layer). As expected, compared to the pure P25 cells, the adding of Ag nanoparticles improve the power conversion efficiency of the DSSCs greatly. More importantly, in this study, the different effects of Ag nanoparticles in these photoanodes of DSSCs are revealed.

2. Experimental

All the reagents in the experiments were analytical grade and used without further purification. The fabrication processes of mixture with Ag photoanode and Ag layer photoanode were shown in Fig. 1.

2.1. Preparation of mixture with Ag composites

As shown in Fig. 1(a) and (b), mixture with Ag composites of different atomic percentages (1.0 at %, 1.2 at % and 1.4 at %) were synthesized by a simple method. Firstly, 3 g of the commercial TiO_2 powder (Degussa P25) was added to 50 mL of deionized water. The solutions were ultrasonicated and stirred for 30 min alternately. Then, 1.265 mL, 1.521 mL and 1.778 mL of 0.6 M $AgNO_3$ aqueous solutions were added separately to the homogeneous solutions under stirring. After stirring continuously for 24 h under the light, the products were centrifuged and washed with absolute ethyl alcohol and deionized water several times, respectively. At last, the obtained products were dried in an oven at 80 °C overnight and reduced at 300 °C for 2 h with a heating rate of 5 °C min^{-1} in 10% H_2.

2.2. Preparation of Ag layer FTO glasses

The preparation of Ag layer FTO glasses is shown in Fig. 1(d) and (e), which consists of two steps ($TiCl_4$ treatment and $AgNO_3$ treatment). The FTO glasses (resistivity of 14 Ω per square, Nippon Sheet Glass, Japan), were ultrasonically cleaned for 30 min in deionized water, anhydrous ethanol and isopropyl alcohol respectively. Firstly, the cleaned FTO glasses were immersed in a 25 mL $TiCl_4$ aqueous solution (0.04 M) in the water bath at 70 °C for 30 min. Then the FTO glasses were washed several times with deionized water and anhydrous ethanol, and the FTO glasses were calcined at 450 °C for 30 min with a heating rate of 2 °C min^{-1} in air. Secondly, the $TiCl_4$-treated FTO glasses were placed in the same concentration (0.03 M) of $AgNO_3$ aqueous solution for 100 min, 130 min and 160min, respectively. After that, the FTO glasses were washed with deionized water and reduced at 300 °C for 2 h with a heating rate of 5 °C min^{-1} in 10% H_2 to get the Ag layer FTO glasses.

2.3. Fabrication of the DSSCs

Fabrication of the mixture with Ag DSSCs: to prepare photoanode films, four kinds of viscous pastes based on P25 powder and mixture with Ag composites (1.0 at%, 1.2 at% and 1.4 at%) was prepared firstly. 1 g of the powder sample was mixed with 4 g of terpinol, 0.5 g of ethylcellulose and 9 g of anhydrous ethanol. The mixture was strongly stirred for 24 h and then removed ethanol with the helping of the rotary evaporation to get the pastes.

As shown in Fig. 1(c), each paste was spread onto an as-cleaned and $TiCl_4$-treated FTO glass via the doctor blade technique. After drying at 120 °C for 15 min, the photoanode films were subsequently annealed at 450 °C for 30 min in air. Then the films were treated with $TiCl_4$ solution as mentioned above. Subsequently, the four films were loaded with dye by immersing it in a 0.4 mM dye solution (dye: N-719, solvent: anhydrous ethanol) for 24 h at room temperature.

At last, the DSSCs were assembled by the photoanode film, I^-/I^{3-} electrolyte and a Pt-coated FTO counter electrode using a vacuum back-filled method. The P25, 1.0 at%, 1.2 at% and 1.4 at% mixture with Ag DSSCs were denoted as P25, M-Ag-1, M-Ag-2 and M-Ag-3, respectively.

Fabrication of the Ag layer DSSCs: as shown in Fig. 1(f), by the doctor blade technique, the P25 paste was spread onto the prepared Ag layer FTO glasses which were immersed in $AgNO_3$ solution for different time. After drying at 120 °C for 15 min, the resulting three films were subsequently annealed at 450 °C for 30 min in air. Then the films were treated with $TiCl_4$ solution as mentioned above. Finally, sensitization of photoanodes and assembly of DSSCs were consistent with above steps. The 100min, 130min and 160min Ag layer DSSCs were denoted as Ag-L-1, Ag-L-2 and Ag-L-3, respectively.

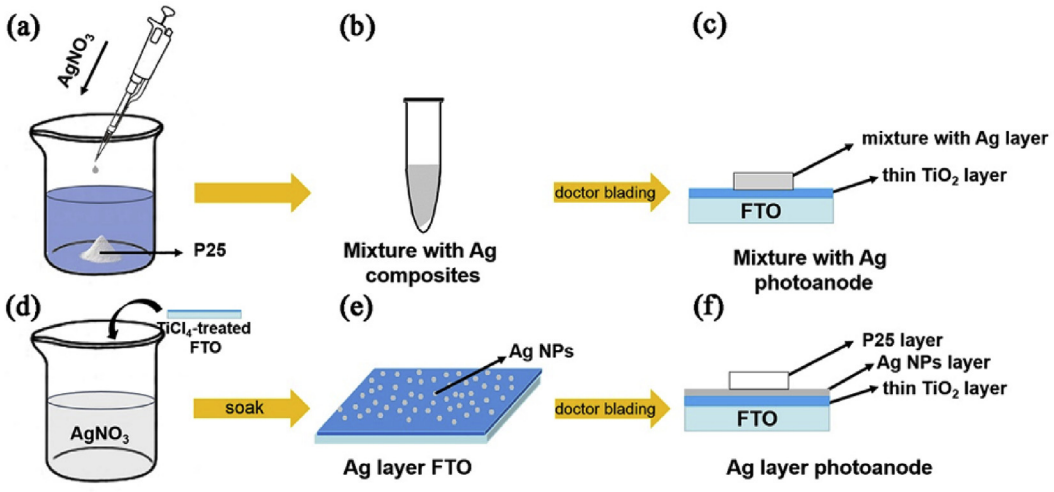

Fig. 1. Simply schematic illustration of the fabrication process of mixture with Ag photoanode (a–c) and Ag layer photoanode (d–e).

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