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Aggregation effect of silver nanoparticles on the energy conversion efficiency of the surface plasmon-enhanced dye-sensitized solar cells

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Abstract

We have fabricated Ag nanoplates that have two broad extinction bands in the visible region, which are found in similar spectral regions of two visible absorption bands of N719 dye. The efficiency of the dye-sensitized solar cells (DSSCs) based on composite films consisting of TiO_2 and Ag nanoplates was affected by the degree of the spectral overlap between these bands and the weight percent of Ag nanoplates to TiO_2 nanoparticles (NPs). By optimizing the size and geometry of Ag nanoplates and the weight percent of Ag nanoplates to TiO_2 NPs, the energy conversion efficiency was improved from 8.7% to 10.3%. The energy conversion efficiency was significantly enhanced by including Ag nanoplates instead of Ag nanospheres. However, the efficiency increased up to 0.35 wt% of Ag nanoplates but then decreased when the weight percent was further increased. The cause of the efficiency decrease for a further increase of Ag weight percent was studied. N719 dye has two strong absorption bands centered at 393 and 533 nm, while black dye centered at 410 and 610 nm. The in-plane mode of the localized surface plasmon of Ag nanoplates near 530 nm is red-shifted when they are aggregated. Therefore, an enhanced absorption is expected on or near the surface of the isolated Ag nanoplates for N719 dye, while aggregated ones for black dye. The extinction of the TiO_2 NP/Ag nanoplate composite films adsorbed N719 dye was the highest when the weight percent of Ag nanoplates was 0.35 wt%, while that adsorbed black dye increased with increasing the weight percent up to 0.7 wt%. This means that aggregation of Ag nanoplates took place significantly when the percent was higher than 0.35 wt%. When the weight percent of Ag nanoplates was higher than 0.35 wt%, the efficiency of the plasmon enhanced absorption of N719 dye might be decreased by aggregation and consequently the energy conversion efficiency was decreased. Therefore, it is suggested that to get a high efficiency of surface plasmon-enhanced DSSCs, the aggregation of metal NPs should be controlled in the fabrication of the composite films.

Keywords: Dye-sensitized solar cell; Silver nanoplates; Localized surface plasmon; Plasmon enhanced absorption

1. Introduction

Dye-sensitized solar cells (DSSCs) have received much attention because of their high energy conversion efficiency and low cost (O'Regan and Gratzel, 1991; Grätzel, 2005; Wang et al., 2004; Kim et al., 2009). In the fabrication of DSSCs, mesoporous TiO_2 films and ruthenium sensitizers have been used as the main component materials. The energy conversion efficiency of DSSCs is affected by several factors: molar absorption coefficients, energetically suitable HOMO–LUMO levels, available surface area for dyes, transport kinetics of the electrons, regeneration by a redox couple, and losses of recombination and back reactions

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(Ghicov et al., 2009). The efficiency of DSSCs will increase when the number of dye molecules adsorbed on a TiO_2 film increases. One could consider increasing the total number of dye molecules adsorbing on TiO_2 film by increasing the thickness of TiO_2 film. However, the electron transfer length to an electrode may also increase as a result of an increase in TiO_2 film thickness. Consequently, an increase in TiO_2 film thickness would not cause a linear increase in DSSC efficiency *via* the increase of dye molecule adsorption. It will be very advantageous if one could increase the effective absorption of dye molecules without increasing the thickness of TiO_2 film.

Diverse optical properties of metal nanoparticles (NPs) like silver and gold are generated mainly by their localized surface plasmon. Localized surface plasmon is excited when the frequency of light photons matches the natural frequency of the collective oscillation of conduction electrons in metal NPs. One of the most interesting features of localized surface plasmon resonance behavior is an enhanced light absorption of molecules that are adsorbed on noble NPs like silver or gold (Ihara et al., 1997; Standridge et al., 2009a,b). The principle of localized surface plasmon has been applied to increase the optical absorption and/or photocurrent in a wide range of solar cell configurations (Ihara et al., 1997; Standridge et al., 2009a,b; Baba et al., 2011; Schaadt et al., 2005; Derkacs et al., 2006; Pillai et al., 2007; Wu et al., 2011; Westphalen et al., 2000; Rand et al., 2004; Morfa et al., 2008; Konda et al., 2007; Jiang et al., 2013; Hagglund et al., 2008; Standridge et al., 2009a,b; Zhao et al., 1997; Wen et al., 2000; Ding et al., 2011; Brown et al., 2011; Muduli et al., 2012; Xu et al., 2014). Therefore, in order to optimize the surface plasmon effect, the size and/or shape of NPs should be controlled to match their absorption band to that of dyes. It is known that bare metal NPs have direct contact with the dye and the electrolyte. It is also known that the recombination and back reaction of photogenerated carriers can take place (Ihara et al., 1997). Therefore, the surface of metal NPs should be protected with an insulator or semiconductor. In order to overcome these problems, core–shell NPs, in which the surfaces of metal NPs are protected as such, have recently been adapted (Brown et al., 2011; Qi et al., 2011; Jeong et al., 2011; Choi et al., 2012; Dang et al., 2013). The energy conversion efficiency of DSSCs based on N719 dye has been improved significantly by adapting core–shell Au NPs (Choi et al., 2012; Dang et al., 2013; Ng et al., 2014). These spherical Au NPs have only one plasmonic absorption band near 530 nm in the visible region, while N719 dye has two broad absorption bands centered at 393 and 533 nm. For all the plasmon-enhanced DSSCs reported, the energy conversion efficiency increased up to a certain weight percent of Ag or Au NPs to TiO_2 NPs but then decreased as the weight percent was increased further (Brown et al., 2011; Qi et al., 2011; Jeong et al., 2011; Choi et al., 2012; Dang et al., 2013; Ng et al., 2014).

Here, we tried to control the size and geometry of Ag nanoplates such that the localized surface plasmon resonances match to two visible absorption bands of N719 dye. By optimizing the size and geometry of Ag nanoplates and the weight percent of Ag nanoplates to TiO_2 NPs, we could achieve energy conversion efficiency for the DSSCs based on TiO_2/Ag nanoplates by up to 10.3%. The energy conversion efficiency increased up to a certain weight percent of Ag nanoplates but then decreased when the weight percent was further increased. The cause of the efficiency decrease for a further increase of Ag weight percent was studied.

2. Experimental section

2.1. Preparation of Ag seeds

0.30 mL of 10 mM silver nitrate solution and 20 mL of 1 mM trisodium citrate solution were mixed together. To this solution, 1.8 mL of ice-cold 10 mM sodium borohydride was rapidly injected and mixture stirred vigorously. The whole solution was aged for 3 h at room temperature.

2.2. Preparation of colloidal Ag nanoplates

Ag nanoplates were prepared by a one-step or two-step seed-mediated process. The size of Ag nanoplates was controlled by varying the volume of the Ag seed solution relative to the volume of the trisodium citrate solution. X (1, 2, 4, or 8) mL of the Ag seed solution, (20 – X) mL of 1 mM trisodium citrate solution and 0.2 mL of 20 mM ascorbic acid solution were mixed together. To this solution, 0.80 mL of 10 mM silver nitrate solution was rapidly injected and mixture stirred vigorously. For the second process, 10 mL of the final mixture solution, 10 mL of 1 mM trisodium citrate solution and 0.60 mL of 20 mM ascorbic acid solution were mixed together. To this solution, 0.80 mL of 10 mM silver nitrate solution was rapidly injected and mixture stirred vigorously.

2.3. Fabrication of DSSCs

FTO (fluorine-doped thin oxide) glass was cleaned in a detergent solution in ultrasonic bath for 20 min and rinsed with water. Then it was cleaned again in ethanol for 10 min. A TiO_2 blocking layer was formed on washed FTO glass by spin-coating with 5 wt% of titanium di-isopropoxide bis(acetylacetonate) in butanol and annealed at 450 °C for 1 h. The photoanodes incorporated with Ag nanoplates and TiO_2 NP paste (ratio of Ag nanoplates to TiO_2 NPs is from 0.15 to 0.7 wt%) were prepared with a modified procedure. Controlled amount of Ag nanoplates were mixed with TiO_2 NP paste (T/SP, solaronix) in methyl alcohol, followed by stirring and sonication, and then the solvent was evaporated in vacuum. The TiO_2 NP paste or sets of TiO_2 NP pastes mixed Ag nanoplates were coated onto the FTO glass by the doctor blade