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Preparation of gold and gold–silver alloy nanoparticles for enhancement of plasmonic dye-sensitized solar cells performance

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Abstract

A two-step method was applied to obtain gold–silver alloy nanoparticles (Au–Ag alloy NPs). First, Au and Ag colloids with average particle sizes of 14.80 and 8.47 nm, respectively, were synthesized by pulsed laser ablation of pure metallic targets immersed in ethanol, subsequent mixing, and re-irradiation of individual Au and Ag colloids (volume ratio of 4:1). In this study, a dense layer of porous titanium dioxide (TiO_2) film with a thickness of ~11 μm was deposited directly on the central area of the conductive face of a fluorine tin oxide (FTO) glass by blade doctor method. A specific amount of N719 dye molecules with and without the plasmonic-metal nanoparticles (NPs) was mixed, incorporated into the porous TiO_2 film, and used as photoanode to fabricate dye-sensitized solar cells (DSSCs). The optical and structural properties of the prepared photoanodes before their application to DSSCs were investigated. The photocurrent density–voltage and external quantum efficiency characteristics of the DSSCs fabricated with these photoanodes were also analyzed and discussed. The experimental results confirmed the plasmonic enhancement effects on the performance of DSSCs, which indicated that cells loaded with the plasmonic-metal NPs yielded larger enhancement. The plasmonic effect of the Au–Ag alloy NPs significantly enhanced the broadband light absorption of dye molecules. The best cell was achieved using the photoanode loaded with Au–Ag alloy NPs, exhibiting a power conversion efficiency of 5.81%, which was ~8.4% and 52.1% higher than that of the DSSCs with Au NPs and the reference cell, respectively.

Keywords: Dye-sensitized solar cell; Localized surface plasmon resonance; Optical properties; Photovoltaic performance

1. Introduction

In the last decade, dye-sensitized solar cells (DSSCs) have received much attention because of their attractive properties: low cost, flexible applications and capability of cell performance control under specific range of light intensity and operating temperature (Gao et al., 2008; Hagfeldt et al., 2010; Kim et al., 2015, 2009). Furthermore, a power-conversion efficiency of DSSC with zinc porphyrin dye as sensitizer and cobalt-based redox electrolyte has been dramatically enhanced to 12.3% (Yella et al., 2011). Recently, a new record power conversion efficiency of 15% for perovskite-sensitized solar cells has been reported

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(Burschka et al., 2013). However, the power conversion efficiency of DSSCs is still lower compared with that of silicon-based solar cells (Chander et al., 2014a). DSSC devices that employ porous semiconducting titanium dioxide (TiO_2) films and organometallic dyes as the main component materials can efficiently convert sunlight into electricity. The dye molecules present onto TiO_2 film absorb light in the photoanode, leading to the production of electron–hole pairs and injection of electrons into the conduction band of the TiO_2 film. The dye molecules are regenerated by electrons transferred from an electrolyte, which is reduced at a counter electrode. The optical properties of the photoanode play an important role in improving the performance of DSSC, which will increase when light absorption and electron transfer are enhanced. An increase in the total number of dye molecules adsorbed on TiO_2 film by increasing the thickness of TiO_2 layer can enhance light absorption. However, this change will result in lower charge collection efficiency as a result of a larger electron transfer length to a collecting electrode. In particular, localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs) has been extensively employed to improve light absorption of dye molecules without increasing the thickness of TiO_2 films at the photoanode. Metallic Ag or Au NPs usually interact with the incident light at the visible region to create a plasmon, resulting in alterations in two characteristic properties: an intense absorption characterization at wavelengths resonant with the electron oscillation, and an extremely enhanced electromagnetic field near the particle. The plasmonic properties of metal NPs, such as the absorption intensity of LSPR, plasmon bandwidth, and stability of metal NPs, play a significant role in controlling the light absorption efficiency (Dang et al., 2013; Kawawaki et al., 2013; Qi et al., 1999; Xie et al., 2006).

Research on bimetallic NPs, either as alloys or as core–shell structures, is of great interest with the tremendous development of nanoscience and nanotechnology. This importance can be attributed to the fact that the bimetallic nanoparticle structure exhibits good stability, the ability to absorb light in a wide wavelength range (broad LSPR peak), and capacity to tune the NPs' optical properties compared with that originating from individual NPs (Chen and Chen, 2002; Devarajan et al., 2005; Hu et al., 2005; Ji et al., 2010; Ma et al., 2010; Messina et al., 2012). The prominent properties of bimetallic NPs, especially Au and Ag NPs, have attracted significant attention for many applications in catalysis (Liu et al., 2005; More et al., 2015; Vadakkekara et al., 2014; Yen et al., 2009; Zhang et al., 2007), biosensors (Deng et al., 2011; Dong et al., 2013; Steinbrueck et al., 2011), optics and photovoltaic devices (Baek et al., 2014; Moskovits et al., 2002; Pellegrini et al., 2007; Sharma et al., 2014; Tan et al., 2014; Xu et al., 2013).

The formation of Au–Ag alloy NPs by irradiating the mixture of individual colloids to laser wavelength of 532 nm has been investigated by several research groups (Compagnini et al., 2007; Intartaglia et al., 2013; Messina et al., 2012; Peng et al., 2006). Given that the 532 nm laser wavelength is near the surface plasmon excitation of Au, Ag, and their alloy NPs, these NPs can significantly interact with laser light (Tarasenko et al., 2006). In brief, the mechanism of Au–Ag alloy NPs formation after exposing the mixture of corresponding colloids to laser radiation can be analyzed based on classical thermodynamics. If the laser energy transferred to the NPs is sufficiently large, Ag and Au NPs can melt to form hot atoms and clusters, inducing the interaction of the NPs with other NPs (Peng et al., 2006). A reaction between metal atoms is extremely greater compared with that between a metal atom and a solvent molecule, so the metal atoms will assemble to produce NPs. The Au and Ag metals compose nearly ideal solid solutions at all compositions (Massalski et al., 1990). Thus, mixing of individual NPs colloids is a thermodynamically proper approach to fabricate homogeneous alloy particles. This mechanism can be controlled by adjusting the preparation conditions, such as concentration of the NPs colloids present in the surrounding medium and laser irradiation time.

The present report describes the formation of Ag–Au alloy NPs obtained by a two-step synthetic approach. In this approach, Au and Ag colloidal solutions were separately prepared by pulsed laser ablation of the relevant metallic target in ethanol. Au–Ag alloy NPs were then composed by mixing and re-irradiating the as-prepared Au and Ag colloids with the volume ratio of 4:1. Initially, the optical and structural properties of Au and Ag NPs, as well as Au–Ag alloy NPs, were investigated. Subsequently, their plasmonic effects on optical absorption of photoanode electrodes and the DSSCs performance were investigated. To the best of our knowledge, this study reports a new approach for three reasons: (i) the preparation of plasmonic-metal colloids for fabricating DSSCs has no chemical reagents compared with chemical methods because contamination may impede the ability of light absorption and electron transport in DSSCs (Zhang et al., 2011); (ii) the TiO_2 film is initially synthesized by coating TiO_2 paste only on FTO surface. Subsequently, this film is soaked in a mixture of plasmonic metal colloids and dye molecules solution in order to ensure that dye molecules and metal NPs are within a minimal spatial range to transfer the resonance energy between the two; and (iii) so far not many reports have been established on the plasmonic enhancement effect of Au–Ag alloy NPs for DSSCs performance, although it produces a broad optical absorption band in the visible region of the electromagnetic spectrum, which is essential for DSSCs fabrication.

2. Experimental section

2.1. Materials

Ultrapure deionized water (pH 7 and 18.2 MΩ resistance), acetone (99.5%), and ethanol (99.7%) were used in