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Original Article

Efficiency improvement in dye sensitized solar cells by the plasmonic effect of green synthesized silver nanoparticles

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ABSTRACT

In the present investigation, the power conversion efficiency of dye-sensitized solar cells has been remarkably increased by incorporation of green synthesized silver nanoparticles into TiO_2 photoanodes. Uniform silver nanoparticles were developed by treating silver ions with *Peltophorum pterocarpum* flower extract at room temperature. The obtained silver nanoparticles have been characterized by UV-vis. spectroscopy, X-ray Diffraction analysis and Transmission Electron Microscopy (TEM). The X-ray diffraction analysis showed that the obtained silver nanoparticles were polycrystalline in nature with face centered cubic lattice. Silver nanoparticles, with an approximate size in the range of 20–50 nm were examined by the TEM. The plasmonic nanocomposite material was prepared by mixing different green synthesized silver nanoparticles (Ag content of 1, 2 and 3 wt%) with P25–TiO_2 nanoparticles and used as photoanodes in dye-sensitized solar cells. Due to the plasmonic effect of the modified electrode, the power conversion efficiency of the solar cell was improved from 2.83% to 3.62% with increment around 28% after incorporation of the 2 wt% of the silver nanoparticles. Maximum increases in open-circuit voltage (up to 12.1%) and in short-circuit current density (up to 10.7%) were observed.

1. Introduction

Utilization of renewable energy sources is one of the best eco-friendly options to refrain from using fossil fuels. Making use of solar energy is positively one of the most feasible ways to mitigate the world's energy crisis. The third generation solar cells such as dye-sensitized solar cell (DSSC) and organic solar cell (OSC) have received great attention as a promising technology for renewable energy exploration. DSSCs have numerous advantages, such as flexibility, relatively high power conversion efficiency, low toxicity to the environment and simple fabrication with low cost. DSSC is comprised of an electrolyte sandwiched between a photoanode and a counter electrode. Titanium dioxide (TiO_2) coated with Indium Tin oxide (ITO)/fluorine doped-tin oxide (FTO) transparent conducting glass is used as the photoanode. A dye molecular layer is coated on the surface of TiO_2 as sensitizer. Under light illumination the dye molecules generate electrons. These electrons are injected into the TiO_2 layer to produce electricity. The light trapping plays a major role in the electricity production. Gratzel *et al.* [1] were the first to fabricate a DSSC. Since then significant improvements have been made in the design of the photoanode, dyes [2,3], electrolytes [4,5] counter electrodes [6], the photoanode semiconducting material as well as the redox shuttle to improve the efficiency of DSSCs. Among these, the photoanode plays a crucial role in determining the cell performance. However, it is ventured to achieve maximum power conversion efficiency. This is due to the insufficient sunlight absorption and the consequently low energy conversion efficiency. Generally, the efficiency of a solar cell is directly proportional to the amount and the intensity of the trapped light. A lot of research has been conducted to enhance the light harvesting efficiency of the photoanode. The light absorption by sensitizers (dye) on the photoanode plays an important role in the energy conversion efficiency of DSSC. The light harvesting efficiency of a DSSC depends on the nature of the response dye molecules, the amount of dye molecules adsorbed on the photoanode [7,8] and the

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thickness of the photoanode [9]. When the thickness of the photoanode increases, the electrons are recombined rather than being collected at the electrode due to the extended length of the diffusion path of electrons. So far the TiO_2-based materials stand as one of the most capable materials for DSSC due to their low cost, availability, non-toxicity, safety, large surface area for maximum dye uptake and band structure. Currently the concept of plasmon resonance has been introduced to the DSSC employing noble metals like silver or gold [10]. It is one of the strategies adopted for the further improvement of DSSC efficiency. The localized surface plasmon resonance (LSPR) phenomena of metal nanoparticles enhance the light harvesting efficiency. The LSPR refers to the resonance between the electromagnetic field and the free-electron oscillation. It amplifies the electromagnetic field near the metal nanoparticles, resulting in the plasmon enhanced light absorption by dye sensitizers in DSSC. Recently silver nanoparticle-enabled plasmonic effect has been proposed and demonstrated as a promising approach to achieve light trapping in solar cells because the relative scattering efficiency of silver nanoparticles is higher than that of other noble metals in the visible range [2–5]. H. Choi *et al.* [11] reported that the efficiency of an N719 dye-sensitized solar cell increased from 9.3% to 10.2% and 9.8% upon incorporation of 0.7 wt. % Au@SiO_2 and Au@TiO_2 nanoparticles, respectively. Kim *et al.* [12] achieved an increase of 10.0% in efficiency of DSSC using double-layered composite films consisting of TiO_2/Ag and TiO_2/Au nanoparticles. Synthesis of nanoparticles is presently an important area of research in the strive to find eco-friendly green materials for the application in electrochemistry. Biological methods have emerged as a green alternative, for it is environment-friendly, cost effective and could be easily scaled-up. Eco-friendly green synthesis of metal nanoparticles using only plant extracts and without any harmful chemicals offers a promising scope in nanotechnology. In this present study, the DSSCs have been fabricated by using green synthesized Ag NPs mixed with TiO_2 photoanode and the plasmonic effect of Ag NPs on DSSC has been studied.

2. Experimental

2.1. Materials

Silver nitrate and Titanium dioxide (P25) from Merck & Co. and Degussa, respectively, were used without any further purification. *Peltophorum pterocarpum* (PP) flowers were collected from the premises of Sona College of Technology, Salem, India. Indium tin oxide (ITO) conducting glass slides (10 Ω sq^{-1}) were commercial products of XIN Yan Technology Limited, China. The N7 dye and Iodolyte Z-100 were purchased from Solarnix.

2.2. Synthesis of silver nanoparticles

Silver nanoparticles were prepared according to previous reports [13,14]. Three grams of fresh PP flowers were immersed in 300 mL of boiling distilled water for 30 min and then filtered. The obtained extract was dripped into 100 mL of 0.01 M aqueous silver nitrate solution in a flask with constant gentle stirring. The yellowish brown appearance of the product indicated the formation of the Ag NPs. The stirring was continued for another 1 h. The product was the dried in an oven at 60 °C and stored in the darkness.

2.3. Fabrication of dye-sensitized solar cells

The anode was prepared by coating the ITO conducting plate with P25–TiO_2 nanoparticles. The green synthesized Ag NPs were mixed with the procured P25–TiO_2 nanoparticles in different weight percentages of 1, 2 and 3. Ethanol was used as a solvent for the preparation of a homogeneous paste. The obtained paste was coated on the conducting side of the ITO plate as a thin film using the doctor-blade technique. Also, a reference electrode was prepared without Ag NPs. The thickness of the thin film was about ≈ 10 μm. After the coating of the film the thickness was checked by the dektak profilometer. In order to get a stable film, the coated slides were dried under ambient conditions, then sintered at 450 °C for 30 min in a furnace and finally allowed to cool down to room temperature. The P25–TiO_2 layers without and with Ag NPs were immersed in an ethanol solution of an 0.5 mM of Ruthenium complex based N7 dye for 18 h and kept in darkness at room temperature. The dye-adsorbed photo-anodes were taken out and gently washed with ethanol and then with distilled water to remove the excess dye molecules. DSSCs were then assembled by sandwiching the prepared photoanode with a platinum coated counter electrode, by inserting a polymer film (50 μm) between the two electrodes, and by injecting the redox iodide electrolyte into the space between the two electrodes. The *J/V* characteristics of the devices were determined under visible light illumination using standard solar irradiation of 100 mW/cm^2 (AM1.5) with a JASCO CEP-25BX spectrophotometer. Three devices have been fabricated for each J-V measurement and the average value was taken for calculation. All measurements were performed soon after the preparation of the devices to avoid any change in the photoelectric properties caused by ageing.

3. Results and discussion

3.1. Characterizations of silver nanoparticles

The obtained green synthesized Ag NPs were characterized by UV-Vis. spectroscopy, XRD Analysis, and HR-TEM. The optical property of obtained Ag NPs was studied using UV-Vis spectroscopy. UV-Vis spectroscopy is employed for primary characterization [15] and it is an indirect method to examine the bio-reduction of the metal ions into the metal nanoparticles [16]. Fig. 1 shows the UV–vis (ELICO-BL-198) absorption spectra of the obtained Ag NPs. The absorption band at about 470 nm is apparently due to the surface plasmon resonance (SPR) band of the Ag nanoparticles and so, it confirms the presence of the Ag NPs. The SPR originates from the interaction of light (the electromagnetic radiation) with the free electrons of Ag NPs. This results in the collective excitation oscillations that lead to strong enhancement of the local electromagnetic fields surrounding the nanoparticles [17].

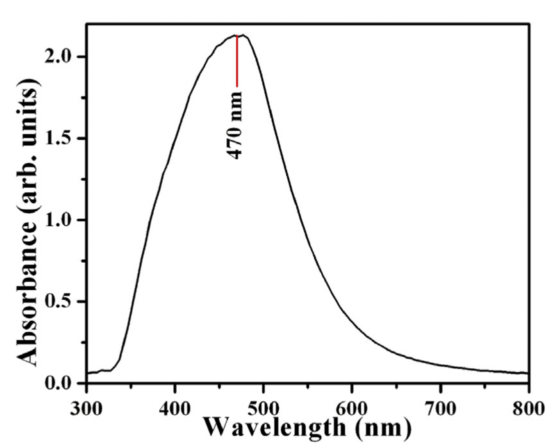

Fig. 1. UV-vis spectra silver nanoparticles.