Solar Energy Materials and Solar Cells 185 (2018) 104–110

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Facile one-pot synthesis of multi-shaped silver nanoparticles with tunable ultra-broadband absorption for efficient light harvesting in dye-sensitized solar cells

Dhavalkumar N. Joshi[a], P. Ilaiyaraja[b], C. Sudakar[b], R. Arun Prasath[a,*]

[a] Laboratory for Energy Materials and Sustainability, Centre for Green Energy Technology, Pondicherry University, Puducherry 605014, India
[b] Multifunctional Materials Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

Keywords:
Broadband absorbance
Multi-shaped AgNPs
Plasmonic
LSPR
DSSCs

ABSTRACT

We report a facile one-pot synthesis of the multi-shaped anisotropic plasmonic Ag nanostructures (Mx-AgNPs) and demonstrated for the broadband plasmonic enhancement in dye-sensitized solar cells (DSSCs). The UV–Vis spectra obtained during the synthesis of AgNPs revealed the fine-tuning of the surface plasmon resonance (SPR) peak and the occurrence of broadband multiple SPR peak with an increase in reaction time. The TEM images confirm the collective presence of different shapes/sizes of the Ag nanoparticles (including sphere, oval, polygon, triangular, rod and some irregular morphologies). The resultant ultra-broadband LSPR from the Mx-AgNPs were utilized to improve the total light absorption coefficient of N719 dye. We observed that the photoanode film incorporated with of Mx-AgNPs enhances light harvesting of the dye up to 60% over an entire visible region. The effects of Mx-AgNPs in the photoanode film on the efficiency and the spectral response of the DSSCs were further evaluated experimentally. Substantial improvement with the considerable broadening in the spectral response was observed in the 'incident photon- to current conversion efficiency' (IPCE) spectra for the plasmonic DSSCs. The 'power conversion efficiency' (PCE) for the best performing plasmonic DSSCs found to improve by ~ 30% for the plasmonic DSSCs. The observed improvement in the efficiency was mainly attributed to the significant enhancement of the light harvesting capacity of the DSSCs resulted by ultra-broadband surface plasmon resonance of the Mx-AgNPs.

1. Introduction

In DSSCs, light harvesting ability of the photoanode is the most important parameter to be considered to improve 'photon conversion efficiency' (PCE) of the device [1–7]. It is well known that the light harvesting of the device can be improved by increasing the thickness of the photoactive layer. However, increasing the thickness beyond the electron diffusion length of photoactive material can have an inferior effect on the performance of the DSSCs [7]. In recent years, several studies have been conducted to improve the light harvesting without manipulating the thickness, which mainly includes (i) to improve the molar extinction coefficient of the dye sensitizers over broad visible and NIR region [8–10], (ii) application of novel mesoporous material with the high surface area, which can improve the adsorption of the dye molecules enhancing the photon absorption efficiency [11–13], (iii) increasing the 'optical path length' of photoanode by applying hierarchical nanostructure with strong light scattering [2,14–16] and (iv) the utilization of the 'localised surface plasmon resonance' (LSPR) and 'far-field scattering' (FFS) properties of the plasmonic nanoparticles (Au, Ag, Al, *etc.*) for improving the 'light scattering' and 'total light absorption coefficient' (α) of the dye molecules in photoanode [7,17–20]. Although there are several studies on the development of the new dye-sensitizers, the light absorption capacity is still restricted for the existing dyes. The best performing N719 and N749 dye have strong absorption around 500 nm wavelength. However, they possess very weak absorption coefficient for longer wavelength region. Further, the application of new dye sensitizers and changing the morphology of the semiconductor oxide results in a change in their energy band positions relative to the redox potential of the electrolyte, which significantly affects charge separation kinetics [7]. In last decade, utilization of LSPR and FFS properties of noble metals (like Ag, Au, Cu, Ni, *etc.*) have emerged as a promising approach to improve the light harvesting in the solar cells [7,17–20]. Moreover, The LSPR and FFS strongly depend on the shape and the size of these plasmonic nanoparticles [19,21,22]. Hence, various plasmonic metal nanoparticles morphologies like a sphere, prism, nanorod, nanowire, popcorn, *etc.* are

* Corresponding author.
E-mail address: raprasath.get@pondiuni.edu.in (R.A. Prasath).

https://doi.org/10.1016/j.solmat.2018.05.018
Received 14 November 2017; Received in revised form 27 March 2018; Accepted 7 May 2018

being explored to tune the surface plasmon resonance and boost light absorption of the dye molecules at different wavelength regime depending on their shapes and sizes [18,23–26]. There are several reports for the enhanced light harvesting *via* plasmonic nanoparticles in DSSCs. However, most of the reported literature primarily focused on spherical/mono-shaped nanoparticles, which is restricted to narrow SPR based enhancement. We demonstrate the use of plasmonic nanoparticles having multiple shapes and sizes with ultra-broadband SPR in the range of 300–1000 nm for application in DSSCs. Recently, improvement in the PCE of 16% was reported by using broadband LSPR enhancement from pop-corn shaped alloy nanoparticles [23]. Ye Zheng *et al.* has also demonstrated plasmon induced broadband light-harvesting using a mixture of gold nanosphere and nanorod of different dispersion which results in the PCE enhancement of 23% [23]. In the current work, we report a facile one-pot chemical reduction method for the synthesis of multiple shaped AgNPs and demonstrated its applicability for PCE enhancement in DSSCs. We further demonstrated the fine-tuning of SPR over 300–1000 nm by increasing chemical reduction time and studied their effect on the spectral response in DSSCs. A maximum PCE enhancement of ~30% has been achieved by incorporation of Mx-AgNPs in the photoactive material of DSSCs.

2. Experimental

Silver nitrate ($AgNO_3$)- Merck, Di-methyl formaldehyde (DMF)-Emplura > 99.8%, Polyvinyl pyrrolidine (PVP-40,000 M.W)-Sigma Aldrich, fluorine doped tin oxide coated transparent (FTO) glass (8 Ω/Sq,)- Sigma Aldrich were purchased and used without any purification. The materials for fabrication like TiO_2 paste (18NR), Ru N719 dye, redox electrolyte (EL-HPE) and Pt paste, Surlyn Sealant were purchased from Dyesol.

2.1. Synthesis of Ag nanoparticles

The synthesis of multi-shaped Ag nanoparticles (Mx-AgNPs) was carried out as reported in earlier procedure with modification [20,22]. In short, about 2.5 gm of $AgNO_3$ was added in 200 ml of DMF solution containing 8.5 g PVP at room temperature. The solution turns to yellow color confirming the formation of Ag seed and the reaction mixture was heated at 90 °C for 8 h. During the reaction, the Ag colloidal dispersion appears different colors in the order of red, pink, blue and green with an increase in reaction time. About ~ 20 ml of the reaction dispersion for each color transition were collected at different intervals. The exchange of solvent from DMF to ethanol was done by centrifugation at 12,000 rpm using acetone as a precipitating agent to get final 0.40% (W/V) AgNPs dispersion in ethanol. The concentrated AgNPs dispersion in ethanol was sonicated for 15 min before performing drop casting.

2.2. DSSCs fabrication

The photoanodes were prepared as stated in our previous work [2]. In brief, a single-layer TiO_2 film was coated using the TiO_2 paste (18NR) of thickness 6–7 μm over an area of 0.125 cm^2 on $TiCl_4$-treated (40 mM, 70 °C) FTO glass substrate by doctor blade technique using 3-M Scotch tape as masking layer. The as-prepared films were annealed at 500 °C for 30 min at a heating rate of 3 °C/min in a furnace. For the fabrication of plasmonic photoanode, the Mx-AgNPs dispersion was incorporated by drop casting (1–3 μL) of AgNPs dispersion on annealed TiO_2 film and heated again at 70 °C in an oven. The as-prepared AgNPs loaded film was again washed with ethanol to remove excess AgNPs. The prepared photoanodes were soaked in the solution of 0.5 M N719 dye (prepared using 1:1 mixture of acetonitrile and butanol) for 18 h for dye adsorption. The Pt counter electrodes were fabricated by coating Pt paste on FTO glass substrate followed by annealing at 450 °C for 30 min. The photoanode and counter electrode were sandwiched together by using Surlyn film (25 μm) as a spacer. The electrolyte was introduced into the inter-electrode gap of a sandwiched device through the hole at counter electrode prior to sealing with Bynel film.

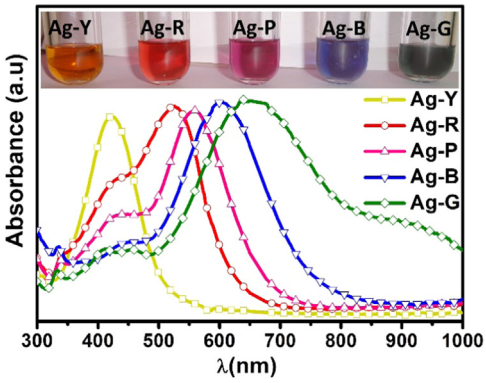

Fig. 1. The UV–Visible spectra during the color transition of the Ag nanoparticles dispersion Ag-Yellow (2 h), Ag-Red (6 h), Ag-Pink (6.20 h), Ag-Blue (6.40 h), Ag-Green (7.30 h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

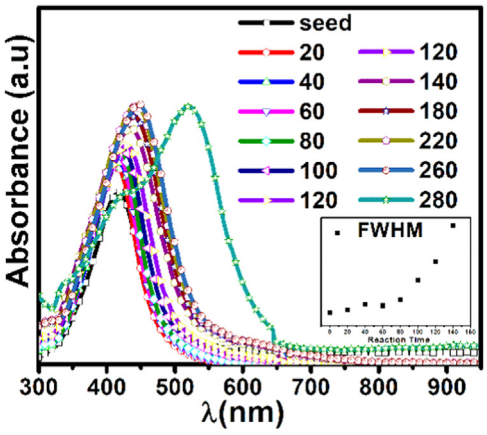

Fig. 2. Time evolution of the UV–Vis spectra during the formation of Ag nanoparticles showing the growth mechanism of the spherical nanoparticles.

2.3. Characterization technique

The high-power UV–Vis fiber light source integrated with thin-film measurement (TFM) spectrophotometer (Angstrom Sun Tech., TF probe 2.4) was used to measure UV–Vis spectra. The size and shape of the AgNPs were analyzed using TEM (JEOL/JEM, 3010). The morphology and thickness of the TiO_2 films were characterized using FESEM (Carl Zeiss Microscopy). The crystallinity of the TiO_2 films was characterized by XRD (Rigaku Ultima IV). The photovoltaic performance of the DSSCs were studied using a Photo Emission Tech (Model # CT50AAA) solar simulator and photocurrent-voltage measurement setup with Keithley 2400 current source meter using Xenon source with 300 W as a light source. The solar simulator with 1 Sun illumination (100 mW/cm^2) was obtained using an AAA class (spectral match ± 25%; non-uniformity ≤ 2%; and temporal instability ≤ 2%) solar simulator fixed with a 1.5AM filter on a 2 × 2 in an area. The Quantum efficiency (QE) was measured using Bentham PVE300-Quantum efficiency measurement system without bias light. The electrochemical properties of the device were studied using electro-chemical impedance spectroscopy (EIS) under illumination. A bias voltage of 0.75 V has been applied and EIS spectra were collected in the frequency range of 0.1–10^5 Hz.