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Size and concentration effects of gold nanoparticles on optical and electrical properties of plasmonic dye sensitized solar cells

Nikhil Chander [a,*], A.F. Khan [a,b], Eshwar Thouti [a], Sanjay K. Sardana [a], P.S. Chandrasekhar [a], Viresh Dutta [a], Vamsi K. Komarala [a]

[a] Photovoltaic Laboratory, Centre for Energy Studies, Indian Institute of Technology Delhi, New Delhi 110 016, India
[b] Department of Electronics and Information Technology, Ministry of Communications & Information Technology, Government of India, New Delhi 110 003, India

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Abstract

Gold nanoparticles (GNPs) of various sizes (range of 5–85 nm) were synthesized and various concentrations (range of 0.1–0.7 wt%) were blended with TiO_2 nanopowder for fabricating conformal TiO_2–Au nanocomposite (NC) films. In optical and electrical studies, we have observed that GNPs of sizes in the range of 15–40 nm, and concentrations in the range of 0.1–0.25 wt% offer the maximum enhancement in dye-sensitized solar cell (DSSC) performance due to the enhanced near-field excitation of dye molecules along with incident light far-field. The best plasmonic DSSC performance was observed with 0.24 wt% of ~36 nm GNPs with an enhancement of 18.44% in photocurrent. Despite the strong absorptance with ~5 nm GNPs, only a modest improvement in photovoltaic behavior was observed due to plasmonic heating effects of strongly localized near-fields instead of dye molecules excitation. With ~85 nm GNPs, we have observed minimal enhancement in device performance due to large scattering cross-sections, which result in the incident energy to be sent back to the far-field after interacting with GNPs instead of localizing around them. The optimized size and concentration of GNPs were also used for fabricating high efficiency DSSCs using commercial TiO_2 paste and two different dyes (N719 and N749) in order to study the effects of apparent extinction coefficients of the dyes as well as device thickness on photocurrent and energy conversion efficiency enhancements of DSSCs.

Keywords: Plasmonics; Dye sensitized solar cell; Gold nanoparticles; Optical properties

1. Introduction

Dye-sensitized solar cell (DSSC) is a third generation photovoltaic technology, which has a potential to significantly lower the cost for generating electricity from solar energy (Gratzel, 2001). The sensitized cell configuration is witnessing a surge in the research activity with the advent of perovskite sensitized solar cells, which are essentially an extension of the dye sensitized concept (Im et al., 2011; Lee et al., 2012; Burschka et al., 2013). But the efficiencies of DSSCs are still lower than other thin film technologies, and much lower than crystalline silicon solar cells. To improve the efficiency of DSSC, one needs to enhance the light absorption and improve the charge collection process. The light absorption can be enhanced by increasing the thickness of the TiO_2 layer so that more

* Corresponding author. Tel.: +91 11 2659 1255; fax: +91 11 2659 1251.
E-mail addresses: nikhilphysics@gmail.com (N. Chander), vamsi@ces.iitd.ac.in (V.K. Komarala).

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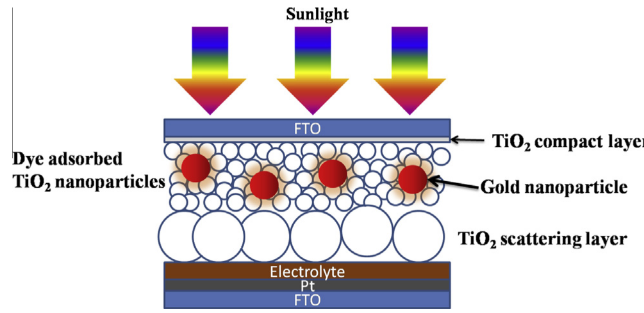
number of dye molecules are available for light harvesting. But this will lead to lower charge collection efficiency as the electrons have to travel a larger distance to reach the collecting electrode.

The researchers are trying to address these problems by utilizing plasmonic properties of metal nanoparticles (NPs) (Atwater and Polman, 2010) as one of the solutions. This can be achieved in two ways, either by enhancing the photon path length in solar cell using the scattering process, or by intensifying the light absorption around NPs, thereby avoiding the need to increase the physical thickness of the TiO_2 film. Scattering due to metal NPs is generally employed in the silicon based solar cells where it is impractical to embed metallic NPs in the active material (Pillai et al., 2007; Catchpole and Polman, 2008; Thouti et al., 2013). But embedding metal NPs in TiO_2 or ZnO layer typically employed in DSSC devices is a viable option for enhancing the light absorption. The commonly used synthetic dyes in DSSCs absorb primarily in the visible region, which is the reason why researchers mainly employ Au and Ag nanostructures in DSSCs because their surface plasmon resonance (SPR) can be tuned in the visible part of the electromagnetic spectrum.

A careful look at the plasmonic DSSC literature reveals that a wide range of metal NPs sizes, from ~2 nm to ~100 nm, have been utilized for improving cell performance (Brown et al., 2011; Qi et al., 2011; Jeong et al., 2011; Nahm et al., 2011; Deepa et al., 2011; Kawawaki et al., 2013; Li et al., 2013). Gold nano-islands and silver nanoparticles, synthesized by physical vapor deposition and sputtering respectively, have also been reported to enhance photocurrents in DSSC (Ng et al., 2014; Lin et al., 2012). It is not clear from these studies as to what size of metal NPs should be used for getting optimum performance from DSSCs. So, there is a need for a systematic study of different sizes of metal NPs incorporated in a typical TiO_2 mesoporous film employed for fabrication of DSSC.

Here, in this work we have studied initially the optical properties of different sizes and concentrations of gold nanoparticles (GNPs) embedded in a 3D TiO_2 mesoporous matrix to find out the optimum particle size and concentration for obtaining maximum absorption enhancement. For this, we have chemically synthesized GNPs of different sizes, blended different concentrations with TiO_2 nanopowder to fabricate conformal nanocomposite (NC) films by conventional doctor blade method. The TiO_2–Au NC films were used to fabricate efficient DSSC devices. Scheme 1 shows the plasmonic DSSC architecture with GNPs embedded inside a TiO_2 matrix. The ‘glow’ around the GNPs represents the conversion of incident electromagnetic far-field into near-field around the GNPs due to the SPRs. Total reflectance, total transmittance and absorptance spectra have been studied to gain insight into the optical properties of NC films containing different sizes and concentrations of GNPs. The photovoltaic performance of DSSCs containing different sizes and concentrations of GNPs has been evaluated by quantum efficiency and current density–voltage measurements. We have tried to correlate and reason the observed optical and electrical behavior of plasmonic films. After identifying the optimum size and concentration of GNPs for obtaining maximum efficiency enhancement using standard N719 dye, the plasmonic effects of GNPs have also been verified with black (N749) dye to look into the effect of SPRs on extinction coefficients of dyes. Finally, we also investigated the observed effects with commercial TiO_2 paste.



Scheme 1. Schematic depicting the near-field enhancement around the gold nanoparticles in Au–TiO_2 plasmonic DSSC.

2. Experimental methods

2.1. Synthesis of gold nanoparticles

GNPs were synthesized by the well known Turkevich method (Daniel and Astruc, 2004). A 30 ml solution of 1 mM hydrogen tetrachloroaurate(III) trihydrate in deionized water was heated to boil on a hot plate. Different quantities of 1% w/w trisodium citrate dihydrate aqueous solution were added to the boiling solution under stirring. Adding different amounts of citrate resulted in formation of GNPs of different sizes. Typically, for a 30 ml gold precursor solution in water, about 1.5 ml, 1 ml and 0.8 ml of 1%w/w trisodium citrate aqueous solution was added to obtain particle sizes of ~17 nm, ~36 nm and ~85 nm respectively (Fig. S1b–S1d, Supplementary material).

A different synthetic route was employed to synthesize GNPs of size ~5 nm (Fig. S1a, Supplementary material). A 100 ml aqueous solution containing 0.25 mM $HAuCl_4$ and 0.25 mM tri-sodium citrate was prepared in a glass beaker. Then ~2.4 ml of 0.1 M ice cold $NaBH_4$ solution was quickly added while stirring the solution. The color of solution immediately changed to reddish pink indicating particle formation.

About 1.5 ml of a 5% polyvinylpyrrolidone (PVP) aqueous solution was added to 30 ml of as synthesized GNPs solution and stirred for 8 h at room temperature. Afterwards the solution was centrifuged at 12,500 rpm for 15 min. The supernatant was removed carefully and the GNPs collected at the bottom of centrifuge tubes were re-dispersed in either ethanol or water. GNPs dispersed