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Photocurrent enhancement by surface plasmon resonance of gold nanoparticles in spray deposited large area dye sensitized solar cells

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ABSTRACT

A facile method for fabricating large area TiO_2 and TiO_2–Au nanocomposite films for dye sensitized solar cells (DSSCs) is presented using a spray technique. Pre-synthesized gold nanoparticles (Au NPs) were sprayed together with the TiO_2 NPs and composite films with brilliant coloration due to surface plasmon resonances of Au NPs were prepared. Composite films containing ~15 nm sized Au NPs exhibited enhanced absorption in the visible region of the electromagnetic spectrum. DSSCs with a large area of ~4.5 cm^2 were fabricated and a photocurrent enhancement of ~10% was obtained for plasmonic DSSC containing 0.3 wt.% of ~15 nm Au NPs. Incident photon to current conversion efficiency data conclusively showed enhanced currents in the visible region of the polychromatic spectrum arising due to plasmon enhanced near-field effects of Au NPs around the absorbing dye molecules.

1. Introduction

Metal nanoparticles (NPs) embedded in dielectric matrices have various technological applications like solar cells [1–3], photocatalysis [4,5] and sensors [6,7]. For plasmonic dye-sensitized solar cell (DSSC) applications large area films of TiO_2–metal nanocomposites (NCs) are required. The fabrication of such thin film NCs can be performed by techniques like magnetron sputtering, liquid phase deposition and chemical vapor deposition [8]. These techniques are either very expensive or unsuitable for depositing large area films on different substrates. In this paper, an easy to use and industrially viable spray deposition technique has been utilized to fabricate TiO_2–Au NC films on glass substrates for plasmonic DSSCs.

The spray technique is inexpensive and can be used to fabricate large area films on various substrates at different deposition temperatures. The spray method has been used previously to deposit Au NP films, synthesis of CdS nanospheres, ZnO thin films and even fluorine-doped tin oxide (FTO) layers on glass substrates [9–12]. An efficiency of 3.2% was reported for a spray deposited small area DSSC [13]. However, there is only one study on the use of the spray technique for fabricating large area TiO_2–Au NC films, in which the researchers reported the fabrication of composite films for glass coatings by mixing metal NPs with a titanium precursor and the tuning of surface plasmon resonance (SPR) was obtained by annealing the films at different temperatures [14]. Here we use commercially available TiO_2 NPs instead of a precursor and chemically synthesized Au NPs to form large area films, which can be used for DSSCs and any other suitable application. We show the application of these large area films for fabricating DSSCs with an active area of ~4.5 cm^2. Plasmonic effects of Au NPs have also been studied and enhanced efficiencies from plasmonic DSSCs are demonstrated.

2. Experimental methods

2.1. Fabrication of large area TiO_2 and TiO_2–Au films for optical studies

TiO_2 films were deposited on glass substrates by modification of a previously reported spray deposition technique [15]. About 1 g of TiO_2 NPs were dispersed in 100 ml of 1-butanol and sonicated for 30 min. This dispersion was sprayed using a specially designed nozzle, on glass substrates kept at ~200 °C on a hot plate. Nitrogen was used as the carrier gas; the solution flow rate and gas pressure were 2 ml/min and 10 kPa, respectively. The distance between the spray nozzle and substrates was kept constant at 20 cm. The solution was sprayed in cycles of 20 s followed by an interval of 20 s to ensure that the substrate temperature was maintained at ~200 °C. The whole spray apparatus was kept inside a specially designed enclosed chamber so as to minimize human contact with the chemical fumes resulting from the spray process (see Fig. 1a). Gold NPs were prepared by the citrate reduction method [16] with chloroauric acid ($HAuCl_4 \cdot 3H_2O$) as the gold precursor. Thus synthesized Au NPs were mixed with TiO_2 NPs (Avg. size ~ 20 nm, Sigma Aldrich) in Au–TiO_2 weight ratio of 0.3%. A similar process as mentioned above was used to fabricate TiO_2–Au NC films. The films thus prepared had a thickness of 4 ± 0.2 μm. The prepared

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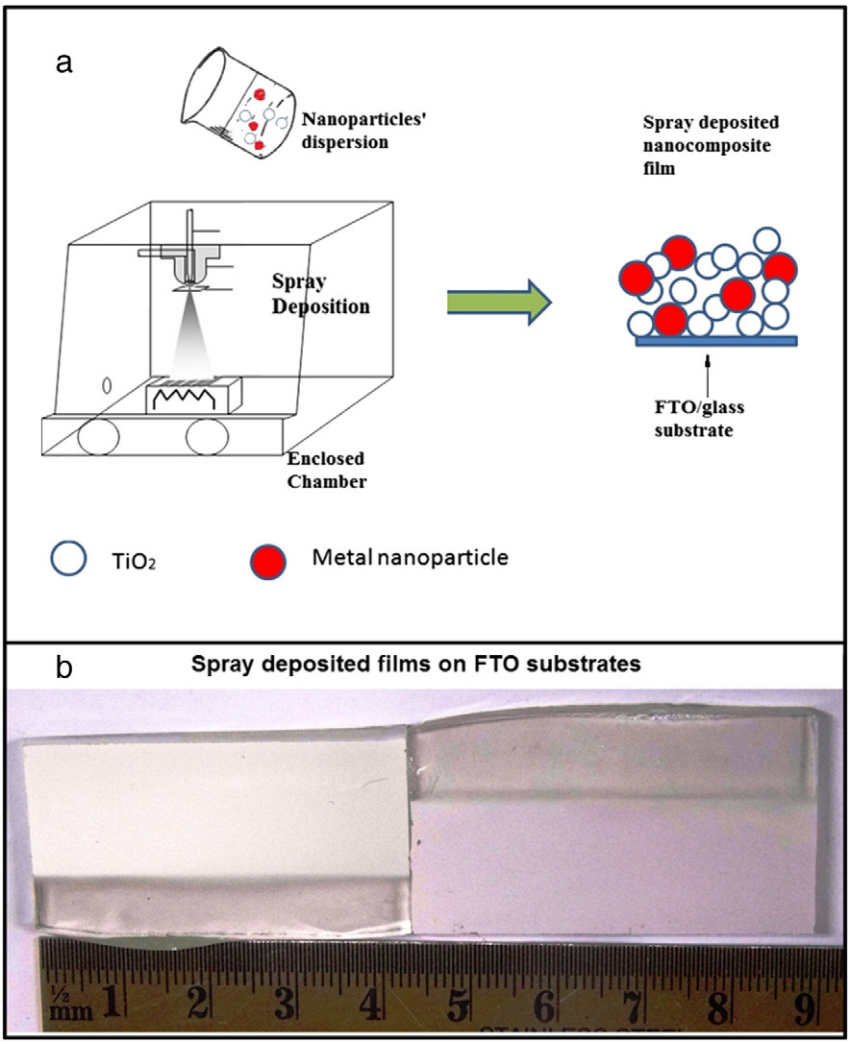

Fig. 1. (a) Schematic of spray deposition apparatus and (b) the digital photograph of fabricated TiO_2 and TiO_2–Au composite films.

films were roughly square in shape with dimensions 2.5 cm × 2.5 cm. The square shaped films were fabricated so as to completely cover the entry and exit ports of integrating sphere assembly of a spectrophotometer to measure the total reflectance and total transmittance, which have diameters of approximately 1 in. All the films were annealed at ~500 °C in air to remove any organic material and to improve adhesion of films on the substrates.

2.2. Fabrication of large area TiO_2 and TiO_2–Au NC films for DSSC preparation

The films for fabricating DSSCs were thicker and prepared on FTO glass substrates by slight modification of the above-mentioned process. FTO glasses were cleaned using soap water, de-ionized water, acetone and propanol in an ultrasonic bath. A compact layer of TiO_2 was formed on FTO substrates by the spray pyrolysis process. For this purpose, a solution of titanium diisopropoxide bis(acetylacetonate) (Sigma Aldrich) diluted in ethanol was sprayed on FTO substrates kept on a hot plate at 450 °C. In this fashion, a compact TiO_2 layer of 70–80 nm was prepared. Following this step the temperature of the substrates was reduced to 200 °C and the dispersion of TiO_2 NPs (or mix of TiO_2–Au NPs) in 1-butanol was sprayed as mentioned previously. The films were annealed at 500 °C following the spray deposition. The substrates were allowed to cool down to room temperature. In this manner, films with an area of ~7.5 cm^2 were deposited. The thickness of the mesoporous titania layers thus prepared was 12 ± 0.5 μm. Afterwards, the prepared TiO_2 and TiO_2–Au NC films were refluxed in a 1 M propanol solution of titanium(IV) isopropoxide (TIP) (Sigma Aldrich) for 15 min and subsequently annealed at 500 °C. The thickness of the films was controlled by adjusting the amount of TiO_2 (or TiO_2–Au) NPs dispersion sprayed on the substrates.

In general, large area films (area > 1 cm^2) could not be prepared by the doctor blade method because of non-uniformity of film thicknesses and inhomogeneous nature of the prepared films. Some large area films (~7.5 cm^2) were fabricated with the doctor blade method and it was found that the thickness varied significantly at different points on the films and the films were not as smooth and uniform as those prepared by the spray method. Due to these reasons, large area doctor bladed films were not used for device fabrication.

2.3. Fabrication of small area films using the spray and doctor blade methods

Apart from the large area films prepared by the spray deposition, some small area films were also prepared using the spray and conventional doctor blade methods for comparing the two deposition techniques. Small area spray films were deposited in the same manner as described earlier, but a metal mask was used to define the deposition area of ~0.2 cm^2. The doctor blade method was also used for fabricating TiO_2 and TiO_2–Au NC films with an area of ~0.25 cm^2 on FTO glasses