Surface Plasmon Resonance of sparsely dispersed Au nanoparticles in TiO_2 photoanode of dye sensitised solar cells

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Plasmonics is an emerging field that makes use of the nanoscale properties of metals, and its application in solar cells has seen a recent surge of interest [1]. Dye-sensitized solar cells (DSSC) were fabricated by incorporating Au NPs into the TiO_2 photoanode. The dye absorption is enhanced by the strong localized electric field from localized surface plasmon and the recombination and back reaction of electrons in DSSC is suppressed by depositing a thin TiO_2 blocking layer over the TiO_2:Au electrode. An increase in photoresponse was observed in the visible region with TiO_2:Au electrode. In particular, we report the observation that a nanoparticles of a noble metal (Au) placed on top of the n-type widegap TiO_2 that control the light emission angle can increase the short circuit current density and the quantum efficiency of the cell.

Keywords Surface plasmons; Dye sensitised solar cell

1. Introduced

Despite the development of Si-based and other thin-film technologies, the dye-sensitized solar cell (DSSC) developed by Gratzel continues to stand out as the most promising low-cost "next generation" technology with photon-to-current conversion efficiencies (η) in excess of 11% [2–4]. These devices mainly consist of a nanocrystalline wide bandgap n-type semiconductor covered with suitable dye molecules, a redox mediator and a counter electrode, usually a thin Pt film. The efficiencies of the devices primarily depend on the properties of the n-type semiconductor, the rate of injection of electrons to the semiconductor by the excited dye molecules and the capture cross-section of the positive charge on the dye cation by a donor species in the electrolyte. Moreover, photo physico-chemical properties and the anchoring ability of dye molecules to the semiconductor greatly affect the conversion efficiency.

However, noble metal nanoparticles (such as Au and Ag) have proven to bear interesting optical and electronic properties which potentially can be used to improve the performance of wide range of applications [1–8]. As Nehl and Hafner reported, the fabrication of monodisperse noble metal nanoparticles has been pursued extensively in the past decade for applications in electronics due to the effect called localised surface plasmon resonance (SPR) [9-10]. When localized surface plasmon on the surface of metal nanoparticles (Ag,Au,etc.) is excited, the irradiated light is scattered and absorbed on the surface of metal nanoparticles, and an evanescent wave with a strong electro- magnetic field is generated on the surface [5]. An evanescent wave is not transported, but rather is localized on the surface of the nanoparticles, and remains about a distance less than the diameter of the metal nanoparticles itself from the surface. Localized surface plasmon effects enhance optical phenomena such as Raman scattering and light absorption [1–5], and the level of enhancement strongly depends on parameters such as dielectric constant, distance, particle size, particle shape, and light wavelength, and thus depends on the combination of materials and the surface states. A considerable increase of the absorbance of Ru complexes in DSSC due to SPR effect has been demonstrated by Ihara et al [10-11]. However, Torrell et al reported using experimental and calculated results for different groups of samples that as grown and low-temperature annealed TiO_2:Au composite films do not possess SPR absorption and higher annealing temperatures are required to produce SPR effect on the optical spectra [12].

Ahmadi et al [13] demonstrated the shape-controlled synthesis of Pt nanoparticles with tetrahedral, cubic, irregular-prismatic and cubo-octahedral particle shapes by changing the ratio of the concentration of the capping polymer material to the concentration of the platinum cations used in the reductive synthesis of colloidal particles in solution at room temperature. Improved photocurrent of organic solar cells by surface plasmon has been reported, although the photocurrent remains low. In this attempt, we have dispersed Au nanoparticles in the nanocrystalline TiO_2 simply by introducing pre-prepared Au nanoparticles into the TiO_2 precursor. Evidence can be found in the literature to the effect that gold doping increases photocurrent. Thus in this study, we investigate the use of gold nanoparticles in the n-type semiconductor, TiO_2, in the enhancement of the photocurrent of the DSSC due to the plasmon effect**.**

2. Experimental

Au nanoparticles were prepared following an aqueous method developed by Turkevich [14]. In order to obtain reproducible results and easy comparison, Nanocrystalline TiO_2 photoelectrodes were prepared using the following simple procedure. 200 mg of P-25 TiO_2 powder (Degussa) was mixed thouroughly with 10 drops acetic acid, one drop of Triton X-100, and 3 ml of Ethanol and ground for 30 min until it reached a semi-solid state. Appropriate amounts of Au nanoparticle suspension were added to the TiO_2 paste and ground again for 15 minutes to obtain a homogeneous consistency. The surface concentration of Au in the TiO_2 film (CAu) was calculated using the amount of Au incorporated into a known quantity of TiO_2. The pastes were used to prepare thin films (< 10 μm) of TiO_2 (with and without Au) on conducting glass substrate (sheet resistance 15 ohm/sq) using conventional doctor blade method. Thin films were then annealed at 500ºC for 20 min before further processing. Thin films were immersed separately in alcoholic Ru bipyridyl (N719 or N3) dye solutions for 10 hours. Photoelectrochemical solar cells were fabricated by sandwiching a platinum sputtered conducting tin oxide (CTO) glass plate with the dyed TiO_2 films. A redox electrolyte containing I3-/I- (0.5 M tetrapropyl ammonium iodide +0.05 M iodine in 1:4 by volume mixture of acetonitrile + ethylene carbonate) was introduced to the solar cell.

Dark conductivity of TiO_2 electrodes was measure using a homemade computer controlled system comprising a Keithley 2410 sourcemeter and a peltier cooler. The morphology of the electrode surfaces was examined using a FEG-SEM Nova Nano SEM 200 scanning electron microscope (SEM). Raman spectroscopy of the thin films was used to characterize the film microstructure, using the 488 nm excitation line of an Ar+ laser, in the back scattering geometry, on a Jobin-Yvon T64000 spectrometer equipped with a liquid nitrogen-cooled CCD detector. The sample incident laser power was kept at 0.91mW and also 90 mW (using a neutral filter) and each scan was under taken at room temperature for over 600 s (60s/scan) while the spectral response analysis, which was recorded using a computer controlled setup with a lock-in amplifier, a calibrated Si photodiode and purpose built amplifiers. The incident light was chopped at a frequency which varied with the surface of the sample used.

3. Results and Discussion

3.1 Dark Conductivity

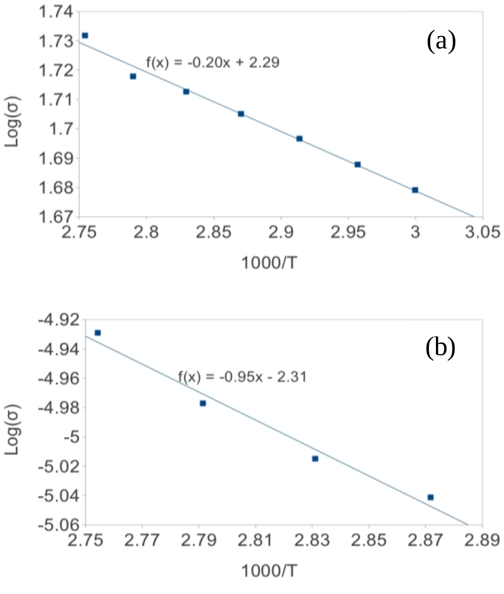

Fig. 1. Dark conductivity of (a) Au doped and (b) undoped TiO_2 electrodes.

The Arrhenius plot (ln(σ) vs. 1/kT) in Fig. 1, shows the change in dark conductivity between Au incorporated and bare TiO_2 electrodes. As can be seen from Fig.1, the dark conductivity of thin films increased by over two orders of magnitude at room temperature as a result of Au incorporation. In addition, the Au incorporation reduced the activation energy ($Ea = Ef - Ev$) in TiO_2 from 0.1 eV to 0.02 eV, which was derived from the slope of the fitting. The decrease of the activation energy with Au incorporation also suggests a strong interaction among the impurities (i.e. shift of Ef closer to the valance band). The homogeneity of the Au distribution in the film can be further improved by performing the Au incorporation separately by immersing bare TiO_2 electrodes in a Au ion solution. The comparatively rough surfaces of the films allows more area of the TiO_2 films to expose to a solution during ion exchange process, which increase the quantity of Au ions adsorbed at the film surface.

3.2 Morphology

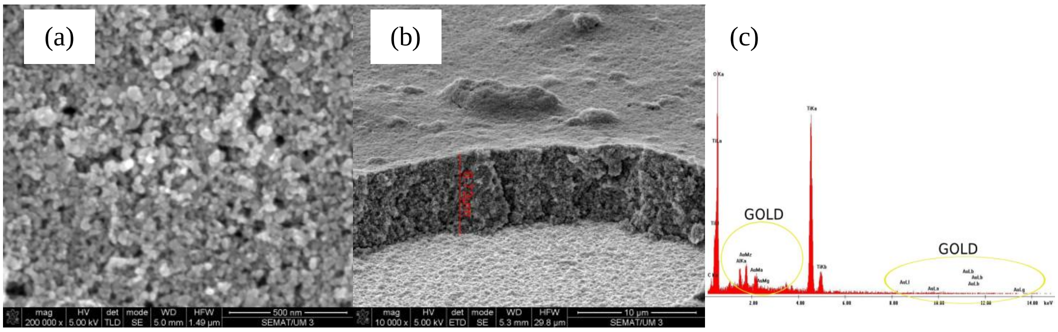

Fig.2. (a) The surface morphology and (b) cross sectional views of SEM micrographs of Au incorporated TiO_2 films.(c) EDX spectrum of a TiO_2 thin film with Au incorporated.

Representative SEM images for the TiO_2 thin films are shown in Fig.2. The composition of the thin films was observed to be a mix of individual particles interconnected with high porosity. The thickness of TiO_2 thin films deposited in this work were ~6-8 µm (Fig.2(b))and the average particle size was ~20-30 nm (Fig.2(a)). Although the films contained some large aggregates (~100 nm), generally they were homogeneous and porous over a large area. There was no apparent difference in morphology between bare TiO_2 films and Au incorporated films within the resolution of the SEM. No cracks on the surface and no gaps between the coatings are observed, indicating excellent inter-particle connectivity and inter-layer attachment. However, all TiO2 films incorporated with Au showed the presence of Au in elemental analysis (energy dispersive X-ray analysis, EDX) (Fig.2(c)).

3.3 Raman Spectroscopy Analysis

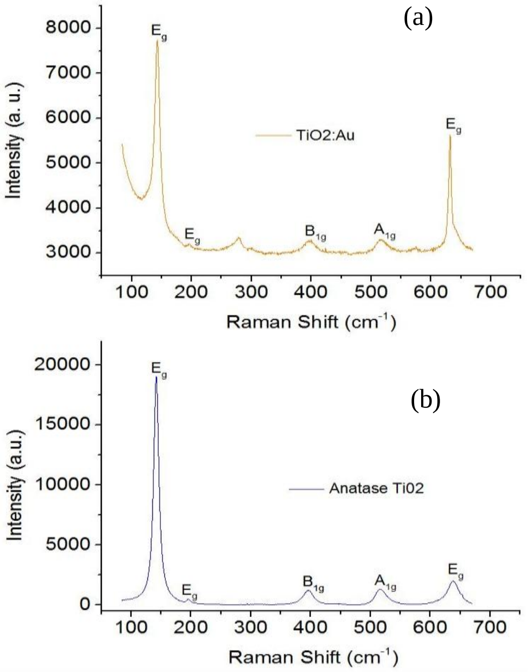

Fig.3. Raman spectroscopy of anatase TiO2 nanoporous thin films (a) doped with Au nanoparticles and (b) undoped.

The intensity of Raman spectrum of bare TiO_2 is much stronger than that of the Au:TiO_2 samples. The Raman lines at 141, 395, 510 and 635 cm^{-1} are assigned to the Eg, B1g, A1g and B2g modes of the TiO_2 anatase phase, respectively. The presence of gold nano-particles on the TiO_2 surface reduced the intensity of the characteristic peak for the anatase phase Eg (141 cm^{-1}), arising from the extension vibration of the anatase structure. As Fig.3 shows, the frequency shift and broadening of the anatase Eg Raman modes at 141 cm^{-1} and 637 cm^{-1} is a consequence of both confinement effect due to the nanosize dimensions of anatase crystallites and the disorder induced by the presence of Au nanoparticles in the samples [15]. Shift and broadening can occur due to oxygen deficiency, stress, presence of organic impurities and phonon confinement effects originated from nanocrystals. In addition, these effects might indicate diffusion of Au into the Anatase layer, which would account for the local enhancement of the electromagnetic field. Also the important role that can be played by the local temperature can be ruled out due to the fact that the laser power used was similar in both cases.

3.4 Spectral Response

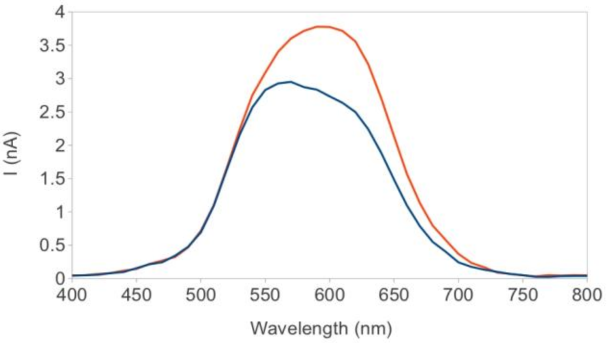

Fig.7. Photocurrent of a typical DSSC as a function of the photon wavelength (blue) bare TiO_2, (red) Au incorporated TiO_2.

Thin and thick films with Au incorporated show enhanced photocurrents and power conversion efficiency under white light, in comparison to bare TiO_2. A typical Spectral Response (SR) is shown in Fig.7, where the highest photoresponse for the bare TiO_2 is at 550 nm (Fig.7). The Au incorporated electrode also has a peak about 610 nm. Such enhancement was always observed for TiO_2 films with Au nanoparticles. The possible explanation is that homogenously distributed Au nanoparticles alters the surface property of the TiO_2 film so that the interaction between TiO_2 and Au becomes stronger and allows for more efficient electron injection due to localised surface plasmonic effect [9]. Furthermore, localised SPR of Au nanoparticles and their frequency can be strongly affected by subtle aspects of their shape [9]. The incident photon to current conversion efficiencies (IPCE) can also be determined using the spectral response at zero bias.

3. Conclusions

Several TiO_2 films with Au incorporated have been systematically investigated using a combination of SEM, Dark conductivity, Raman spectroscopy and spectral Response. The structure of TiO_2:Au has been found to be generally a single phasic anatase phase. EDX and Raman spectra show the presence of Au nanoparticles in the Au nanoparticle incorporated TiO_2 electrode structure and the localised SPR effect from Au nanoparticles is evident from SR analysis. The results also show that the combination of incorporating au nanoparticles and controlling the shape of nanoparticles in the TiO_2 thin films is an effective way to enhance the photoresponse, which is promising for photovoltaic (PV) and photoelectrochemical applications. The collective oscillations of electrons are induced by certain wavelength of the incident light. In the Au-TiO_2 interfacial region, where bands of TiO_2 are bent, the transport of electrons to TiO_2 bulk from the excited dye molecules can occur. It appears that further electrochemical linkages between TiO_2-dye and TiO_2-TiO_2 are built by these polarized Au nano particles.

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