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Research Article

Enhanced photovoltaic effects of dye-sensitized solar cells of SnO_2 surface modified with gold nano particles

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Abstract

The photovoltaic properties of dye-sensitized solar cells of SnO_2 are improved by depositing gold nano-particles on the surface of SnO_2 particles. The enhancement of the efficiency is attributed to increment of both the photocurrent and the photo voltage of the cells. This is described by the shift of the conduction band edge of SnO_2 to a higher energy level when SnO_2 particles are in contact with gold nano-particles.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) based on nanoporous films of metal oxides have gained much attention as alternative approach to the silicon solar cells because of their prospect for the low cost photovoltaic energy conversion [1]. In this contest, promising solar energy into electrical energy conversion efficiencies of more than 10% have been achieved for DSSCs based on TiO_2 [2]. However the efficiency of DSSCs constructed with other candidates of metal oxides such as ZnO, Nb_2O_5, SnO_2 etc., lies much more behind [3-5]. Even though, an impressive enhancement of the efficiencies comparable to TiO_2 have been noted in cells made from composite films of ZnO / SnO_2 [6] and SnO_2 films coated with an ultra thin layers of MgO [7] and other insulating oxides [8-10], the mechanisms involved here are not fully understood.

SnO_2 is an attractive semiconductor material for DSSCs as well as for other optoelectronic devices because of its high photo stability and good carrier mobility [11]. SnO_2 is a high band gap semiconductor like TiO_2 or ZnO. But the conduction band edge of

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SnO_2 locates at a lower level in the energy scale. Due to this reason, open circuit photo voltage of DSSCs constructed with SnO_2 are low comparable to DSSCs of TiO_2 or ZnO [6].

In this article we have reported our experimental results of construction of a dye-sensitized solar cell with composite film made by embedding gold nano particles on the film of SnO_2. When SnO_2 particles are in contact with gold nano particles the conduction band edge of SnO_2 shifts up in the energy scale increasing the photovoltage of the DSSC. Simultaneously, the shallow traps and the Fermi level of the SnO_2 also shift together with the conduction band edge. The existence of these shallow traps of SnO_2 far apart from the redox level of the electrolyte suppresses recombination via trap states, so that photocurrent of the cell increases. Thereby the efficiency of solar cells made from SnO_2 and gold composite enhances by increment of both the photocurrent and the photovoltage.

2. EXPERIMENTAL

We have prepared gold embedded SnO_2 films which we refer as Au/SnO_2 to fabricate films of dye-sensitized solar cells. The performance of the dye-sensitized solar cells constructed with above films was compared with bare SnO_2 films in this study. In the preparation of the Au/SnO_2 films, 1 ml of SnO_2 colloidal solution (Alfa chemicals, 15 % SnO_2 colloidal in H_2O), few drops of glacial acetic acid and sufficient amount of ethanol were added together into an agate mortar and mixed well. Known volume of gold chloride hydrate ($AuCl_4H$) from 3 x 10^{-5} M solution was added to the above mixture. The mixture was dispersed in 30 ml of ethanol and ultrasonically agitated for several minutes. The solution was sprayed onto 0.5x 1.0 cm^2 fluorine doped tin oxide (FTO) glass plates (sheet resistance 15 Ω /sq) heated to 150 °C and then sintered at 550 °C in a furnace for 30 min. The thickness of the film was maintained at ~ 10μm. Bare SnO_2 films were prepared following the same method described above without the incorporation of $AuCl_4H$ solution. Indoline 149 dye was coated on the surface of the electrode by soaking plates in the dye-solution (1.5x 10^{-4} M in *t*-butyl alcohol + acetonitrile, 1:1 by volume) for one and half hours. Photoelectrochemical cells (PECs) were fabricated by clamping a Pt sputtered FTO glass plate onto the dyed surface and filling the capillary space with the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.05 M iodine in 1:4 by volume mixture of acetonitrile + ethylene carbonate). I-V characteristics of the cells were recorded using a Keithley 2420-3A source meter and a 1.5 AM, 1000 Wm^{-2} solar simulator lamp. Photocurrent action spectra were recorded with a monochromator (Nikon Monochromator Autoscanner). An Eko pyranometer (MS 80) measured the light intensities. Absorption spectra of the dye solution were recorded with a Shimadzu UV-1600 Spectrophotometer. The flat band potential of SnO_2 and Au/SnO_2 electrodes were measured by Mott-Schottky measurements. 0.5 M Na_2SO_4 solution was used as the electrolyte and voltage is measured with respect to a standard calomel electrode (SCE).

2. RESULTS AND DISCUSSION

Significant difference could not be observed in the action spectra of dye coated bare SnO_2 electrode and the gold embedded SnO_2 electrode, other than the higher photocurrent of the Au/SnO_2 electrode as seen in Fig. 1(b) and (c) respectively. The absorption of the Indoline 149 dye peaked at around 532 nm, Fig. 1(a). Chelation of Indoline 149 dye on the surface of SnO_2 red shift the action spectra of the cell to 600 nm. Since the action spectrum of Au/SnO_2 composite film also red shift by the same amount to 600 nm, the dye is most probably adsorb on the surface of SnO_2 rather than on Au nano particles of the Au/SnO_2 composite film. It is clear from the action spectra that the photo excitation of the dye contributes to the photocurrent of the cell.

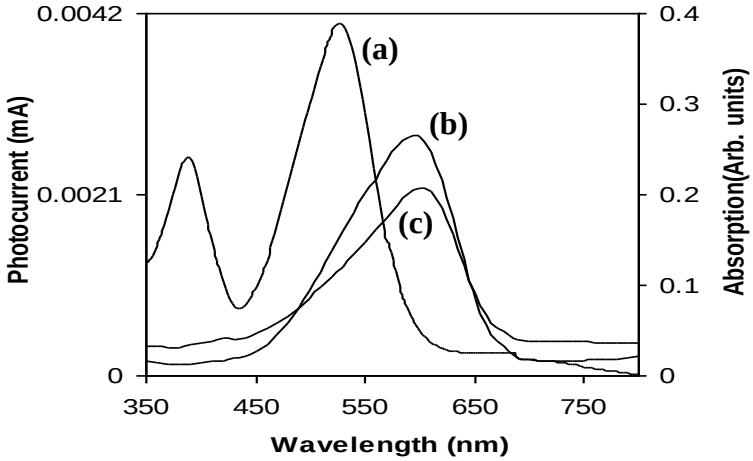

Fig. 1 Absorption spectrum of (a) Indoline dye and action spectra of DSSCs of (b) Au/SnO_2 film and (c) SnO_2 film.

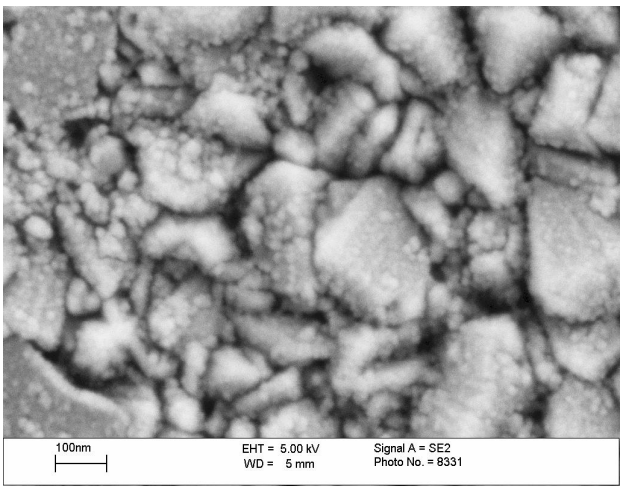

Fig. 2 SEM images of the Au/SnO_2 composite film deposited on the FTO glass

Gold nano particles embedded in SnO_2 film are visible in the SEM picture (Fig. 2). The average particle size of SnO_2 is around 100 nm and average particle size of gold is around 10 nm. XRD pattern for the gold nano particles embedded in SnO_2 film could not be obtained because the percentage of gold in the composite film is very small (less than 2.35×10^{-3} by weight).

I-V characteristic curves given in Fig. 3 show the variations of photocurrent and photovoltage of the cell with different amounts of gold on the Au/SnO_2 composite film. Introduction of gold to the composite film gradually increases both the photocurrent and the photovoltage of the cell and reaches the maximum when the gold content of the

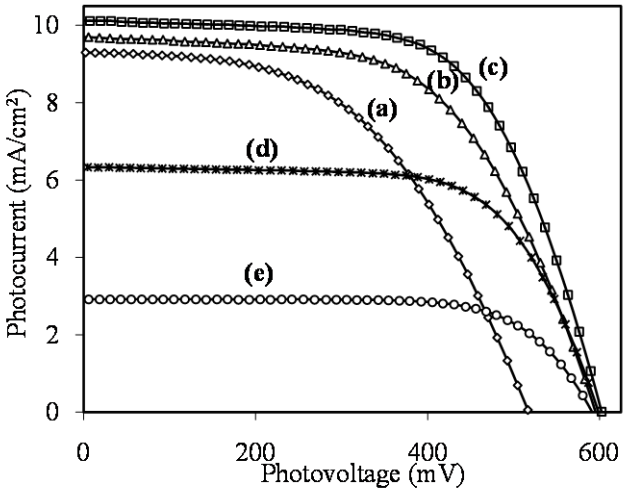

Fig. 3 I-V characteristic curves of DSSC made of Au/SnO_2 composite films of (a) 0 % (b) 9.4×10^{-4} (c) 1.41×10^{-3} (d) 1.88×10^{-3} (e) 2.35×10^{-3} of gold by weight.

Au/SnO_2 film is 1.4×10^{-3} % by weight. The open circuit photovoltage, short circuit photocurrent, fill factor and efficiency of the cells with different amount of gold are given in Table 1 for comparison.

Table1 I-V parameters of DSSCs made of Au/SnO_2 composite films depicted in Fig. 4.

Cell configuration	Au by weight (% x 10^{-3})	I_{sc}(mA/cm^2)	V_{oc}(mV)	FF (%)	η (%)
a	0.0	9.2	524.4	48.6	2.4
b	0.9	9.7	598.0	57.9	3.4
c	1.4	10.1	604.7	63.0	3.9
d	1.9	6.3	600.9	66.4	2.5
e	2.4	2.9	594.9	70.4	1.2

Increment of gold in the composite film beyond the optimum decreases the photocurrent of the cells keeping the photovoltage at the maximum voltage of 600 mV. The photocurrent of dye sensitized solar cells based on TiO_2 also increased incorporating nanoparticles of gold to the film. However increment of the photovoltage due to incorporation of Au to TiO_2 is marginal because of TiO_2 alone produces a higher photovoltage with Indoline 149 dye. This is one of the reason for selecting SnO_2 as the semiconductor material of our study to fabricate the Au/SnO_2 composite films since it shows enhancement in both the photocurrent and photovoltage. The enhancement of photovoltage and the photocurrent can only be described by the rise of the conduction band edge during the formation of schottky junction at the metal semiconductor interface.

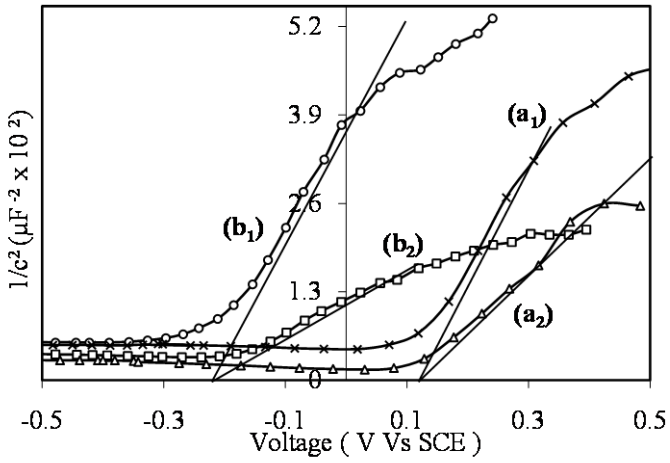

Fig. 4 Mott-Schottky plots of (a_1) SnO_2 (1.5 kHz) (a_2) SnO_2 (1 kHz) and (b_1) Au/SnO_2 composite (1.5 kHz) and (b_2) Au/SnO_2 composite (1 kHz) films.

The shift of the conduction band edge due to the addition of gold to the Au/SnO_2 composite is calculated with Mott-Schottky measurements. Fig. 4 shows the mott-schottky plots of bare SnO_2 film and Au/SnO_2 film deposited on FTO glass. It clearly indicates that the potential of conduction band edge of the Au/SnO_2 film shifts up by ~ 0.34 eV.

When two materials having different work functions are in contact, free carriers in the material with a lower work function material transfer to the material with high work function, and consequently Fermi levels of both materials coincide. When an n-type semiconductor is in contact with a higher work function metal, electrons in the conduction band of the semiconductor are transferred to the metal. The density of free carriers in the semiconductors are usually low, and hence, free carriers lying in the semiconductor from the surface to the deep bulk must be transferred to the metal in order to line up the Fermi levels. As a consequence, bands of semiconductor bend at the interface forming a depletion layer, which could extend even to a depth of one micrometer, Fig. 5(b). But the situation is rather different at a metal semiconductor interface when the particles are in nano range. Build up of a depletion layer in the interface is questionable because of the small size of the

semiconductor and the metal particles [12, 13]. However, still their energies have to be equalized when they are in contact. Therefore electrons in the material with higher Fermi level have to transfer to material with lower Fermi level even these particles are in nano scale. The Fermi level of SnO_2 is high compared to the gold, Fig. 5(a). Therefore electrons in the conduction band of SnO_2 transfer to gold to gain an equilibrium energy state. Since the particles are in nano range the potential of the conduction band edge of SnO_2 rises up together with the shallow traps [14] and the Fermi level of the Au/SnO_2 composite, Fig. 5(c). As a consequence the photovoltage of the cell increases because the conduction band edge of SnO_2 is now at a higher level. Since the gold nano-particles are good electron acceptors [15], one can interpret this result as a surface modification process to describe the shift of the conduction band when gold particles are in contact with SnO_2.

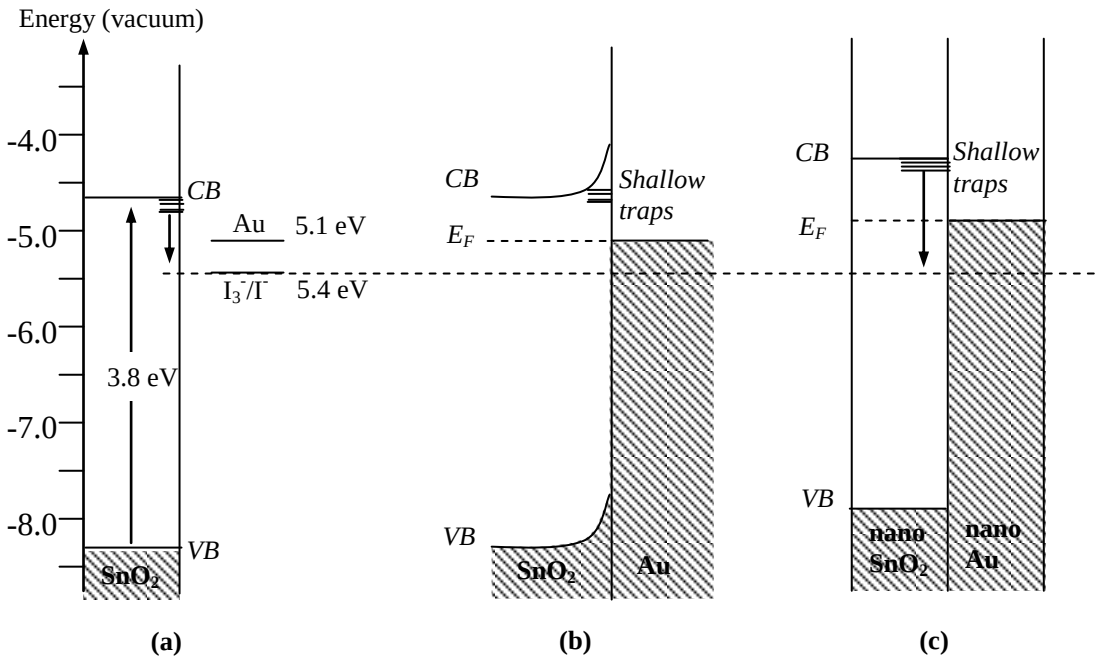

Fig. 5 Band diagram of (a) SnO_2 and Schottky junction of (b) SnO_2 and gold (c) SnO_2 and gold nano-particle contact.

When electrons are injected to the Au/SnO_2 film by excitation of the dye molecules they travel across SnO_2 and Au nano-particles in the composite film. The band structure of the Au/SnO_2 film is depicted schematically in Fig. 6. Here electrons suppose to transport ballistically across the gold nanoparticles in between two SnO_2 particles when the particle size of gold is comparatively small [16]. But when the gold particles grew bigger, the structure become more alike a multiple quantum well where electrons possibly fall or trapped in the quantum wells. This is attributed to the retardation of photocurrent of the cells when the gold content in the film is increased. But this will not effect on the photovoltage, which is decided by the conduction band position of the Au/SnO_2 composite relative to the energy position of the redox-couple (I^-/I_3^-), so that the photovoltage of the cell remains further unchanged.

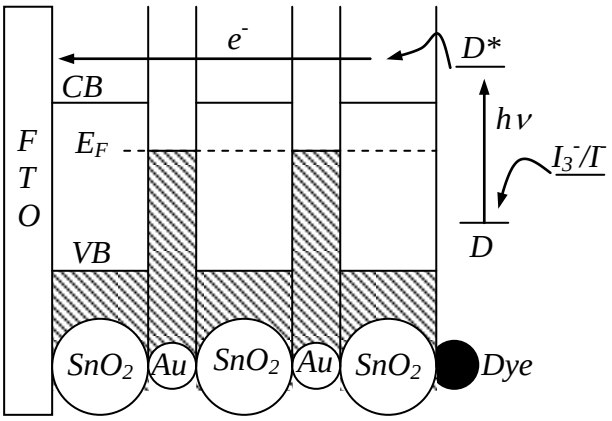

Fig. 6 Schematic band diagrams of Au/SnO_2 composite to illustrate the electron transportation through the film.

4. CONCLUSION

The present study shows that DSSCs made of composite films of metals and semiconductors of nanometer size particles enhance the charge separation and transportation when the work function of the metal is greater than that of the semiconductor. In this study we have taken gold as the metal and SnO_2 as the semiconductor taking into account their work functions. According to our investigation it is clearly seen that the conduction band edge of the semiconductor move to a higher potential when the Fermi level of the contact metal particle lies below the Fermi level of the semiconductor though the band bending at the semiconductor metal interface would not appear in particles of nano range. Since SnO_2 has high density of shallow traps near the conduction band edge, their potential also moves up to a higher energy with the shift of the conduction band edge. This will result to suppress the recombination of germinated electrons with the electrolyte which in turn increase the photocurrent. The shift of the conduction band edge to a higher level attributes to higher photovoltage of 604 mV and photocurrent of 10 mA of the cell. I-V characteristics and Mott-Schottky measurements provided sufficient evidences to support this idea. Previously we have shown that composite films made combining different types of semiconductors and semiconductors with insulators improve the performance of DSSCs. With this issue it is opening up the field to construct films of DSSC with composites of semiconductors and metals to enhance the performance of DSSC.

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