

Composite SnO₂/ ZrO₂ Dye-sensitized Photo Electrochemical Solar Cells

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Abstract

SnO₂ is among one of the many high band gap semiconductor materials utilized in dye-sensitized solar cells¹. Nevertheless, the performance of these cells has been found to be inferior when compared to other semiconductor materials such as TiO₂ because the existing shallow trap levels lead to high recombination of injected electrons with acceptors in electrolytes at the semiconductor/ electrolyte interface. However, the use of SnO₂² mixed with ZrO₂ at a low concentration can lead to the formation of an ultra-thin ZrO₂ shell around SnO₂ nanocrystallites, which can suppress recombination by creating a quantum well structure in [SnO₂] ZrO₂ films.

In the preparation of [SnO₂] ZrO₂ films, 1 ml of SnO₂ colloidal solution, a few drops of glacial acetic acid and a sufficient amount of ethanol were added together into an agate mortar and mixed well. A known weight of zirconyl chloride (ZrOCl₂) dissolved thoroughly in glacial acetic acid was added to the above mixture. The mixture was dispersed in 30 ml of ethanol and ultrasonically agitated for several minutes. The solution was then sprayed onto a 0.5 x 1.0 cm² fluorine doped tin oxide (FTO) conducting glass plates (sheet resistance 13 Ω /sq), which were heated to 150°C and sintered at 550°C (ZrOCl₂ decompose to ZrO₂ at 400°C) in a furnace for 30 minutes. Bare SnO₂ films were prepared by the same method without incorporating ZrOCl₂. Indoline D-149 dye was coated on the surface of the electrode by soaking the films in the dye-solution for 1.5 hours. Photo electrochemical cells (PECs) were fabricated by clamping a Pt sputtered FTO glass plate onto the dyed surface and filling the capillary space with the electrolyte.

The photo-generated high energetic electrons could tunnel through the ultra thin barrier of ZrO₂ to confine in SnO₂ nano crystallites. The consequence is a rise in the Quasi-Fermi Level (QFL) of SnO₂ enhancing both the photovoltage as well as photocurrent of the cell. According to the experimental evidence obtained in this study and also available literature, the formation of a ZrO₂ shell around the SnO₂ crystallites cannot be ruled out.

Introduction

Over the past decade, the study of dye sensitized (DS) solar devices based on nanocrystalline films of high band gap semiconductors¹⁻⁴ has emerged as an attractive field of research that is being carried out by the scientists the world over. One of the main reasons for this may be the associated photovoltaic conversion of solar energy at low cost ensuring a likely avenue to meet the increasing energy demands of the future, as conventional sources of energy are being rapidly depleted. Among the many semiconductor materials utilized for DS solar devices, SnO₂ is a high band gap semiconductor that has been widely used for this purpose. However, its performance is inferior when compared to other semiconductor materials like TiO₂ in devices working under similar conditions (comparable film thickness and morphology, same level of loading,

same electrolyte etc.). A previous report⁵ has indicated that the high recombination of injected electrons in a DS device via the shallow trap levels of SnO₂ is the prime factor for their poor performance.

The efficiency of solar cells could be enhanced by controlling recombination in such devices, which may take place through four distinct channels:

a. germinate electron, e⁻ recombination with the dye cations D⁺; b. non-germinate electron, e⁻ recombination with the dye cations D⁺; c. recombination of injected electrons, e⁻ with an acceptor in the electrolyte at the semiconductor/ electrolyte interface; and d. recombination of injected electrons, e⁻ with an acceptor in the electrolyte at the exposed conducting glass / electrolyte interface.

Of these four avenues, channel a. can be neglected because of the rapidity of electron injection and the slow pace of the back reaction. Since the swiftness of

hole transportation to the electrolyte, the recombination through channel b. could also be ignored. As the surface of the conducting fluorine doped tin oxide (FTO) glass is nearly about three orders of magnitude smaller than that of the surface of rough nano-crystalline SnO₂, voids in this film account only for a small fraction, and the rate of channel d similarly could be ignored as it is negligible. Therefore, channel c. becomes the most significant route in the recombination process.

Electrons injected to a semiconductor from the excited dye molecule could transport directly through conduction band or traps in shallow levels. The electrons in traps diffuse towards the counter electrode by hopping from trap to trap. Because of the high existence of trap levels in SnO₂, it is obvious that recombination of injected electrons through channel c. in trap-to-trap hopping is the major reason for the inferior performance in SnO₂ films. The delay time τ_D of electrons to the back contact can be expressed as $\tau_D = d^2/4D_n$, where D_n and d are respectively, the diffusion coefficient, and the thickness of the film. As the diffusion coefficients of electrons associated with trap-to-trap hopping are smaller than those corresponding to transport in the conduction band, the recombination of electrons with acceptors in the electrolyte is favorable in trap-to-trap hopping since, such electrons take a longer time to reach the back contact.

In dye sensitized electrochemical solar cells (DSECSCs), open circuit photovoltage is theoretically determined by means of the difference between the energy positions of the redox-couple (I^-/I_3^-) and the conduction band edge of n-type semiconductor materials. Since the trap-to-trap transport is highly favorable in DS solar devices based on nano-crystalline films of SnO₂, open circuit photovoltage is determined by the difference between the energy positions of the redox-couple (I^-/I_3^-) and the trap levels of SnO₂, which is situated below the conduction band edge of SnO₂. Therefore the open circuit photovoltage is always below that of the theoretical upper limit. Besides, recombination via traps reduces the short-circuit photocurrent. However, there are many published articles that have reported higher efficiencies of DSECSCs, in which SnO₂ crystallites in the film are coated with an ultra-thin outer shell of insulators such as MgO, Al₂O₃ (we denote such films by the symbol [X]Y, where X and Y are core and shell materials, respectively). It has also been reported that the enhancement of photocurrent is

only possible by the formation of an ultra-thin outer shell of insulators around the crystallites of the high band gap semiconductor in composite semiconductor insulator films (capped type hetero structures).

ZrO₂ is an insulating material whose energy gap lies between 5–7 eV. It has the monoclinic crystal structure at room temperature and converts into the cubic or the tetragonal structure at higher temperatures. The pressure, which is exerted with the accumulation of tetragonal forms at higher temperatures, could again convert the tetragonal form into a monoclinic form with the retardation of further growth accompanied by volume expansion. This would enhance the fracture toughness of the material, significantly extending the reliability and lifetime of the device made by this stabilized ZrO₂. This paper then describes the enhancement of both the photovoltage and the photocurrent of DSECSCs constructed using films of SnO₂ crystallites coated with an ultra-thin outer shell of ZrO₂ insulator, abbreviated by [SnO₂] ZrO₂. The results obtained are compared with DSECSCs of bare SnO₂ films. Or in other words, in this study the performance of DSECSCs constructed by [SnO₂] ZrO₂ films is compared with those made of bare SnO₂ films.

Experimental details

In the preparation of [SnO₂] ZrO₂ films, 1 ml of SnO₂ colloidal solution (Alfa chemicals, 15 % SnO₂ colloidal in H₂O), a few drops of glacial acetic acid and a sufficient amount of ethanol were added together into an agate mortar and mixed well. A known weight of zirconyl chloride (ZrOCl₂) dissolved thoroughly in glacial acetic acid was added to the above mixture. The mixture was dispersed in 30 ml of ethanol and ultrasonically agitated for several minutes. The solution was then sprayed onto a 0.5 x 1.0 cm² fluorine doped tin oxide (FTO) conducting glass plates (sheet resistance 13 Ω /sq), which were heated to 150 °C and then sintered at 550 °C (ZrOCl₂ decompose in to ZrO₂ at 400 °C) in a furnace for 30 minutes. The size of SnO₂ particles in the film was around 100 nm and the thickness was maintained at ~ 10 μ m. The film area was determined by adsorption of monolayer of dye on mesoporous film. Bare SnO₂ films were prepared by the same method without incorporating ZrOCl₂. The surface of the electrode was coated with indoline D-149 dye by soaking the films in the dye-solution (1.5x 10⁻⁴ M in *t*-butyl alcohol + acetonitrile, 1:1 by volume) for 1.5 hours. Photo electrochemical 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 a mixture of acetonitrile and ethylene carbonate 1:4 by volume). I–V characteristics of the cells were recorded using a Keithley 2420–3A source meter and a 1000 Wm⁻² solar simulator lamp at 1.5 AM. Photocurrent action spectra were recorded with a monochromator (Nikon Monochromator Autoscaner). An Eko pyranometer (MS 80) was used to measure the light intensities. Absorption spectra of the dye solution were recorded with a Shimadzu UV–1600 Spectrophotometer. A Spectrofluorophotometer (Shimadzu RF-5000) was utilized to obtain emission spectra of the relevant samples. The flat band potential of SnO₂ and [SnO₂] ZrO₂ electrodes were measured by Mott–Schottky measurements. A 0.5 M Na₂SO₄ solution was used as the electrolyte, while the voltage was measured with respect to a standard calomel electrode (SCE).

Results and Discussion

Since the SnO₂ and ZrO₂ particles are in nano scale, SnO₂ crystallites in the [SnO₂] ZrO₂ film are assumed to be coated with an ultra thin over layer of insulating material ZrO₂ which acts as a barrier against recombination of photo generated electrons. The thickness, T of the shell material, ZrO₂ in [SnO₂] ZrO₂ film, with SnO₂ as the core material is estimated using the formula,

$$T = \frac{r}{3} \frac{W_{ZrO_2} \rho_{SnO_2}}{W_{SnO_2} \rho_{ZrO_2}} \quad (1)$$

Where, r is the median radius of SnO₂ particle. W_{ZrO₂} and W_{SnO₂} are the respective weights and ρ_{ZrO_2} and ρ_{SnO_2} are the respective densities of ZrO₂ and SnO₂.

The DSECSCs constructed utilizing composite [SnO₂] ZrO₂ films produce high efficiencies accompanied by the development of both photocurrents as well as photovoltages, compared to those using bare SnO₂ films. Figure 1, shows the I–V characteristics of solar cells made of [SnO₂] ZrO₂ films with different ZrO₂ compositions and sensitized by indoline D–149 dye, along with the I–V characteristics of a solar cell made of bare SnO₂ electrodes (Fig. 1a). As the concentration of ZrO₂ in the composite film is gradually increased, both the photocurrent and the photovoltage of the cell increase and reach their maximum values when the

content of ZrO₂ in the [SnO₂] ZrO₂ film is 0.9 % by weight. At that optimum point, the efficiency of the ZrO₂ coated cell reaches 3.8 % compared to 2.2 % for an equivalent cell with bare SnO₂ film.

Besides, the incorporation of ZrO₂ has enhanced the fill factor as well. Table 1 illustrate the improvement of all I–V parameters, short-circuit photocurrent (I_{sc}), open circuit voltage (V_{oc}), efficiency (\square), fill factor (FF) of the cells with introduction of ZrO₂ in [SnO₂] ZrO₂ films. Further increment of ZrO₂ in the composite film decreases the photocurrent where the photovoltage increased slightly than the other cells. The indoline D–149 dye is well adsorbed onto the bare ZrO₂ films. This is further confirmed by the photocurrent (though very small) and photovoltage of the DSECSCs made of ZrO₂ films alone (Table 1).

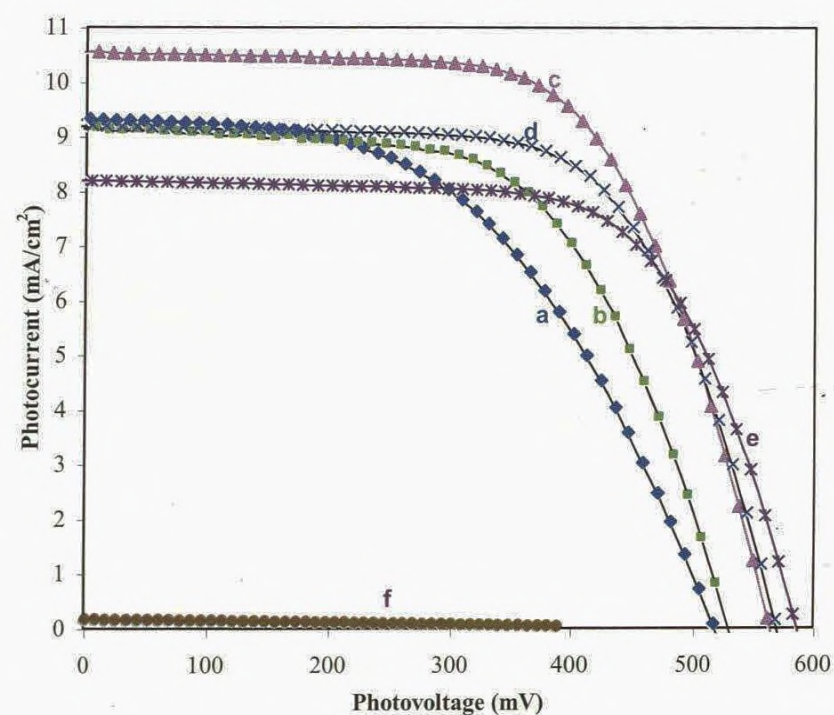


Fig. 1. I–V characteristic curves of dye-sensitized photo electrochemical solar cells made of a. bare SnO₂ and SnO₂ incorporated with b. 0.45 % c. 0.90 % d. 1.35 % e. 1.80 % of ZrO₂ by weight, and f. for pure ZrO₂ respectively.

When SnO₂ and ZrO₂ particles are in nano scale, the formation of ultra thin over layer of ZrO₂ around SnO₂ crystallites could be expected and the dye is entirely adsorbed onto the ZrO₂ surface. The introduction of ZrO₂ to the composite film further increases the thickness of this shell which acts as a quantum barrier to suppress recombination of photo-generated electrons. High energetic electrons (hot electrons) generated by the excitation of the indoline D–149 dye, tunnel through this barrier and relax to the conduction band (CB) or shallow traps of the SnO₂ particles (Fig. 2).

Table 1. I–V parameters (I_{sc} –short circuit photocurrent, V_{oc} –open circuit photovoltage, η –efficiency, FF –fill factor) of different $[\text{SnO}_2]$ ZrO_2 films sensitized with indoline D–149 dye.

Cell configuration	ZrO_2 by weight (%)	I_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
a	0.00	9.3	524.4	49.5	2.22
b	0.45	9.0	533.0	59.7	2.90
c	0.90	10.5	562.7	63.8	3.77
d	1.35	9.2	569.2	65.4	3.42
e	1.80	8.1	584.4	66.9	3.19
f	100.0	0.1	390.6	31.1	0.02

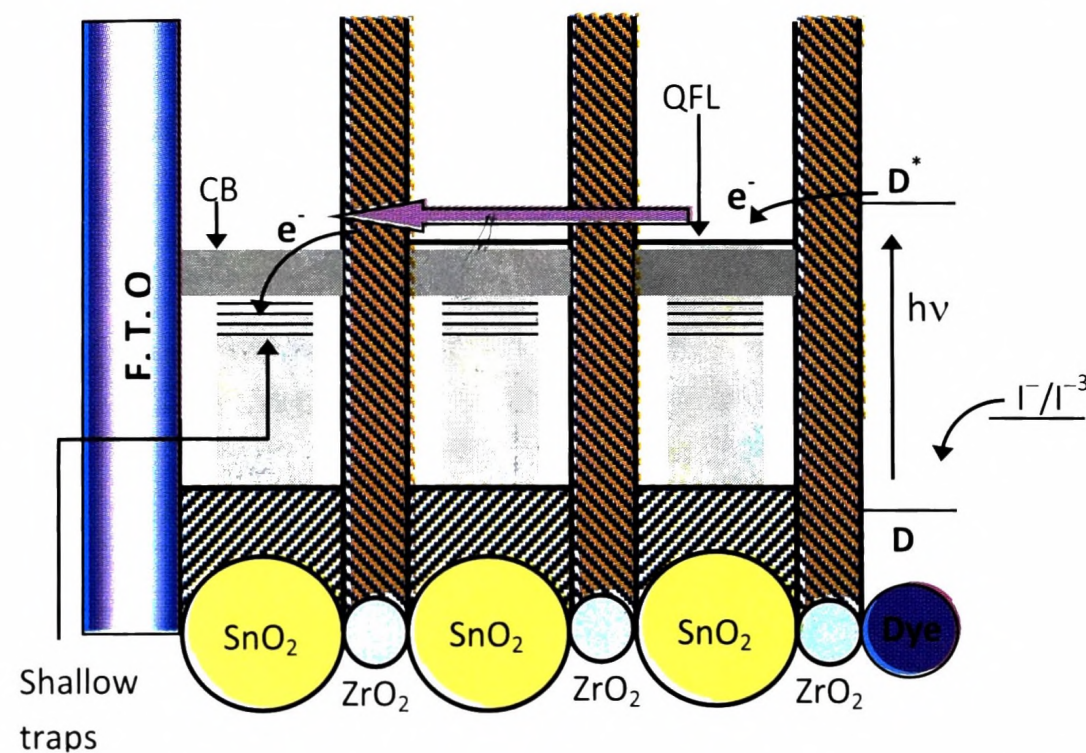


Fig. 2. Schematic band diagrams of $[\text{SnO}_2]$ ZrO_2 composite film to illustrate electron transportation through the ultra thin barrier of ZrO_2 towards the FTO back contact.

These electrons are not allowed to penetrate through the barrier again because of the diminution of their energy. Thus it suppresses recombination of these electrons with acceptors in the electrolyte at the semiconductor/electrolyte interface or with the dye cations D^+ again. However, further injection of these hot electrons fills the shallow traps as well as the CB of SnO_2 particles. Under these circumstances, the upper most occupied energy level of the electrons in the CB, or the so called Quasi-Fermi Level (QFL) which in turn, determines the value of V_{oc} with respect to the energy position of the redox couple (I/I_3), gradually increases. When the barrier width is narrow, newly generated hot electrons have enough energy to penetrate through the narrow barrier and transport towards the FTO back contact (Fig. 2). At the optimum efficiency of the cell, the thickness of the ZrO_2 shell calculated by equation 1 is about 0.2 nm.

The shift of the flat band potential (under these circumstances) of SnO_2 nano-particles due to the addition of ZrO_2 in $[\text{SnO}_2]$ ZrO_2 composite film

was calculated with Mott–Schottky measurements. Fig. 3 shows the Mott–Schottky plots of bare SnO_2 film and $[\text{SnO}_2]$ ZrO_2 film deposited on FTO glass. It clearly indicates that the flat band potential of the $[\text{SnO}_2]$ ZrO_2 film shifts up by ~ 0.48 eV for the optimum cell with the highest efficiency. Thus rising up of flat band potential increases the photovoltage whereas the suppression of recombination increases the photocurrent of the cell.

However, thicker shells of ZrO_2 decrease the photocurrent of the cell while increasing only the photovoltage (Table 1). When the thickness of the shell is high, the width of the barrier increases preventing penetration of photo-excited electrons across it. The rising of QFL due to the collection of injected electrons, increases the photovoltage of the cell. Broad width of the ZrO_2 barrier confines these electrons in SnO_2 particles. In this case, the suggestion is that the electrons are transferred to trap states of ZrO_2 shell. The existence of trap states in ZrO_2 acting as an intermediate to transport

electrons to the next SnO₂ particle cannot be ruled out (Fig. 4). When the thickness of the ZrO₂ layer is further increased, the electrons hop from one trap state to another trap state of ZrO₂ particle following a trapping and de-trapping mechanism until they meet the next SnO₂ particle. The thermal excitation

of electrons causes the de-trapping, transferring them to the next trap state or back to a CB of some other SnO₂ particle. And thus, when the thickness of ZrO₂ layer is increased, a drastic drop in photocurrent could be observed.

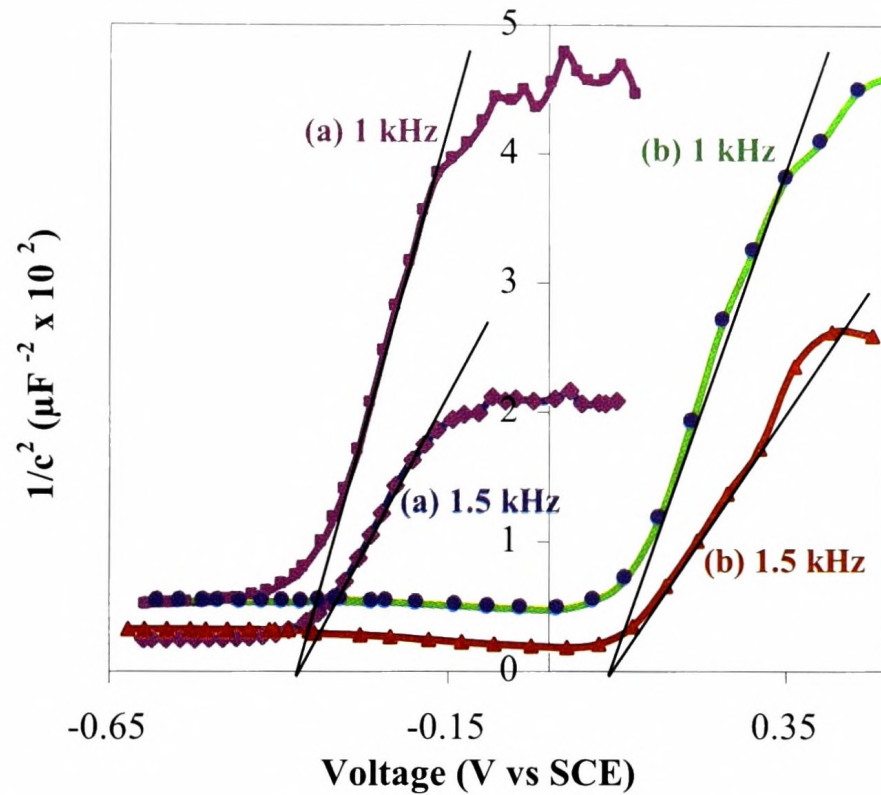


Fig. 3. Mott-Schottky plots of (a) [SnO₂] ZrO₂ composite and (b) SnO₂ films

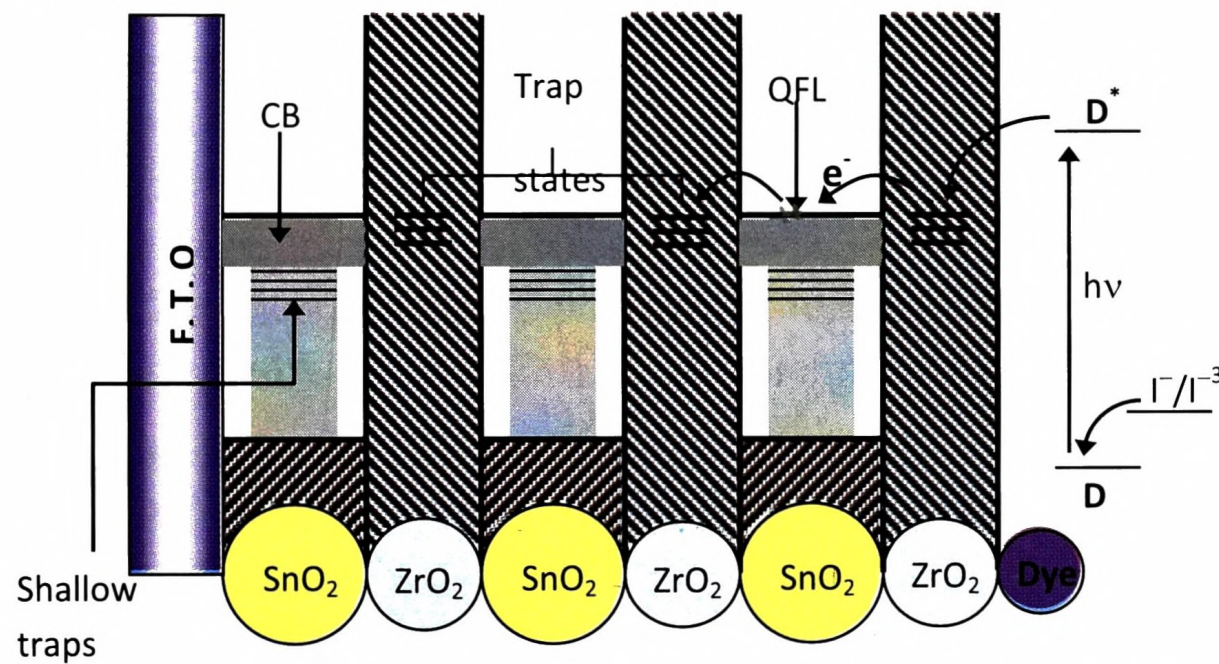


Fig. 4. Schematic band diagrams of [SnO₂] ZrO₂ composite to illustrate electron transportation through the thick barrier of ZrO₂ layer by hopping electrons over the trap states in ZrO₂ towards the FTO back contact

The transportation of photo-excited electrons through the trap states of ZrO₂ is reported in many literature articles⁶. DSECSCs constructed utilizing bare ZrO₂ films displayed a photovoltage and a low photocurrent (Table 1). The transportation of these electrons through the CB of ZrO₂ can not be expected. However, a certain photo-generated current was experimentally observed. The hopping of these electrons from one trap state to another trap state of some other ZrO₂ particle following a trapping and de-trapping mechanism, could

produce the observed low photocurrent, which is agreeable with the experimental results.

Conclusions

The above investigation may lead to the conclusion that the inferior performance of DSECSCs made from SnO₂ films alone may be due to the recombination of electrons injected into SnO₂ with the acceptors in the electrolyte at the semiconductor/electrolyte interface. Suppression of recombination process by incorporation of the insulating material ZrO₂ has improved the cell

performance significantly. The formation of a ZrO₂ shell around the SnO₂ crystallites in the [SnO₂] ZrO₂ film could enhance both the photovoltage as well as the photocurrent of the cell. The ZrO₂ layer on SnO₂ particles could not be identified with the SEM images because of its ultra thin nature. However, according to other experimental evidences including shell thickness calculations and also the reported data in many literature articles, the formation of ZrO₂ shell around the SnO₂ crystallites in the [SnO₂] ZrO₂ composite film cannot be ruled out.

The authors acknowledge the National Institute of Fundamental Studies, Sri Lanka, the Sabaragamuwa University of Sri Lanka and the Open University of Sri Lanka for the support extended to this work.

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