



Efficient passivation of SnO₂ nano crystallites by Indoline D-149 via dual chelation

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ABSTRACT

For the first time in SnO₂ based dye solar cells, here we report, efficiency exceeding 3% of the cells consisting with Indoline D-149 dye with unmodified SnO₂ nano-crystallites. The cells sensitized with metal free D-149 dye together with liquid electrolyte comprising with 0.5 M tetrapropyl ammonium iodide and 0.05 M iodine in a mixture of acetonitrile and ethylene carbonate (1:4 by volume) delivered a short circuit current density of 10.4 mA cm⁻² with an open circuit voltage of 530 mV under the illumination of 100 mW cm⁻² (AM1.5) having an efficiency of 3.1%. As evident from the FTIR measurement, strong surface passivation of recombination centers of SnO₂ crystallites due to the dual mode of attachment of dye molecules to the surface of SnO₂ via both COOH and S-O direct bond might be the possible reason for this enhancement in these SnO₂ based cells.

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1. Introduction

Dye sensitized photoelectrochemical (DSPEC) solar cells based on nano-crystalline film of high band gap semiconductors are receiving much attention as promising alternative to conventional solar cells. The performances of these devices depend on the material, and the morphology of the electrode, photophysical and structural properties of the sensitizer and the redox electrolyte. DSPEC solar cells made of Ru-bipyridyl dye coated TiO₂ films with I⁻/I₃⁻ redox electrolyte have incident photon to photocurrent efficiency (IPCE) of nearly 100% and energy conversion efficiency (η) of ~10% [1]. However in the ruthenium dye sensitized SnO₂ based DSPEC solar cells, despite any optimization, it is not possible to achieve efficiency greater than ~0.5% with an open circuit voltage exceeding 260 mV. One of the main reasons for these differences is dissimilarities in effective electron masses (m^*) (m^* of TiO₂ = ~10–50 m_e and m^* of SnO₂ 0.1 m_e) [2–6]. The spreading of the hydrogenic wave function of a trapped electron is inverse exponential and increases with the effective electron mass so that the electron leakage and their recombination with acceptors is higher in SnO₂ (crystallite size ~4 nm) than TiO₂ (crystallite size 10–30 nm) [7]. Recombination of the electrons injected into the conduction band (by photoexcitation of the dye) with dye cations or

I₃⁻ ions in the electrolyte are the main dissipative processes limiting the efficiency of the DSPEC cells. During the past few years, it has been reported in literature affirming high efficient DSPEC solar cells made from SnO₂ specially reducing the recombination by preparing composite materials with SnO₂ [8–12]. Apart from the usage of composite materials with SnO₂ crystallites, on the other hand, it is also possible to reduce this recombination via strong surface passivation using suitable dyes such as Indoline [13]. For example the dye molecules can totally and strongly cover the SnO₂ crystallites via multiple chelating mechanisms, minimizing the recombination. In this context, metal free Indoline (D-149) dye consisting with both COOH and C=S moieties could be one of the best candidate to fulfill the above requirements. Due to the availability of the above moieties, it might be possible to have double chelation of these moieties with SnO₂ crystallites which eventually reduce the recombination and enhance the efficiency of the cells [14]. Therefore in order to see this phenomenon and also to enhance the efficiency of the SnO₂ based dye solar cells, investigations are being carried out with Indoline based SnO₂ dye solar cells. Hence here we report the highest efficiency obtained from dye solar cells based on SnO₂ crystallites and evidence for this possible dual chelation mechanism.

2. Experiment

Colloidal aqueous solution of SnO₂ (2 ml, 15% SnO₂ Alfa Aesar) and 100 μ l of acetic acid glacial (Fisher Scientific) were mixed well with a drop wise addition of 80 ml of ethanol in an agate motor.

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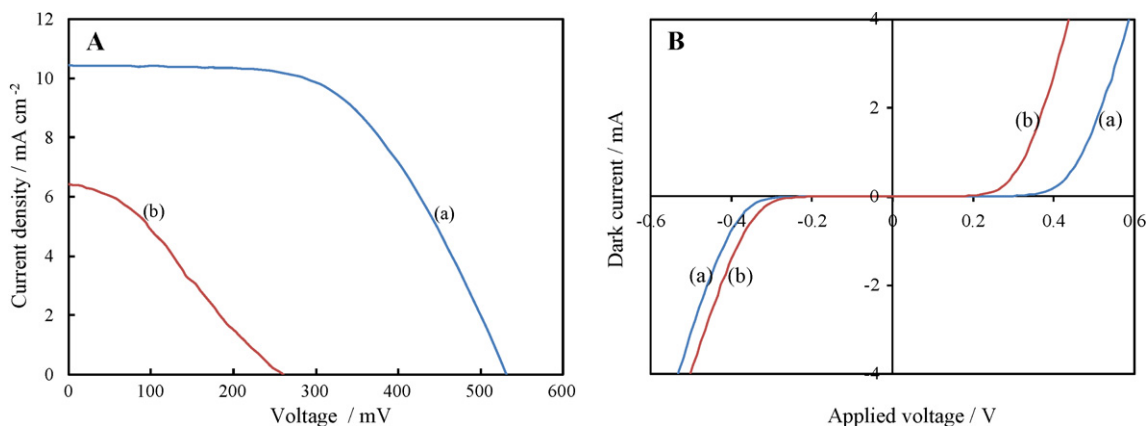


Fig. 1. (A) Current–voltage characteristics of SnO₂/D-149 system (a) SnO₂/N-719 system (b) under illuminated. (B) Current–voltage characteristic of SnO₂/D-149 system (a) SnO₂/N-719 system (b) under dark condition.

The dispersion is then sprayed onto fluorine doped SnO₂ conducting substrates (sheet resistance 15 Ω sq⁻¹, 0.5 cm × 1.5 cm, active area 0.25 cm²) placed at 150 °C. The films were sintered at 530 °C for 20 min and allowed to down to 80 °C. Then electrodes were immersed separately in Ru-bipyridyl N-719 dye solution (0.5 mM in ethanol) and D-149 dye solution (0.5 mM in a mixture of acetonitrile and tert-butyl alcohol 1:1 by volume) and kept at room temperature for 24 and 4 h, respectively (it was found that four hour immersion in D-149 dye solution gives the best photo responses). After the dye adsorption, films were rinsed with absolute ethanol and sandwich with platinum sputtered conducting glass substrates using clips. The cells were filled with the electrolyte consisting of 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 measured under the illumination of 100 mW cm⁻² (Am1.5) simulated sunlight (Xe 500 lamp with AM 1.5 filter) with home made computer controlled setup consisting Keithly 2000 multimeter and Potentiostat/Galvanostat HA-301. Incident photon to current efficiency (IPCE) was estimated using a computer controlled Nikon (G 250) monochromator and Keithly 2000 multimeter, calibrated with Si photodiode (S1223-BQ). The dark rectification *I*–*V* curves of these cells were recorded with the help of potentiostat controlled by computer (THJ Instruments potentiostat). For the transient studies, A He–Ne laser and mechanical shutter were used with a digital storage oscilloscope (Tektronix TDS 3032B). In situ FTIR measurements were carried out by Horizontally Attenuated Total Reflection Infra-Red (HATR-IR) spectroscopy (Nicolet 6700). Internal reflecting element (IRE) used was ZnSe cell (trapezoidal shape crystal with 70 mm × 6 mm dimensions). Thin layer of D-149 dye and D-149 dye coated on SnO₂ were deposited on ZnSe cell and examined by HATR-IR spectra in the wave number between 4000 and 650 cm⁻¹ with 4 cm⁻¹ resolution. Spectra were analyzed by OMNIC tools (version 7.3) built in with the FTIR spectrometer. The coverage of the dyes (D-149 and N-719) on SnO₂ the electrode were estimated by spectroscopic technique (Shimadzu UV-2450 UV–vis spectrophotometer).

3. Results and discussion

Fig. 1 shows the *I*–*V* characteristic of DSSC comprising with D-149 (a) ruthenium N-719 (b) under illumination (A) dark (B) conditions. The main cell parameters, open circuit voltage (*V*_{oc}), short circuit photo current density (*J*_{sc}), fill factor (FF) and efficiency (*η*) are shown in Table 1. As it is evident from the table, and Fig. 1 (A) the solar cells fabricated with SnO₂/D-149 shows superior photo responses than the cells sensitized with N-719. Moreover, higher voltage and the fill factor of SnO₂/D-149 cells than the Ru N-719

Table 1

I–*V* parameters (*J*_{sc}: short circuit photo current density, *V*_{oc}: open-circuit voltage, *η*: efficiency and FF: fill-factor) of SnO₂/D-149 system and SnO₂/N-719 system.

Cell configuration	<i>J</i> _{sc} (mA/cm ²)	<i>V</i> _{oc} (mV)	FF (%)	<i>η</i> (%)
SnO ₂ /N-719	6.4	258.5	30.7	0.5
SnO ₂ /D-149	10.4	532.9	55.9	3.1

cells suggest that the overall recombination of D-149 sensitized cells are smaller than the other type which can also be observed from the dark *I*–*V* characteristic curves as shown in Fig. 1(B). As depicted in Fig. 1(B), the cells with SnO₂/D-149 configuration shows better dark rectification than SnO₂/N-719 system. Further, it can be seen that a shift of onset of the dark current curve of SnO₂/D-149 system towards a higher position. Therefore from these observations it is evident that the recombination in the cells having SnO₂/D-149 configuration are lower than the cells sensitized with N-719. The photovoltage transients of the above two cells further support this fact as shown in Fig. 2. The fast decay of photovoltage transient in D-149 sensitized cells indicates a low carrier trapping density which is one of the main causes of recombination [6]. In other words, the fast decay of photovoltage of SnO₂/D-149 cell than the cell with N-719 clearly shows a higher suppression of recombination. One of the reasons for this suppression of recombination in SnO₂/D-149 cells might be due to the passivation of traps in SnO₂ surface by Indoline D-149 dye. Further

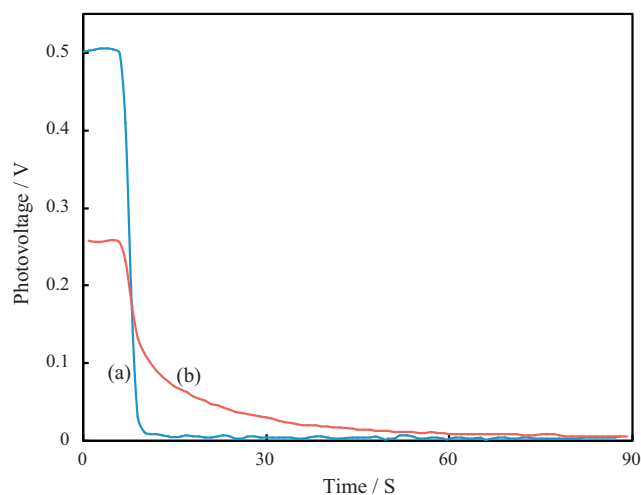


Fig. 2. The photovoltage transient characteristics of the solar cells sensitized with D-149 (a) and with N-719 (b).

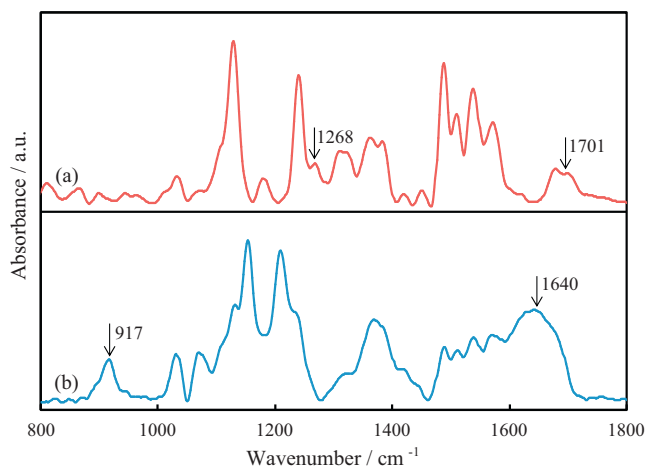


Fig. 3. ATR-FTIR spectra for D-149 (a) and D-149 coated SnO₂ electrode (b) (800–1800 cm⁻¹).

the estimated number of D-149 dye molecules by spectroscopic methods reveals that the coverage of SnO₂ electrode by D-149 is approximately three times higher than that by the N-719 dye. The estimated values were 3×10^{16} and 1×10^{16} , respectively for cells with an area of 0.25 cm². Possible higher degree of chelation via COOH and C=S moieties of D-149 dye molecules and SnO₂ crystallites which enhance the dye coverage, could act as a thin insulating layer on SnO₂ crystallites as observed in cases of SnO₂-MgO and SnO₂-Al₂O₃ systems [10]. In order to examine and confirm this effect, FTIR experiment were carried out on D-149 dye and D-149 dye coated on SnO₂. Fig. 3 shows the FTIR spectra of (a) D-149 dye and (b) D-149 coated on SnO₂ crystallites. The disappearance and formation of new bonds can be seen clearly. As depicted in Fig. 3, the FTIR measurements of samples shows clear differences in major peak positions confirming this phenomenon. The peak position at 1268 cm⁻¹ (curve a) of the D-149 dye disappeared and formation of a new bond can be seen around 917 cm⁻¹ (curve

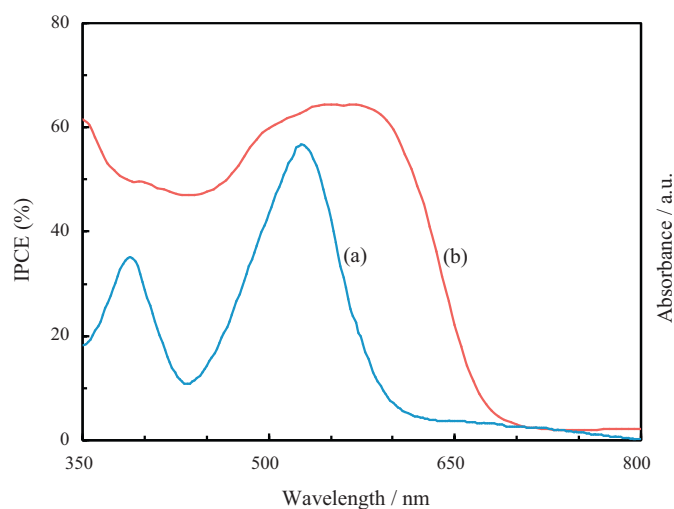


Fig. 5. Incident photon to photocurrent efficiency (IPCE) of SnO₂ cell sensitized with D-149 (a) and (b) absorption spectrum of D-149 dye in mixture of acetonitrile and tert-butyl alcohol 1:1 by volume.

b) when the dye is attached to the SnO₂ crystallites. The peak at 1268 cm⁻¹ and 917 cm⁻¹ in these figures ((a) and (b)) can be assigned to the stretching vibration modes of the C=S bond and S-O bond, respectively [15,16]. The peak at 1701 cm⁻¹ in curve a can be assigned to the C=O bond stretching in D-149 [16].

The broadening and shifting of this vibration mode to low wavenumber indicate (curve (b)) that the chelation of dye molecules and SnO₂ crystallites via COOH. The schematic diagram for the chemical structure of D-149 and possible dual modes of attachment of dye molecule to the surface of SnO₂ are depicted in Fig. 4(A) and (B), respectively. Therefore it is evident from these observations, enhanced surface coverage of the SnO₂ crystallites by D-149 dye molecules than N-719 dye. Therefore the high efficiency of DSPEC solar cell based on SnO₂ sensitized with D-149 is attributed due to the passivation of the trap states in SnO₂ film by

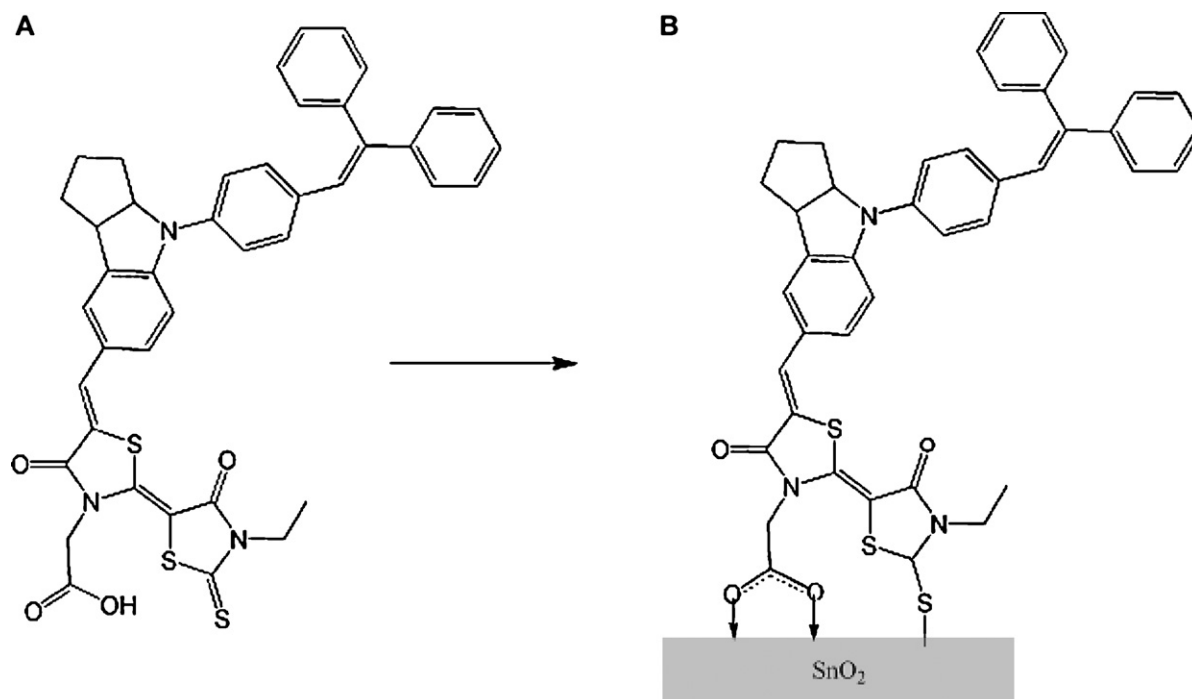


Fig. 4. Schematic representation of the structures of D-149 (A) and the possible dual chelating mechanisms via COOH and S=O moieties (B).

dual chelating of the D-149 dye via carboxylic groups and sulphur sites. Since the dye is an insulator, it could act as a barrier against recombination of electrons. Thus this effect enhances the performance of SnO₂ DSPEC solar cell when D-149 is used as a sensitizer. Fig. 5 shows IPCE action spectra of SnO₂ cell sensitized with D-149 and absorption spectrum of D-149 dye. A photocurrent action spectrum was broader because of the dye aggregation and J aggregates [17].

4. Conclusions

DSPEC SnO₂ cell with conversion efficiency of 3.1% and open circuit voltage of 530 mV was fabricated without any modification in the SnO₂ electrode or electrolyte using D-149 dye as the sensitizer. This enhancement is attributed to the suppression of recombination of electrons due to the passivation of trap sites in SnO₂ film by the attachment of D-149 dye. Attachment of the Indoline dye by carboxylic groups and sulphur sites to the SnO₂ film is strongly supported by the FTIR measurements. Such efficiency could not be achieved for DSPEC SnO₂ cells with N-719 dye, although high efficiencies have been recorded for Ru-bipyridyl dye for TiO₂ DSPEC cell with similar light absorption cross sections. This could be explained by the donor ability of electrons of oxygen and sulphur. In general sulphur is a good electron donor than oxygen in carboxylic groups, thus trap sites in SnO₂ is better passivated by attachment of sulphur sites in D-149 than carboxylic groups in N-719. Ordered orientation due to π - π stacking of the intermolecular aromatic rings of D-149 attached on SnO₂ also helps to achieve a complete coverage of the dye on SnO₂ surface. Therefore D-149 dye layer also acts as a barrier against recombination of germinated electrons.

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