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Enhanced Photovoltaic Performance via Co-sensitization of Ruthenium (II)-Based Complex Sensitizers with Metal-Free Indoline Dye in Dye-Sensitized Solar Cells

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Abstract: Co-sensitization is shown to be an effective method to improve the efficiency of dye-sensitized solar cells wherein ruthenium (ii)-based complex sensitizers (N749, N719) is co-sensitized with the metal-free indoline dye (D149), where photovoltaic efficiency of 5.40% is achieved by co-sensitized N749+D149 and efficiency of 4.94% is achieved by co-sensitized N719+D149. The assembled dye-sensitized solar cells were studied by UV-vis absorption measurements of dye solutions, the absorption spectra of the dye-sensitized TiO_2 film along with co-sensitized TiO_2 film and current–voltage characteristics. The co-sensitized based device exhibits better photovoltaic performance compared to the devices fabricated from individual sensitizers. Upon optimization, the device made of co-sensitized N749+D149 yielded J_{sc} = 13.6 mA/cm^2, V_{oc} = 690 mV, FF = 0.576 and η = 5.40% and the device made of co-sensitized N719+D149 yielded J_{sc} = 13.3 mA/cm^2, V_{oc} = 660 mV, FF = 0.563 and η = 4.94%. This demonstrated that the performance of co-sensitized devices is improved from that of the devices sensitized with either N749 (4.56%), N719 (4.24%) or D149 (4.06%) under the same fabrication conditions.

Keywords: Dye-sensitized solar cell; Co-sensitization; Ruthenium (II)-Based Complex Sensitizers; Metal-Free Indoline Dye; Enhanced Efficiency

1 Introduction

Solar energy is considered one of the most positive ways to decrease the climate change resulting from the use of fossil resources for energy generation [1–4]. The low-cost as well as environmentally friendly properties of dye-sensitized solar cells (DSSC) make the DSSCs one of the most promising classes of photovoltaic cells for the conversion of photon energy to electricity [5]. DSSCs were first reported by O'Regan and Grätzel in 1991 [6]. A DSSC is composed of a working electrode in which mesoporous nanocrystalline TiO_2 is deposited on the surface and enclosed with a monolayer of dye molecules, a redox-couple electrolyte and platinized coated fluorine-doped tin oxide (FTO) glass substrate as counter electrode. When a photon strikes the surface of the photoanode, the incident photon energy is absorbed by a sensitizer on the nanoporous TiO_2 layer that ensures charge separation and the transfer of electrons from the excited dye molecule to the photoanode [7, 8]. The sensitizer is then regenerated by an electrolyte containing a redox-couple. The photosensitizer is one of the key components of DSSCs for achieving good efficiency. Photosensitizers work as solar light harvesters of Photovoltaic (PV) cells. In addition their electronic properties are recognized to affect light harvesting efficiency along with power conversion efficiency (PCE) [9, 10]. In DSSCs, the majority of low efficiencies are based on traditional photosensitizers undergoing low absorption, narrow absorption spectra, along with the loss of energy absorbed by the electrolyte [5]. For this reason, an approach using co-sensitization was demonstrated and implemented to recover the performance of the DSSC [11, 12].

Much of the research has targeted the improvement of new and efficient photosensitizers, including sensitizers like ruthenium complexes [13–15], zinc porphyrins [16–18] as well as metal-free organic dyes [19–22]. Ruthenium-based sensitizers such as the N3 dye/ N719 dye [9, 10, 23] and black dye [24] were rigorously tested as light har-

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vesters and reached remarkable overall power conversion efficiency (η) in the range of 11% under Air Mass 1.5 (AM 1.5) irradiation while organic photosensitizers have reached power conversion efficiency (PCE) in the range of 5-8% [25–31]. Metal-free indoline dye (D149) is the most effective photosensitizer for DSSCs and has attained very high efficiencies of 9% [32]. Recently, devices fabricated by using ruthenium (II) complexes with cobalt (3+/2+) based electrolytes have achieved efficiencies of 9.4% [33]. A heteroleptic copper (I)-based sensitizer combined with a squaraine derivative dye (SQ2) based device has been reported to produce increased photovoltaic efficiency by 65.6% relative to ruthenium-based sensitizer (N719) set at 100% [34]. DSSCs fabricated by a co-sensitized porphyrin dye (FNE57 or FNE59) and an organic dye (FNE46) with a quasi-solid-state gel electrolyte have obtained photovoltaic efficiencies of 7.88% and 8.14% [35]. DSSCs made of porphyrin dyes co-sensitized with chenodeoxycholic acid (CDCA) have been successfully demonstrated with a high PCE of 8.6% [36]. However, a device made of a porphyrins sensitizer (XW4) co-adsorbed with an organic dye C1 illustrated an increased in short circuit current density (J_{sc}) by 24% and an increased in open circuit voltage (V_{oc}) by 5%, together with an enhanced PCE of 10.45% [37]. A device based on a nanoporous semiconductor film with co-sensitization of an amphiphilic heteroleptic ruthenium complex (Ru) sensitizer and a (D–Π–A) metal free organic sensitizer (Y3) demonstrated an improved PCE of 6.29% [38]. The porphyrin sensitizers [39, 40] between the Soret and Q bands displayed very weak absorption in the spectral region so that co-sensitization with different sensitizers (cocktail-type) has been demonstrated to be an efficient way to broaden the photoelectric response range of the DSSCs [41]. Co-sensitization of TiO$_2$ electrodes with organic dyes based on indigo and thioindigo has been reported to enhance the performance of dye sensitised solar cells [42]. Devices fabricated by using a ruthenium-based complex co-sensitized with an organic dye have resulted in a PCE of 6.29% [43]. The performance of a device relies on the light harvesting property of the sensitizer.

Co-sensitization is a significant approach to enhance the spectral response of a sensitizer for which the mixing of two or more sensitizers adsorbed together on a TiO$_2$ electrode and dyes have complementary absorption properties. The co-adsorbent should have three main properties: (i) a large molar extinction coefficient in the near IR region or below 450 nm, (ii) both the sensitizers should not adsorb competitively with each other while efficiently restraining the aggregation of sensitizers on the nanoporous TiO$_2$ film, and (iii) the co-absorbent should be capable of decreasing the charge recombination by the formation of a compressed monolayer coating the bare nanoporous TiO$_2$layer. The chemical names of the sensitizers are as follows: N749 (black dye) is triisothiocyanato-(2,2’:6’,6”-terpyridyl-4,4,4”-tricarboxylato)ruthenium(II)tris(tetrabutylammonium) [24]; N719 is Di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) (TBA)$_2$[Ru(NCS)$_2$(Hdcbp y)$_2$] [9]; and metal free organic dye D149 indoline dye is 5-[[4-[4-(2,2-Diphenylethenyl)phenyl]-1,2,3-3a,4,8 bhexahydrocyclopent [b]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolid [44]. The chemical structures of the sensitizers N749 dyes, N719 dyes & D149 dyes are shown in Figure 1.

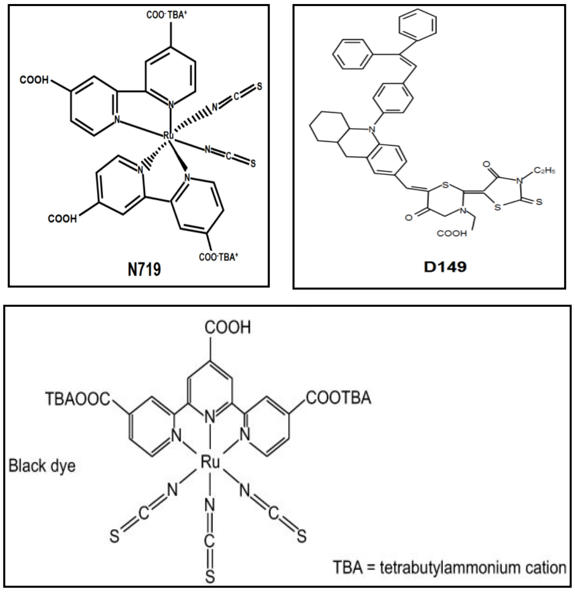


Fig. 1. The structure of: (a) N719 dye, (b) D149 dye & (c) N749 dye (Black dye).

In this paper, the performance of DSSC devices were investigated with the nanocrystalline TiO$_2$ photoanode of the DSSCs photosensitized by co-sensitization of a metal-free indoline dye (D149) as co-adsorbed with ruthenium (II) based complex sensitizers (N719 & N749) and the performance of the device were investigated. The Current density-Voltage (J-V) curves and UV-visible absorption spectra were also studied in this work. The photovoltaic performance of the cells from the individual sensitizers N749, N719 and D149 are compared with that of co-sensitized devices (N719+D149) and (N749+D149). The short circuit photocurrent and PCE of the co-sensitized device were notably improved relative to that of devices sensitized with individual dyes.

2 Experimental Section

2.1 Chemicals

A FTO electrode (2.2 mm, 7 ohm/sq), a platinum electrode (2.2 mm, 7 ohm/sq FTO), Iodolyte AN-50 (50mM iodide/triiodide in acetonitrile) and Ruthenizer 535-bis TBA (N719) dye were purchased from Solaronix; Labogent (detergent solution) was purchased from S.d.fine; nanoporous TiO_2 powders (particle size 20 nm, 97% anatase), indoline dye (D149), α-terpineol, acetonitrile, methanol and ethanol were purchased from Sigma-Aldrich.

2.2 Fabrication of Dye-Sensitized Solar Cells

Nanoporous TiO_2 paste was prepared by mixing 4g of nanoporous TiO_2powder (particle size 20 nm, 97% anatase; Sigma-aldrich), 0.8mL of acetic acid, 2 mL of α-terpineol and 4mL of deionized water. Afterwards 100 mL of ethanol was steadily mixed and at the same time sonicated the blend for 3 hours. The mixture was thorough stirred at room temperature for 2hours and lastly the mixture was stirred for 4hours at 100°C to form a colloidal paste [39]. F-doped tin oxide (FTO)-coated glass substrates were cleaned with a detergent solution using an ultrasonic bath for 15 min; and then respectively rinsed with ethanol and deionized water and dried in hot air. The electrodes were prepared by coating TiO_2 paste on the conductive surface of the FTO-coated glass substrates using the doctor blade method followed by annealing at 300°C for 1hour and cooling at room temperature. The resultant average thickness of the TiO_2 film was 12 µm.

Five different solutions of composite dye – i.e. 0.4 mM N719 in ethanol; 0.4 mM N749 in ethanol; 0.3 mM D149 in acetonitrile; 0.3 mM N719 + 0.2 mM D149 in 1:1 ethanol/acetonitrile mixed solvent; 0.3 mM N749 dye + 0.2 mM D149 dye – were prepared. The TiO_2 coated films were immersed in the dye solutions at 25°C for 20 hours. The dye sensitized TiO_2photoanode and the platinum coated counter FTO glass were assembled together. One drop of electrolyte solution composed of iodolyte (50mM iodide/tri-iodide in acetonitrile) was introduced via a predrilled hole in the counter electrode. The active area of the solar cell was 0.25 cm^2.

2.3 Measurement

The current–voltage (I–V) characteristics of the DSSCs were measured by the solar simulator of Air Mass 1.5 (Oriel Sol3A Solar Simulator) to provide an irradiance of 100 mW/cm^2. The absorption spectra of both dye solutions adsorbed on TiO_2 films were recorded by a UV–visible spectrophotometer (UV-1800, Shimadzu). The morphology of the porous TiO_2 film was characterized by scanning electron microscopy (SEM, Olympus BX-51). The crystalline structures were analyzed by X-ray diffraction (XRD, Bruker APEX CCD diffractometer). I–V curves were recorded using a Keithley model 2400 digital source meter.

3 Results and Discussion

Fig. 2(a-b) present a plain-view SEM image of a nanocrystalline TiO_2 film electrode. As seen in the SEM micrograph the TiO_2 anatase film was well-established and held the homogeneously dispersed nanoporous TiO_2 over the surface without aggregations. The TiO_2 film demonstrated a compact microstructure of approximately spherical shape with no apparent long-range order with frequent nanoporous size of about 20nm, which supplied passageways for diffusion of electrolytes and adsorption of dye molecules. The thickness of the TiO_2 film was 12 µm.

Absorption spectra of the Dye solutions and Dye-Sensitized TiO_2 thin films along with co-sensitized approach: In the present study we used a ruthenium II complex (N749 & N719) as the sensitizer and metal-free indoline D149 as the co-sensitizer. In the ruthenium (II) polypyridyl complex sensitizer, the presence of hydrophobic moiety on the bipyridine ligand increases the stability of the DSSCs. The co-sensitizer D149 is a central indoline group which performs as an electron donoring unit, maintained by additional phenyl rings, while the cyanoacrylic acid acts as an acceptor and as a binding group to the semiconductor film. The best metal free organic sensitizers produce higher molar absorption coefficients. The absorption spectra of N749, N719, D149, D149+N749 & D149+N719 dyes solution are shown in Figure 3(a). The N749 dye in ethanol

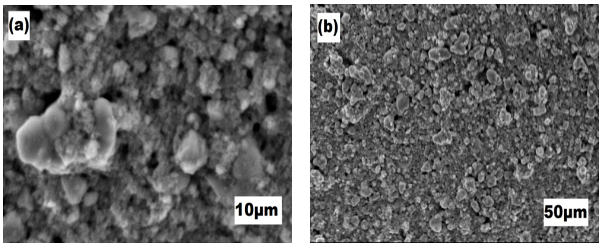
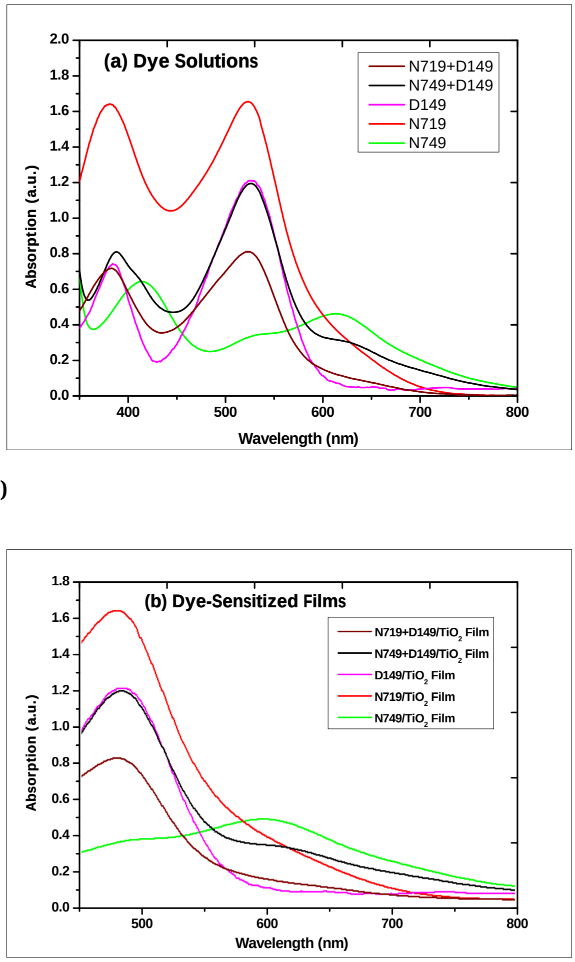


Fig. 2. SEM plain-view image of (a). 10 µm nanocrystalline TiO2 films. (b). 50 µm nanocrystalline TiO2 films.



(a)

(b)

Fig. 3. (a) UV-Vis Spectra of N749, N719, D149, D149+N749 & D149+N719 Dye Solution. (b) UV-Vis Spectra of N749, N719, D149, D149+N749 & D149+N719 on TiO$_2$ Film.

gives two broad peaks in the visible region at 614 nm and 413 nm due to metal-to-ligand charge transfer (MLCT). The two broad peaks of the N719 dye in ethanol in the visible region at 525 nm and 380 nm are assigned to metal-to-ligand charge transfer (MLCT). Likewise, the two distinct absorption bands of the D149 dye in acetonitrile produces the following: a first band in the region of 350 nm-430 nm due to (π–π^*) electron transitions of the conjugated molecules and a second band in the region of 430 nm-614 nm due to an intermolecular charge transfer (ICT) between the electron-donor and electron-acceptor anchoring moieties. Furthermore, the mixed ethanol/acetonitrile solution of both the co-sensitizers N749+D149 and N719+D149 give more intense and broader bands because of the synergistic effect of two dyes comparison to the individual dye.

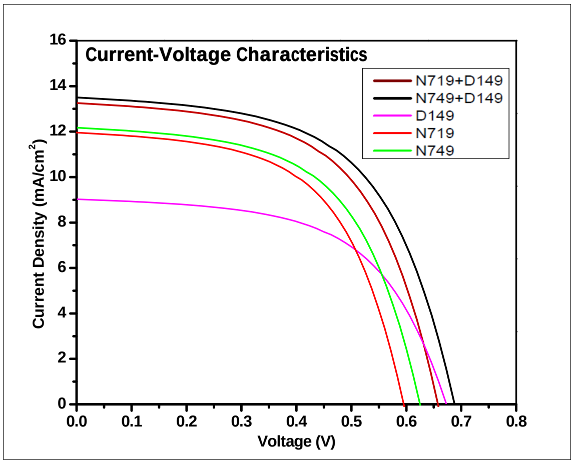


Fig. 4. J–V Characteristics of the TiO2 Sensitized/Co-sensitized based DSSCs.

The absorption spectra of N749, N719, D149, N749+D149 & N719+D149 anchored to TiO$_2$ films are shown in figure 3(b). Similar absorption features were analyzed for both the sensitizers N749 and N719, where the individual dye molecules were anchored onto the semiconductor TiO$_2$ film in the dye solutions respectively. While a very slight hypochromic shift of the sensitizer D149 was analyzed, this was credited to the H-type aggregation of the D149 sensitizer on the TiO$_2$ film. It was observed that the intensity was increased for the both the co-adsorbed TiO$_2$film with N749+D149 and N719+D149. It was verified that a broad and strong spectral response was achieved for the co-sensitized TiO$_2$ films from N749+D149 and N719+D149, which can absorb more photons than the individual sensitized TiO$_2$ films. Thus, light harvesting efficiency (LHE) can be improved by co-sensitization

Figure 4 shows the Current–Voltage characteristics for the DSSCs sensitized/co-sensitized with N749, N719, D149, N749+D149 and N719+D149. The photovoltaic parameters of DSSCs such as the short circuit current density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (FF) and efficiency (η) are summarized in Table 1. The results from the DSSCs show that the N749 sensitized DSSC yielded J_{sc} = 12.2 mA/cm^2, V_{oc}= 630 mV, FF = 0.594 and η = 4.56%; and the N719 sensitized DSSC yielded J_{sc} = 12 mA/cm^2, V_{oc} = 600 mV, FF = 0.589 and η = 4.24%. Furthermore, the metal free organic dye (D149) sensitized DSSC yielded J_{sc} = 9 mA/cm^2, V_{oc} = 660 mV, FF = 0.674 and η = 4.06%. The photovoltaic results clearly show the efficiency for the individual-dye sensitized devices in the following order: N749 (PCE = 4.56%) > N719 (PCE = 4.24%) > D149 (PCE = 4.06%). Upon co-sensitization, the device made of co-sensitized N749+D149 yielded $J_{sc=}$ 13.6 mA/cm^2, V_{oc} =

Table 1. Photovoltaic parameters of DSSCs.

Device	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
N749 Sensitizer	12.2	630	0.594	4.56
N719 Sensitizer	12	600	0.589	4.24
D149 Sensitizer	9	670	0.674	4.06
N749+D149 Co-sensitizer	13.6	690	0.576	5.40
N719+D149 Co-sensitizer	13.3	660	0.563	4.94

690 mV, FF = 0.576 and η = 5.40% and the device made of co-sensitized N719+D149 yielded J_{sc} = 13.3 mA/cm^2, V_{oc}= 660 mV, FF = 0.563, and η= 4.94%. Upon optimization, the co-sensitized based devices indicated an effective enhancement in efficiency in comparison to the devices sensitized by N749, N719 or D149 only. The efficiency of the co-sensitized devices strongly depend on the enhanced values of the short circuit current (J_{sc}) and the open circuit voltage (V_{oc}), which are strongly associated with high light absorption in the visible region and a decrease in charge recombination. Furthermore, the enhancement in efficiency for the DSSC based on co-sensitization can also be recognized to the fact that the co-sensitizer successfully overcomes the competitive photon absorption by ionic species in the electrolyte (I^-/I_3^-), lower dye aggregation, and decreases charge recombination.

4 Conclusion

In conclusion, the combination of a ruthenium II complex (N749 & N719) as the sensitizer and a metal-free indoline (D149) as co-adsorbent, were effectively demonstrated to enhance J_{sc} and the cell efficiency of the DSSC. The homogenously mixed solutions of N749, N719 and D149 in Ethanol/Acetonitrile in a ratio 1:1 were used for the co-sensitization of TiO_2 coated photoanodes of DSSCs. The results indicate that the Ethanol/Acetonitrile (1:1) solutions of co-sensitization N749+D149 and N719+D149 shows more intensive and broader bands as compared to that of individual sensitizers N749, N719 and D149 dyes due to the combined effect of two sensitizers. The photovoltaic performances of individual dye sensitized and co-sensitized devices are related to the absorption properties of the sensitizer anchored TiO_2 film and the charge recombination rate for the device. Hence an improvement in the open circuit current (J_{sc}) and efficiency is achieved. Under optimal conditions, the power conversion efficiencies (PCE) of N749+D149 of 5.40% and N719+D149 of 4.94% are achieved, which is higher than those based on individual dyes, N749 (4.56%), N719 (4.24%) and D149 (4.06%). In conclusion, the enhancement in efficiency is primarily dependant on the increase in J_{sc} and V_{oc}, which are strongly implicated to improve light absorption and decrease charge recombination, respectively.

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