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N719 and D149 dyes: Appropriate sensitizers for bare SnO_2 and MgO coated SnO_2 based dye-sensitized solar cells

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ABSTRACT

SnO_2 is an attractive semiconducting material suitable for application as the photoanode in dye sensitized solar cells (DSSCs) due to its favourable properties such as wide band gap and notable photo stability. However, improved solar cell performances can be achieved by using composites of SnO_2 with several other materials like Al_2O_3 or MgO. In this study photovoltaic performances of DSSCs with pristine SnO_2 and SnO_2 coated MgO composite photoanodes were investigated with two different dyes, namely Ruthenium N719 and metal free Indoline D149. Significant difference in the efficiencies was observed in DSSCs made with liquid electrolyte having I^-/I_3^- redox couple and Pt counter electrode. DSSC fabricated with D149 sensitized pristine SnO_2 showed higher efficiency of 2.07% compared to the efficiency of 1.07% for the DSSC sensitized with N719. Higher energy level of the, lowest unoccupied molecular orbital (LUMO) of D149 than that of N719 and the higher insulating nature of the metal free D149 could be possible reasons which could help rapid electron transfer from the excited dye molecules to the conduction band (CB) of the semiconductor and reduction of recombination of the electrons in the device. It was also observed that DSSC fabricated with N719 sensitized SnO_2/MgO composite photoanode exhibited higher efficiency of 3.43% than the efficiency of 0.67 % for the DSSC having D149 sensitized photoanode. Higher insulating nature of the metal free D149 layer and the SnO_2/Dye interface due to the insertion of MgO would have reduced the electron transfer from the excited dye molecules to the CB of the semiconductor. Therefore, metal free dyes could be used effectively to sensitize pristine SnO_2 photoanode.

Keywords: tin dioxide, stannic oxide, Indoline D149, Ru-dye, tunneling

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are emerging as promising candidates to replace expensive silicon solar cells because of reasonably high efficiency and lower production cost. Photoanodes of these DSSCs generally comprised with oxide semiconductor like TiO_2, ZnO and SnO_2 [1–3]. Tin oxide (SnO_2) has exceptional optical and electrical properties, chemical stability and flexible morphological transformations with a wide band gap (E_g = 3.62 eV at 27 °C), notable photo stability and high charge mobility (~250 $cm^2\ V^{-1}\ s^{-1}$). Hence, the SnO_2 is an attractive semiconductor material for many applications such as DSSCs, gas sensors, optoelectronic devices, anti-reflective coatings and batteries. Though, SnO_2 is not much popular in DSSCs, because of the low power conversion efficiencies (PCE) due to the high recombination rate of electrons. Some unconventional approaches for enhancing dye-sensitized solar cell performance have also been actively demonstrated. In particular, improved solar cell performances can be achieved by using composites of SnO_2

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with several other materials like Al_2O_3, $CaCO_3$ or MgO [4–6]. As Tennakone *et al.* [7] reported, on coating the SnO_2 crystallite surfaces with a thin insulating layer of MgO, an oblivious enhancement of Short-circuit current density (J_{SC}) open-circuit voltage (V_{OC}) and efficiency was observed.

Moreover, in order to get high performed DSSCs, all three major components in the system named photoanode, electrolyte and sensitizer/dye should efficiently play their role. As indicated by Shalini *et al.* [8], dye in particular should possess certain important features for efficient performance, namely, a broad and strong absorption from visible to near-infrared region, chemical stability of the appropriate lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels for effective charge injection into the semiconductor, and dye regeneration from the electrolyte, high-molar extinction coefficients in the visible, and near-infrared region for light-harvesting, good photo stability, and solubility to hamper the recombination [8,9]. At present, DSSC is fabricated by using inorganic ruthenium (Ru)-based dyes, metal-free organic dyes, quantum-dot sensitizer, perovskite-based sensitizer, and natural dyes as sensitizer. But in terms of PCE and stability Ru- based dyes are the most successful dyes. Because of the higher absorption in the visible range of solar spectrum, excellent electron injection, and efficient metal-to-ligand charge transfer of Ru-based dyes. Even though Ru-based dyes are most successful, metal-free dyes have become a viable alternative to expensive and rare Ru-based dyes because of low cost, ease of preparation, easy attainability, and environmental friendliness [8–10]. Metal-free organic dyes offer superior molar extinction coefficients, low cost, and a diversity of molecular structures. Photosensitizers such as Indoline, phenothiazine and tetrahydroquinoline have achieved efficiencies up to 6% for SnO_2-based DSSCs and up to 9% for TiO_2-based DSSCs [4,8,10]. In unmodified bare SnO_2-based dye-sensitized solar cells, Ariyasinghe *et al.*[11] reported higher efficiency for the cells consisting with Indoline D-149 dye than with Ru-based N719 dye. As per Ariyasinghe *et al.* this enchantment is due to the possible higher degree of chelation of D-149 dye molecules and could act as a thin insulating layer on SnO_2 crystallites as observed in cases of SnO_2/MgO and SnO_2–$CaCO_3$ systems [7,11,12]. In order to compare the performance of the DSSCs sensitized with different dyes, four types of DSSCs have been prepared by sensitizing with (a) N719 dye and (b) D149 dye. The two dyes with concentration of 0.3 mM used to sensitize the both bare-SnO2 and SnO2/MgO composite film-based DSSCs.

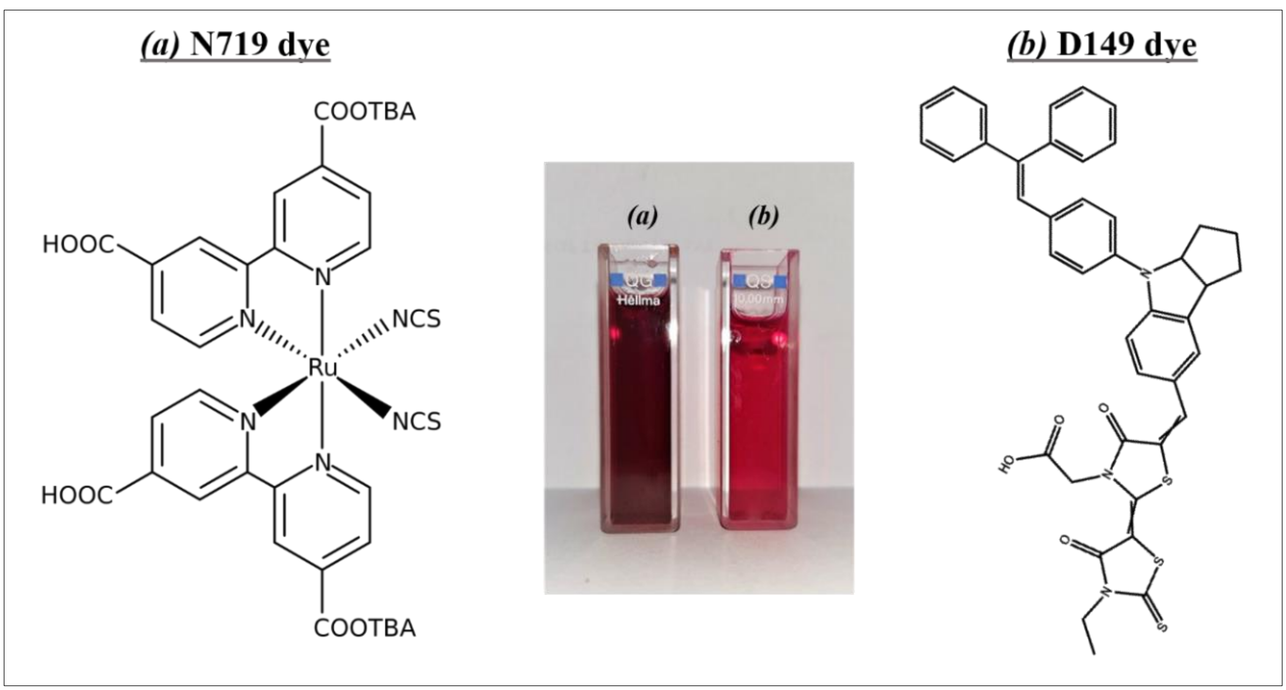

Figure 1: Chemical structures of two dyes, (a) N719 and (b) D149, and physical appearances of prepared 0.3mM dye solutions.

2. METHODOLOGY

2.1 Optical absorption measurements

Optical absorption spectra of two dye solutions, (1) cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) known as N719 and (2) 5-[[4-[4-(2,2-Diphenylethenyl)phenyl]-1,2,3-3a,4,8b-hexahydrocyclopent[b]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)-4-oxo-3-thiazolidineacetic acid known as D149, were taken by using the Shimadzu 2450 UV-VIS spectrophotometer in the wavelength range from 200 nm to 1200 nm.

2.2 Preparation of SnO_2-based photoanodes and *J* –V characterization

To prepare the bare SnO_2 films, SnO_2 colloidal solution (Alfa chemicals, 15 % SnO_2 colloidal in H_2O) was grounded together with 3 drops of glacial acetic acid and 3 drops of Triton-X 100 using an agate mortar. The mixture was dispersed in 40 ml of ethanol and ultra sonicated for 10-15 minutes. The sonicated dispersion was sprayed on to 1.0 × 2.0 cm^2 area of cleaned fluorine doped tin oxide (FTO) glass plates (7 Ω/sq FTO from Solaronix) and kept on a hot plate maintained at 150 °C and then sintered at 550 °C in a furnace for 45 min.

SnO_2/MgO composite photoanodes were prepared by using 2.0 ml of SnO_2 colloidal suspension, 0.025g of anhydrous MgO nanoparticles and 3 drops of glacial acetic acid were mixed together in an agate mortar and grounded well with 3 drops of Triton X-100. The mixture was dispersed in 40 ml of ethanol and then sonication, spraying & sintering process were carried out same as done for bare SnO_2 film. Prepared SnO_2 based films (bare SnO_2 & SnO_2 / MgO composite) were then separately immersed in a 0.3mM N719 dye solution (in absolute ethanol) for 24 hours and in a 0.3 mM Indoline D149 dye solutions (in t-butyl alcohol : Acetonitrile, 1:1 by volume) for 1 hour and 45 minutes and gently rinsed with absolute ethanol. Figure 1 shows the chemical structure of two dyes, N719 and D149, with physical appearances of prepared dye solutions.

The prepared liquid electrolyte containing tetrapropyl ammonium iodide salt and iodine in molten ethylene carbonate and acetonitrile. The I^-/I_3^- redox mediator was injected into the space between the photoanode and the counter electrode to form a sandwich structure for each photoanode type. The fabricated DSSCs were in the configuration of (a) FTO/ N719:SnO_2/ electrolyte/ Pt (b) FTO/ D149:SnO_2/ electrolyte/ Pt (c) FTO/N719: SnO2/MgO electrolyte/Pt FTO/ and (d) FTO/ D149:SnO2/MgO /electrolyte/Pt. The photocurrent density versus voltage measurements were taken for these DSSCs under the illumination of 100 mW cm^{-2} (1.5 AM filter) simulated sunlight with a 100 W Ozone Free Xenon Lamp and an Oriel LCS-100 solar simulator using a Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128. The active area of each cell was 0.25 cm^2.

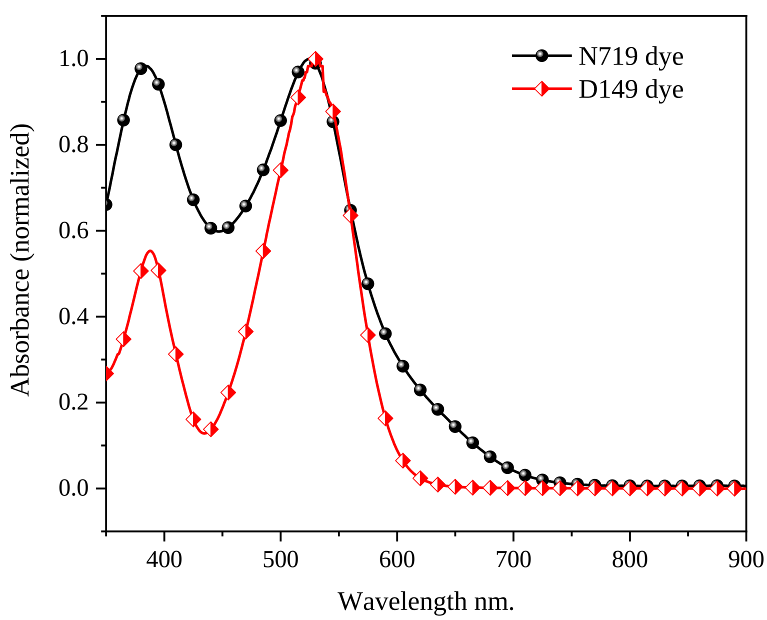

Figure 2: The optical absorption spectra for N719 and D149 dye solutions

3. RESULTS AND DISCUSSION

3.1. Dyes and UV- Visible absorption of dyes

The chemical structures of Ru-based N719 dye and Indoline D149 dye are shown in Figure 1. As it shows, D149 is a metal-free dye with a higher insulating nature than N719. The D-149 dye consisting with both -COOH and C=S functional groups. Due to the availability of the above moieties, it might be possible to have double chelation of these moieties with SnO_2 crystallites which eventually reduce the recombination and enhance the efficiency of the cell [11].

The optical absorption spectra for (a) 0.3 mM N719 dye solution (in absolute ethanol) and (b) 0.3 mM D149 dye (in a 1:1solvent mixture of acetonitrile and tertiary-butyl alcohol) are shown in Figure 2. As shown in Figure 2, broaden absorption graph was observed to the N719 than D149. The absorption maximum, which corresponds to dye solutions, N719 and D149, are 524.6 nm and 531.6 nm respectively. There are three important steps to convert solar power into electrical energy, those are: the visible photoexcitation of dyes triggering an electron transfer into the conduction band of the SnO_2 semiconductor, followed by regeneration of the oxidized dye molecules by the electron donation from the I^-/I_3^- redox couple in the electrolyte, and finally migration of electron through the external load to complete the circuit. Figure 3 shows the schematic energy level diagram indicating the position (eV) of the conduction band (CB) and valence band (VB) of SnO_2, ground (LUMO) & excited (HOMO) levels of the N719 and D149 dyes and the I^-/I_3^- redox potential level of electrolyte. For the effective electron injection in to the CB of SnO_2 is depend on the position and chemical stability of HOMO and LUMO. As shown in Figure 3, when compare the LUMO energy level of two dyes the LUMO of D149 is higher than LUMO of N719 dye. Hence, due to the higher energy difference, the electron injection efficiency to CB of SnO_2 from the excited state (D*) of D149 dye is more favorable than N719 dye. The rapid electron transfer from the excited dye molecules to the conduction band (CB) of the semiconductor could also be a reason to enhance the photocurrent, I_{SC} [8,13,14].

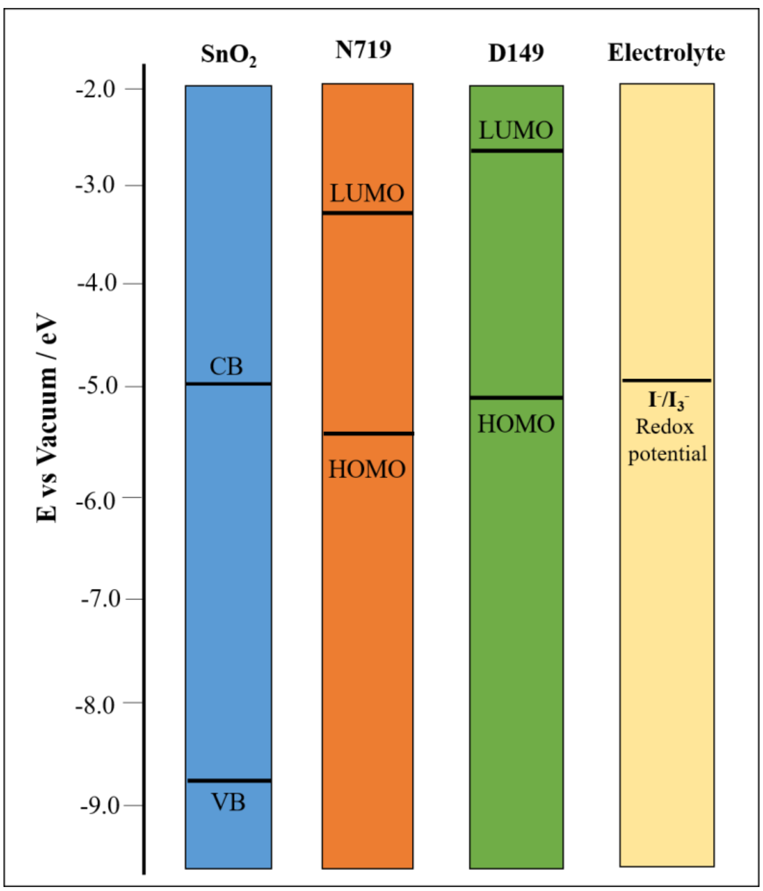

Figure 3: Schematic energy level diagram indicating the position (eV) of the bands of SnO_2, ground (LUMO) & excited (HOMO) levels of the N719 and D149 dyes and the I^-/I_3^- redox potential level of electrolyte.

3.2 Photovoltaic performance (*J-V* characterization) of DSSCs

Figure 4 shows the *J*-V graphs for the four types of DSSCs, fabricated with two different photoanodes (1) bare SnO_2 film, (2) SnO_2/MgO composite film and sensitized with two different dyes (1) N719 and (2) D149, under the same illumination condition. And Table 1 summarizes the corresponding photovoltaic parameters. As shown in Table 1 and Figure 4, DSSCs made with bare-SnO_2 and sensitized with D149 (cell A) shows the higher PCE than sensitized with N719 (cell B), but it was opposite for the DSSCs made with SnO_2/MgO composite. i.e. the higher efficiency was observed to the cell which was sensitized with N719 dye (cell D) than D149 dye (cell C) for SnO_2/MgO composite.

The enhanced PCE of 2.07% and improved-V_{OC} of 533.1 mV was observed for DSSCs using D149 as the sensitizer, without any modification in the SnO_2 electrode or electrolyte. As mention in literature, the improvement of photovoltaic performance is attributed to the suppression of recombination of electrons due to the passivation of trap sites in SnO_2 film by the dual chelating attachment of D-149 dye. Such efficiency could not be achieved for bare SnO_2 based DSSCs with N-719 dye [11,15]. When compared the DSSCs fabricated with SnO_2/MgO composite and sensitized with N719 dye (cells B and D), a thin MgO insulating layer coated around SnO_2 semiconductor particle in the photoanode, it remarkably reduces the recombination of the photo-generated electrons. This lead to a dramatic enhancement in V_{OC}, J_{SC}, FF and efficiency of the DSSC made with SnO_2/MgO composite photoanode compared to the DSSC made with bare SnO_2 photoanode (Table 1, cells B and D). A comparison of *J*-V curves in Figure 4 (a), also shows the dramatic increase in both *J*sc and *V*oc of the DSSCs due to the effect of the insulating nature of D149 layer (shell) around the SnO_2 semiconductor grains. As discussed earlier, this effect arises due to the impressive inhibition of electron back transfer from SnO_2 to the redox electrolyte (I_3^-) as like the MgO insulating layer. According to Tennakone *et al.*[7], the optimum MgO layer thickness is expected to be around few angstroms, suggesting that electron transfer from the excited dye attached to the MgO oxide surface to the underlying SnO_2 occurs by tunneling through the thin insulator layer. Since the D149 dye is an insulator, when the metal-free D149 used to fabricate DSSCs with SnO_2/MgO composite as the sensitizer, it could act as another insulating layer on top of SnO_2 crystallites in addition to MgO layer. Hence, it could act as an extra barrier would have reduced the forward electron transfer too. Further in the SnO_2/MgO composite, MgO reduces the surface coverage of the D149 dye on SnO_2 crystallites. So, the possible degree of chelation via COOH and C=S moieties of D149 dye could be very low compare to the bare SnO_2. In consequence, the J_{SC} and FF of Cell-C was worst than Cell-A (Table 1 and Figure 4 (b)). [7,11,16]. Because of the capability of efficient metal-to-ligand charge transfer and excellent electron injection of the Ru-based N719 dye, that DSSC fabricated with N719 sensitized SnO2/MgO composite photoanode exhibited higher efficiency of 3.43% than the efficiency of 0.67 % for the DSSC having D149 sensitized photoanode.

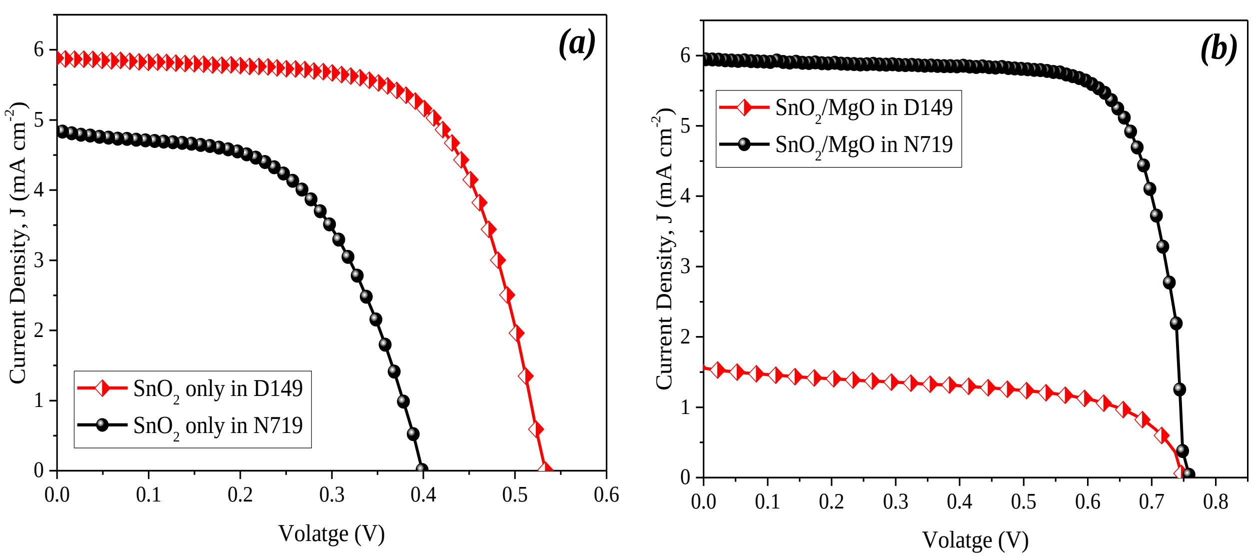

Figure 4: Photocurrent density–voltage characteristics of **(a)** bare SnO_2 based DSSCs (cells A & B) and **(b)** SnO_2/MgO based DSSCs (cells C & D) fabricated with two different dyes, N719 and D149, under illuminated condition.

Table 1: I–V parameters (short circuit-current density, open-circuit voltage, efficiency and fill-factor) of SnO_2 system and SnO_2/MgO system sensitized with two different, D149 & N719, dyes.

Cell	Photoanode	Dye	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	η %
A	SnO_2	D149	533.1	5.88	66.2	2.07
B		N719	398.6	4.84	55.6	1.07
C	SnO_2/ MgO	D149	756.8	1.56	56.8	0.67
D		N719	768.7	5.95	74.9	3.43

4. CONCLUSIONS

In order to investigate the performance of the SnO_2-based DSSCs, fabricated with two different photoanodes (1) bare SnO_2 film, (2) SnO_2/MgO composite film with two different dyes, four types DSSCs were prepared, (A)Bare SnO_2 with D149 dye, (B) Bare SnO_2 with N719 dye, (C) SnO_2/MgO with D149 dye and (D) SnO_2/MgO with N719 dye. The reported power conversion efficiencies for these DSSCs are 2.07%, 1.07%, 0.67% and 3.43% respectively, under same condition. Hence the corresponding PCE of DSSCs, Indoline D149 dye is most appropriate sensitizer than N719 for bare-SnO_2 based DSSCs and Ru-based N719 dye is most appropriate sensitizer than D149 for SnO_2/MgO composite based DSSCs.

5. REFERENCES

[1] O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature* **353**, 737 (1991).

[2] Gong, J., Sumathy, K., Qiao, Q. & Zhou, Z. Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends. *Renew. Sustain. Energy Rev.* **68**, 234–246 (2017).

[3] Andualem, A. & Demiss, S. Review on Dye-Sensitized Solar Cells (DSSCs). *Edelweiss Appl. Sci. Technol.* **2**, 145–150 (2018).

[4] Zainudin, S. N. F., Abdullah, H. & Markom, M. Electrochemical studies of tin oxide based-dye-sensitized solar cells (DSSC): a review. *J. Mater. Sci. Mater. Electron.* **30**, 5342–5356 (2019).

[5] Senadeera, G. K. R., Weerasinghe, A. M. J. S., Dissanayake, M. A. K. L. & Thotawatthage, C. A. A five-fold efficiency enhancement in dye sensitized solar cells fabricated with AlCl3 treated, SnO2 nanoparticle/nanofibre/nanoparticle triple layered photoanode. *J. Appl. Electrochem.* **48**, 1255–1264 (2018).

[6] Baraneedharan, P., Chidambaram, S., Kasi, N. & Muthusamy, S. Recent advances in SnO2 based photo anode materials for third generation photovoltaics. in 25–38 (2014).

[7] Tennakone, K., Bandara, J., Bandaranayake, P. K. M., Kumara, G. R. A. & Konno, A. Enhanced Efficiency of a Dye-Sensitized Solar Cell Made from MgO-Coated Nanocrystalline SnO2. *Jpn. J. Appl. Phys.* **40**, L732–L734 (2001).

[8] Shalini, S. *et al.* Status and outlook of sensitizers/dyes used in dye sensitized solar cells (DSSC): a review. *Int. J. Energy Res.* **40**, 1303–1320 (2016).

[9] Giribabu, L., Kanaparthi, R. K. & Velkannan, V. Molecular engineering of sensitizers for dye-sensitized solar cell applications. *Chem. Rec.* **12**, 306–328 (2012).

[10] Mehmood, U., Rahman, S., Harrabi, K., Hussein, I. A. & Reddy, B. V. S. Recent Advances in Dye Sensitized Solar Cells. *Adv. Mater. Sci. Eng.* **2014**, 974782 (2014).

[11] Ariyasinghe, Y. P. Y. P. *et al.* Efficient passivation of SnO2 nano crystallites by Indoline D-149 via dual chelation. *J. Photochem. Photobiol. A Chem.* **217**, 249–252 (2011).

[12] Bhande, S. S. *et al.* DSSCs synergic effect in thin metal oxide layer-functionalized SnO2 photoanodes. *J. Photochem. Photobiol. A Chem.* **295**, 64–69 (2014).

[13] Solaronix. Ruthenizer 535-bisTBA, High Performance Ruthenium Photo-Sensitizer for Dye Solar Cell Application. 1–4 https://shop.solaronix.com/sensitizing-dyes/ruthenium-dyes/ruthenizer-535-bistba.html (2013).

[14] Xu, J. *et al.* DFT Studies on the electronic structures of indoline dyes for dye-sensitized solar cells. *J. Serbian Chem. Soc.* **75**, 259–269 (2010).
[15] Ito, S. Investigation of Dyes for Dye-Sensitized Solar Cells: Ruthenium-Complex Dyes, Metal-Free Dyes, Metal-Complex Porphyrin Dyes and Natural Dyes. *Sol. Cells - Dye. Devices* 18–48 (2011) doi:10.5772/19960.
[16] Horiuchi, T., Miura, H., Sumioka, K. & Uchida, S. High Efficiency of Dye-Sensitized Solar Cells Based on Metal-Free Indoline Dyes. *J. Am. Chem. Soc.* **126**, 12218–12219 (2004).