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Investigation of effect of thiophene-2-acetic acid as an electron anchoring group for a photovoltaic device

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ABSTRACT

Different anchoring groups such as thiophene-2-acetic and malonic acid were investigated for synthesis of new photosensitizers. The new dyes (photosensitizers) were made pure and determined by various analytical techniques. The chemical structure of synthesized materials was certified by analytical studies. UV-Visible and fluorescence spectra revealed intense fluorescence and absorption for organic photosensitizers. The cyclic voltammetry results showed that the two photosensitizers were suitable for dye sensitized solar cell preparation. The work electrode was gathered using tin (IV) oxide nanoparticles in dye-sensitized solar cells structure. The new photosensitizers and tin (IV) oxide were used for photovoltaic devices preparation. The power conversion efficiency was obtained as about 4.12 and 4.29% for Dye 1 and Dye 2, respectively.

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1. Introduction

Nowadays energy supply is of great importance for life and industries. Another important issue is protecting the environment. Dye-sensitized solar cells (DSSCs) technology can produce green and environmentally friendly energy [1,2]. These devices are composed of several major components which include the following: photoanode (containing mesoporous semiconductor metal oxide film and sensitizer), electrolyte/hole transporter, and counter electrode [3]. Most DSSCs research have focused on two main components: sensitizer as the electron donor and semiconductors as the electron acceptor [4,5]. TiO₂ nanocrystalline material as a semiconductor has been applied as in DSSC devices. Other n-type metal oxide nanocrystalline compounds, such as ZnO, SnO₂, In₂O₃ and Nb₂O₅ can also be used in DSSCs based on investigation on photoelectrochemically active thin semiconductor substrate [6–8]. Several studies have reported different groups of various sensitizers containing organometallic, metal-free, and natural dyes in preparation of DSSCs towards a higher power conversion efficiency [9]. Two types of SnO₂ nanocrystalline were synthesized by Wang *et al.* The prepared devices exhibited appropriate conductivity and efficiency of about 4–5% for N719 [10]. The ZnO crystalline film was prepped on a conductive substrate and sensitized by N719 as a photosensitizer. The DSSCs based on this component resulted in an efficiency of 0.4 percent [11]. To improve the performance of photoanodes, Saito and Fujihara prepared a ZnO film via the squeegee method and obtained a power

conversion efficiency of 6.58 percent [12]. A ZnO/TiO₂ electrode via anion-vacuum solution method was prepared by Chou *et al.* employing the DSSCs structure. The device showed an efficiency of about 6.62% [13]. Elsewhere, TiO₂ doped with F was synthesized by Yang *et al.* and employed in dye-sensitized solar cell devices with 8.07% of power conversion efficiency [14].

A series of new sensitizers based on indoline containing phenylethynyl, thienlethynyl as π -conjugated bridge was synthesized by Srinivas *et al.* The organic photosensitizers showed good efficiency in photovoltaic devices with theoretical studies proving the charge conduction at a molecular level [15]. Two new organic sensitizers to form a donor-acceptor- π -acceptor (D-A- π -A) configuration were prepared by Singh *et al.* and applied in a photovoltaic structure. The thiophene group was utilized as a conjugated bridge and obtained an efficiency of about 4–5% [16]. TDDFT and theoretical method was utilized for the investigation of chemical properties of indoline dyes as photosensitizers with D-A- π -A configuration by Ding *et al.* The results show that the longer conjugated bridge caused increase efficiency of the devices [17]. Slodek *et al.* synthesized two new dyes based on phenothiazine with multi donor and acceptor substituents and applied these in DSSCs structures. The results show that the photovoltaic devices presented good performance and efficiency around 6.11 and 5.03% [18].

In this study, two different anchoring groups were utilized for preparation of new photosensitizers. Analytical methods such as FTIR and NMR were utilized for identification of synthesized intermediates and dyes. The absorption of dyes was investigated in the solution and applied on the photoanode by UV-Visible method. Photovoltaic devices were then assembled using these photosensitizers and their performances were tested. Figure 1 presents the route of preparing the synthesized organic dye.

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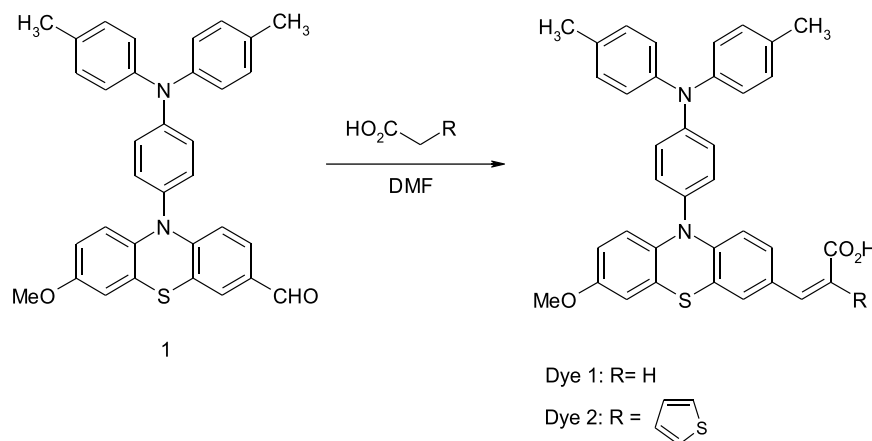


Fig. 1. Synthesis route for the organic sensitizers.

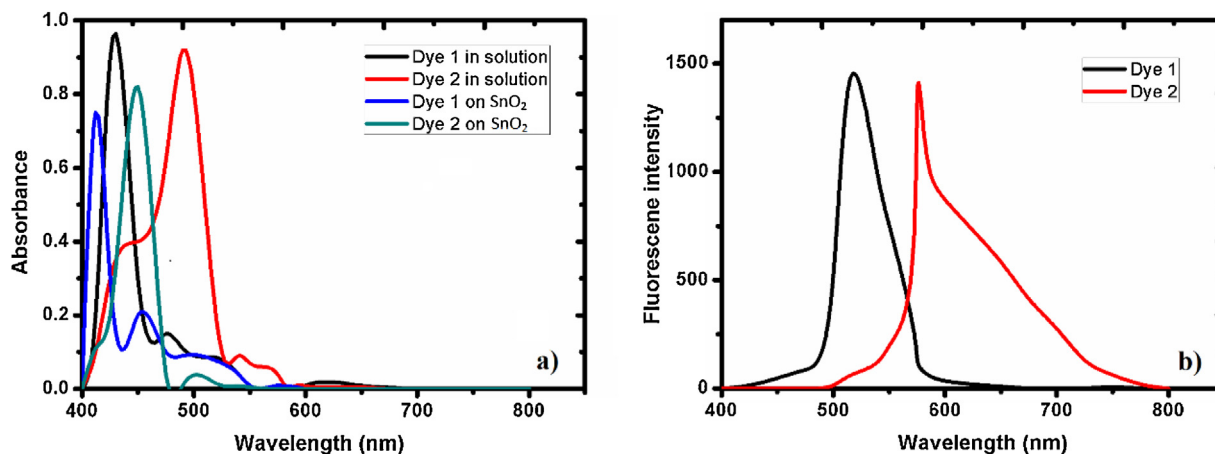


Fig. 2. a) UV-Visible absorption and b) fluorescence spectra of dyes.

2. Experimental

2.1. Materials and instrumentation

All chemical ingredients were bought from Merck Company and consumed without purification. The preparation path of component 1 has been described in a previous published paper [19]. Fluorine doped thin oxide (FTO) substrate, scattering layer, N719 as a standard photosensitizer, and titanium dioxide paste were bought from Sharif Soar Company. Differential scanning calorimetry (DSC) analyses were carried out on a DSC 214 Polyma-NETZSCH thermal analyzer. The infrared (FTIR) spectra were recorded on a Perkin Elmer instrument using pulverized samples. The NMR spectra were recorded on a Bruker Avance 400 MHz instrument using CDCl_3 and acetone- d_6 as solvents. UV-Visible and fluorimetry measurements were done on a Cecil 9200 spectrophotometer and Ocean Optics fluorometer, respectively. The X-ray powder diffraction (XRD, D8-Advance Bruker, and made in Germany) and Field Emission Scanning Microscopy (FESEM) were employed for investigation of SnO_2 nanoparticles. FESEM characterization was performed by a MIRA3TESCAN-XMU microscope operating at 15 kV. The solar device investigation was done under 100 mW/cm^2 (1.5 Air Mass) illumination conditions by a solar simulator (III-S NanoSAT 210+Iran) (Solmetric I-V Curve Tracer SIV-200+Iran).

2.2. SnO_2 nanoparticles procurement

Stannic oxide nanoparticles were prepared by a hydrothermal technique. For this purpose, 1.7353 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 20 ml deionized water, 20 ml absolute ethanol, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were mixed in a beaker under pH=9 and intense magnetic stirring. The resulting mixture was placed in an oil bath at 70°C and after 30 min stirring, placed in an autoclave of 50 ml capacity heated to 180°C for 24 h. The autoclave then cooled

naturally at room temperature. Eventually, the resulting powder was drained with deionized H_2O and ethanol several times and dried in air atmosphere.

2.3. Dye 1 procurement

20 ml CH_3CN were added to 17.6 mmol **1** (N-(N,N-diparatolylamino)-7-methoxy-3-yl phenothiazine), 42 mmol malonic acid and 8 drops of piperidine and mixed for 3 h under 90°C . The resulting powder was filtered and purified by silica gel column chromatography (chloroform:methanol, 6:1). Yield = 88 percent; mp: 319°C ; FTIR (KBr) (Cm^{-1}): 3049: CH str. Ar, 1707: C=O str. Acid, 1611, 1439: C=C str.; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 2.28 (s, 6H, CH_3), 3.88 (s, 3H, OCH_3), 6.82–6.79 (d, 4H, ArH, $J=7.1 \text{ Hz}$), 7.21–7.25 (dd, 2H), 7.84–7.80 (d, 4H, ArH, $J=7.5 \text{ Hz}$), 7.89 (s, 2H, ArH), 8.06–8.66 (d, 4H, ArH, $J=7.3 \text{ Hz}$), 8.66–8.70 (d, 4H, ArH, $J=7.2 \text{ Hz}$), 9.71 (s, 1H, CO_2H); $^{13}\text{CNMR}$ (100 MHz, CDCl_3 , δ /ppm): 202.87 (C=O, Ket), 163.22 (C=O, Acid), 112.83, 116.26, 117.78, 118.16, 119.82, 120.35 (2C), 121.72, 122.95, 123.44, 124.22 (2C), 125.44, 126.44, 127.12, 128.31, 129.27 (2C), 130.87, 131.02, 131.34 (2C), 132.67, 134.45, 135.01, 136.11 (2C), 137.57, 138.83, 139.14, 140.54, 143.51 (C Ar), 56.47, 86.48 (C Aliphatic); Elem. Anal. Calcd. For $\text{C}_{36}\text{H}_{30}\text{SO}_3\text{N}_2$: C, 75.78%; H, 5.26%; N, 4.91%. Found: C, 75.62%; H, 5.08%; N, 5.03%.

2.4. Dye 2 procurement

Similarly, 20 ml CH_3CN was added to 8 mmol **1** (N-(N,N-diparatolylamino)-7-methoxy-3-yl phenothiazine), 16 mmol thiophene-2-acetic acid and 9 mmol of piperidine and stirred for 6 h under 90°C . The obtained powder was filtered and purified by silica gel column chromatography (chloroform:methanol, 10:1). Yield = 89 percent; mp: 326°C ; FTIR (KBr) (Cm^{-1}): 3033: CH str. Ar, 1700: C=O str.

Table 1
Absorption and emission properties of the synthesized dyes.

Dye	$\lambda_{\max}(\text{nm})^a$	$\epsilon (\text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\max}(\text{nm})^b$	$\lambda_{\text{F}}(\text{nm})^c$	E_{F}	$(\text{Cm}^{-1}) \nu_{\text{A}}-\nu_{\text{F}}$
D1	428	24272	412	512	0.21	4023
D2	491	25136	453	574	0.22	4234

^a Maximum absorption in CHCl_3 solution (10^{-5} M) at 25°C .

^b Maximum absorption on SnO_2 film.

^c Maximum emission in CHCl_3 solution (10^{-5} M) at 25°C .

Acid, 1606, 1421: $\text{C}=\text{C}$ str.; $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 2.38 (s, 6H, CH_3), 3.81 (s, 3H, OCH_3), 6.70–6.73 (d, 4H, ArH, $J=7.3$ Hz), 7.25–7.30 (d, 1H), 7.37–7.40 (d, 6H, ArH, $J=7.2$ Hz), 7.44 (dd, 1H, ArH), 7.56 (s, 2H, ArH), 7.70–7.78 (d, 4H, ArH, $J=7.0$ Hz), 7.80–7.86 (d, 4H, ArH, $J=7.5$ Hz), 10.13 (s, 1H, CO_2H); $^{13}\text{CNMR}$ (100 MHz, CDCl_3 , δ/ppm): 192.10 (C=O, Ket), 160.91 (C=O, Acid), 110.23, 112.45, 113.74, 114.45, 115.28, 117.22 (2C), 119.36, 120.68, 121.17, 122.68 (2C), 123.68, 125.61, 126.25, 128.95, 129.25 (2C), 130.76, 131.49, 131.71 (2C), 132.61, 133.80, 135.41, 136.77 (2C), 137.25, 138.48, 139.26, 140.19, 143.17 (C Ar), 57.32, 81.29 (C Aliphatic); Elem. Anal. Calcd. for $\text{C}_{40}\text{H}_{32}\text{S}_2\text{O}_3\text{N}_2$: C, 73.61%; H, 4.90%; N, 4.26%; Found: C, 73.21%; H, 5.09%; N, 4.89%.

2.5. Electrochemical measurements

Electrochemical measurements of the synthesized dyes were carried out in an acetonitrile solution. The oxidation potential (E_{ox}) was measured using three small-sized electrodes. Ag quasi reference electrode (QRE) was used as the reference. Platinum wires were used as working and counter electrodes. All electrode potentials were calibrated with respect to ferrocene(Fc)/ferrocenium (Fc^+) redox couplet. An acetonitrile solution of each dye containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) and ferrocene (ca. 1 mmol dm^{-3}) was also prepared. The electrochemical measurements were performed at a scanning rate of 100 mV s^{-1} [20,21].

2.6. Dye sensitized solar cells assembly and photovoltaic characteristics

A nanocrystalline TiO_2 or SnO_2 film was coated on a FTO coated glass support. The dye was adsorbed by dipping the coated glass for several hours in a 5×10^{-4} M ethanolic solution of the dye. The visible bands in the absorption spectrum of the dyes on the nanostructure film appeared only after the photoelectrodes were dipped in the dye solution for at least 10 h. Finally, the film was washed with an acetonitrile-ethanol 1:1 mixed solvent. Acetonitrile-ethylenecarbonate ($v/v=1:4$) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as an electrolyte. The dye-adsorbed photoelectrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [21,22].

An action spectrum was measured under monochromatic light with a constant photon number ($5 \times 10^{15} \text{ photon cm}^{-2} \text{ s}^{-1}$). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) through a shading mast ($5.0 \text{ mm} \times 4 \text{ mm}$) using a Bunko-Keiki CEP-2000 system.

3. Results and Discussion

The organic dyes were prepared via Knoevenagel reaction as aldol condensation (Fig. 1). In this reaction, as nucleophilic addition, a carbonyl substituent was prepared via a dehydration reaction in which a molecule of water is eliminated. The supply is often an α,β -unsaturated ketone and the catalyst is a weakly basic amine. Many commercial compounds, such as drugs, are synthesized using the Knoevenagel reaction [23,24]. For dye preparation, component 1 reacted with malonic and thiophene-2-acetic acid, separately in basic media. The synthesized dyes were then purified and identified by FT-IR, $^1\text{HNMR}$, $^{13}\text{CNMR}$, and CHN. The synthesis yield of Dye 1 and Dye 2 were calculated as 89 and 88 percent, respectively.

Table 1 and Figure 2 present the absorption and emission information of organic dyes. The intramolecular charge transition [25] caused intense absorption around 428 and 491 nm for Dye 1 and 2, respectively.

Table 2
Photovoltaic performance of DSSCs based on Dye 1, Dye 2 and dye N719.

nanoparticle	Dye	V_{oc} (V)	J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	FF	η (%)
TiO_2	Dye 1	0.64	11.06	0.61	4.32
	Dye 2	0.65	11.63	0.62	4.69
	N719	0.82	14.27	0.71	8.31
SnO_2	Dye 1	0.63	10.72	0.61	4.12
	Dye 2	0.65	10.81	0.61	4.29
	N719	0.81	13.56	0.70	7.69

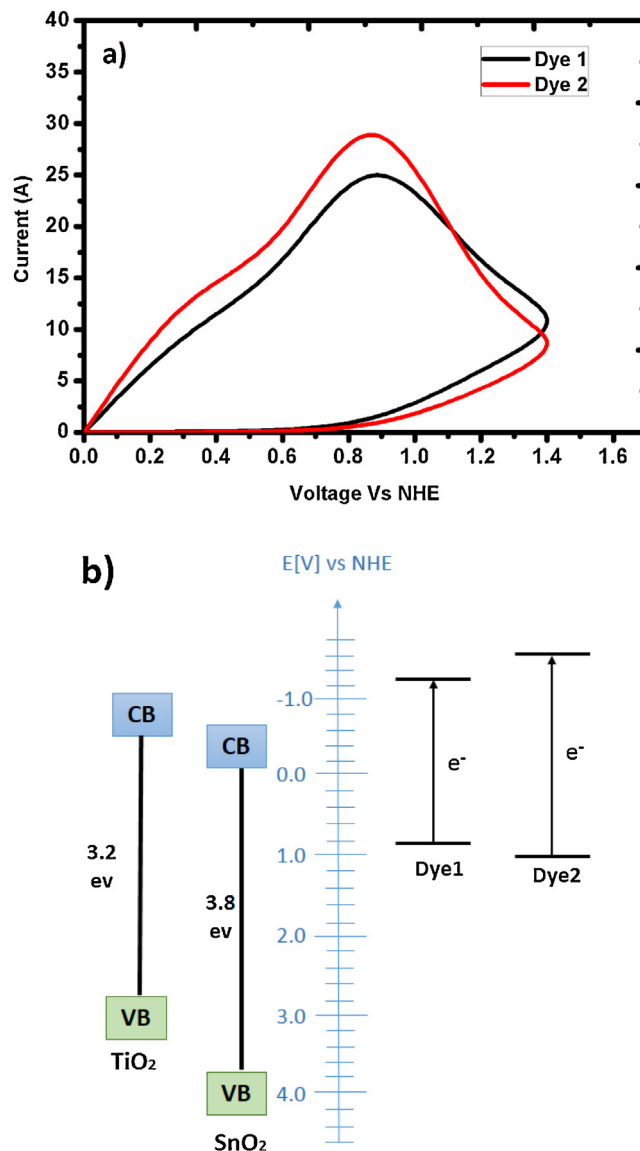


Fig. 3. a) CV curves and b) energy level of organic photosensitizers.

The vinyl and thiophene groups were bonded for Dye 2 (491 nm) and caused a blue shift in absorption spectra of this dye compared with Dye 1 (428 nm). The results in Table 2 show that the absorption peak shifted to longer wavelengths due to using the thiophene group as a stronger anchoring substituent [26] compared to acrylic substituents in Dye 1. The N,N -diparatolylaniline substituent has increased the λ_{\max} for Dye 2 compared with organic photosensitizer containing thiophene group such as BT1 with λ_{\max} around 388 nm [27]. The obtained dyes were coated on SnO_2 for DSSCs preparation. The λ_{\max} of the synthesized SnO_2 decreased by about 16 and 38 nm, respectively, due to H-aggregation of dyes on semiconductor surface [28]. The ϵ_{\max} of organic photosensitizers (Dye 1 and Dye 2) was 24272 and $25136 \text{ M}^{-1} \text{cm}^{-1}$, respectively.

That the results of UV-Visible absorption spectra of the N719 sample in ethanol solution reveals four broad bands. The two broad visible

bands at 531 and 390 nm are assigned to metal-to-ligand charge-transfer (MLCT) origin. The bands in the UV region at 313 and 215 nm with a shoulder at 253 nm are attributed to intraligand and (π - π^*) charge-transfer transitions. The low-energy MLCT maximum in N719 dye has considerably shifted upon adsorption onto these films compared to the solution spectra. The blue shifts of the low-energy MLCT band have occurred onto TiO₂ and SnO₂ films.

The results indicate that the morphology and size of nanocrystals particles (TiO₂ and SnO₂) can lead to a shift in the low-energy MLCT of N719 dye. The shift is due to the change in the energy of the lowest unoccupied molecular orbital (LUMO) of the ligand, causing the π - π^* and $d\pi$ - π^* transitions to occur at higher or lower energies [28,29].

The fluorescent properties of the synthesized dyes studied in CHCl₃ media are also shown in Table 1. The charge transfer arising from the presence of electron accepting groups caused red fluorescence in both photosensitizers. The fluorescence emission maxima of the two photosensitizers Dye 1 and Dye 2 in the solution were 512 and 574, respectively. The fluorescence emission maxima of the those of thioindigo dyes were higher than the thiophen-based dyes such as, BT1 (451 nm) [27] due to the presence of the *N,N*-diparatolylaniline groups in the structure of thioindigo organic dyes.

The E_{ox} of Dye 1 and 2 was investigated by the cyclic voltammetry (CV) technique [20,30]. Accordingly, the oxidation peak potential (E_{pa}) for Dye 1 and 2 can be measured as +0.85 and 0.92 V in the solution, respectively. The suitable method for energy investigation is the density functional theory (DFT), though CV can be used experimentally for obtaining this information [31]. In many cases, theoretical and experimental results are similar or acceptable. The E_{ox} - E_{0-0} of Dye 1 and 2 can, therefore, be measured to be -1.3 and -1.33 V, respectively. The cyclic

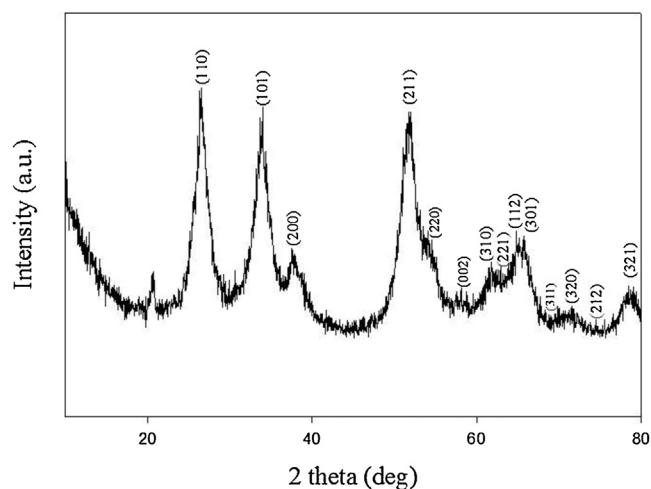


Fig. 4. XRD spectra of the rutile SnO₂.

voltammetry curves and energy level of organic photosensitizers can be viewed schematically in Fig. 3.

The X-ray spectra of organic photosensitizers are illustrated in Fig. 4. The results indicate that the specific peaks (110), (101), and (211) have appeared at 26.28°, 33.85° and 51.68°, respectively; thus the rutile SnO₂ was successfully prepared. The average crystal measure of the rutile SnO₂ was computed using XRD data and the Scherer equation [Eq. (1)] [32]:

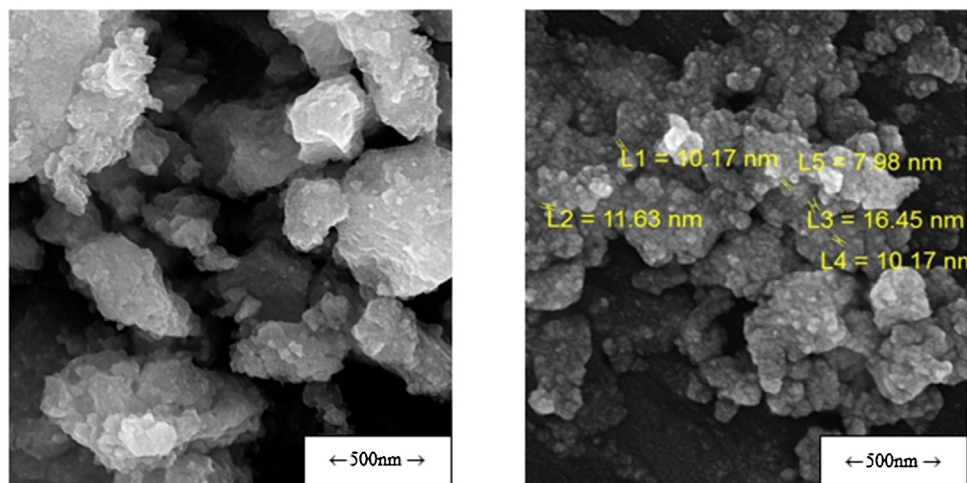


Fig. 5. FE-SEM images of the synthesized SnO₂ nanoparticles.

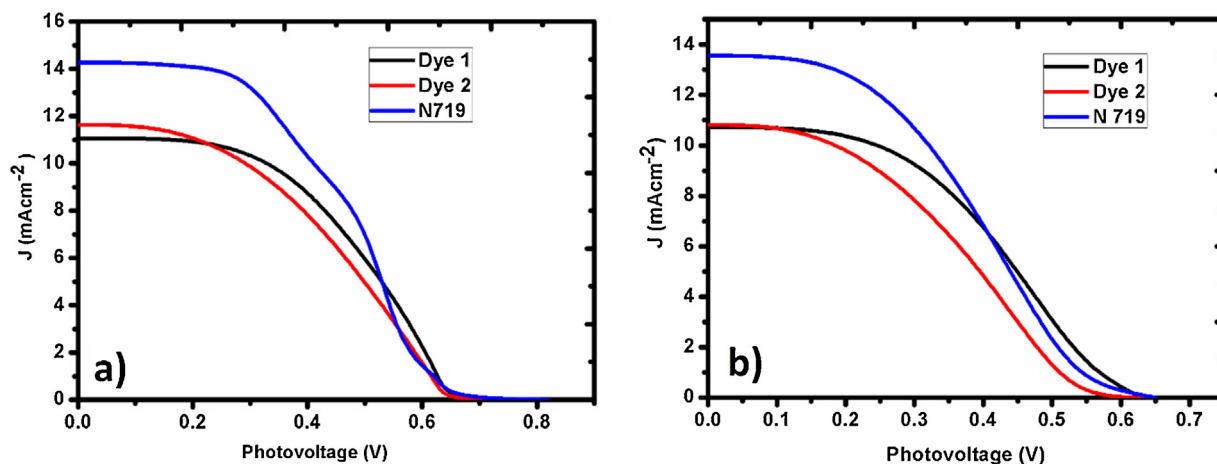


Fig. 6. J-V curve of DSSCs based on organic dyes, a) TiO₂ and b) SnO₂ photoanode.

$$D = \frac{0.89\gamma}{(\beta \cos \theta)}, \quad (1)$$

where D , γ , β and θ are the crystal size, the X-ray wavelength, the half peak width and the Bragg angle. The results show that the nano-crystal measure of rutile SnO_2 was about 7 nm. Figure 5 has been illustrated the FESEM image of nano-crystal of rutile SnO_2 . SnO_2 nanoparticles synthesized have a smaller, uniform size.

The microwave-assisted technique was utilized for rutile SnO_2 preparation as photoanode preparation of DSSCs. The results of X-Ray powder diffraction (XRD) illustrated phase pure SnO_2 nanocrystals tetragonal space group with the SnO_2 crystal size being measured as 9 ± 0.15 nm [32,33].

Dye-sensitized solar cells (DSSCs) devices were prepared and investigated, to explain the relationships between the excitement of photosensitizers and their chemical structures. Two synthesized photosensitizers were applied in DSSCs based on TiO_2 and SnO_2 . The J-V curves and optical data for photovoltaic devices sensitized by Dye 1 and 2 and N719 are illustrated in Fig. 6 and summarized in Table 2.

Table 2 shows that the efficiency of photovoltaic DSSCs assembled by Dye 1 and 2 and SnO_2 was 4.12 and 4.29 percent, respectively. The thiophene ring has stronger withdrawing potency compared to acrylic acid, thus, the Dye 2 presented larger η compared to Dye 1. The performance of organic photosensitizers can be enhanced in two ways: 1) enlarging the conjugated bridge and 2) adding appropriate anchoring group(s) [34]. For example, a novel series of organic dyes with thiophene bridge was designed and prepared by Dhar et al. [35]. The organic photosensitizers offered good stability and efficiency of about 6 percent. Estrela et al. set up four new organic photosensitizers for using the DSSCs structure with efficiency of 4.56–6.23% [36]. The DSSCs containing synthesized dyes found to have appropriate efficiency due to the facile motion of electron in such a dye structure. The prepared DSSCs using N719 as standard organometallic photosensitizer revealed an efficiency of about 7.69% with SnO_2 . This η is higher compared to the efficiency of organic dyes, but the dyes do not contain expensive Ruthenium.

4. Conclusions

Two organic photosensitizers with a donor- π -acceptor (D- π -A) structure were engineered and prepared. To this end, thiophene-2-acetic and malonic acid were utilized as anchoring groups. These dyes were identified by FTIR, ^1H NMR, ^{13}C NMR, elemental analysis, and UV-Visible spectroscopic. The UV-Visible spectra of organic photosensitizers were investigated in the solution and on the photoanode surface. The λ_{max} of the Dye 2 appeared at a longer wavelength compared to Dye 1 having employed thiophene-2-acetic acid in the dye structure. The results revealed that the organic photosensitizers had H-aggregation on the photoanode surface (SnO_2 film). The purified dyes were applied to the DSSCs structure and their optical performance was investigated. The efficiency values of 4.12 and 4.29% were achieved for Dye 1 and 2, respectively. Dye 2 containing thiophene-2-acetic acid offered higher conversion efficiency compared to Dye 1 containing acrylic acid as the acceptor unit which is attributable to the stronger electron withdrawing ability of Dye 2.

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