Enhanced photovoltaic performance of dye-sanitized solar cell with tin doped titanium dioxide as photoanode materials

Z. H. Mahmoud^{a,b,*}, R. A. Al-Bayati^a, A. A. Khadom^c

^aDepartment of Chemistry, College of Science, Al-Mustansiriyah University, Baghdad, Iraq ^bDepartment of Chemistry, College of Science – University of Diyala – Baquba City 32001, Diyala governorate, Iraq ^cDepartment of Chemical Engineering, College of Engineering – University of Diyala – Baquba City 32001, Diyala governorate, Iraq

Tin doped TiO_2 (Sn-TiO₂) nanoparticles were synthesized using a simple photolysis method and X-ray diffraction (XRD) studies confirm that they have a 4.59 nm crystallite size and crystallized as an anatase phase of TiO2. Field emission-scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) reveals the formation of spherical and fusiform agglomeration nanoparticles with mesoporous structure and size equal 20nm approximately. The preparation of 5% Sn:TiO₂ is confirmed by energy dispersive X-ray (EDX), and the empirical formal is Sn_{0.05}TiO₄. X-ray photoelectron spectroscopy (XPS) revealed that 1% Sn was successfully doped with anatase TiO₂ and that Ti⁺³ was present as an electron trap. Raman spectrum shows a red shift of anatase peaks with doping Sn:TiO₂. The adsorption spectrum of Sn doped TiO₂ has an excellent transmittance with increasing Sn doping until 5% mole ratio and reaching 85%, as well as decreasing the band gap with increasing Sn doping ratio and reaching a minimum value of 2.62eV corresponding to 5% Sn:TiO2. The results obtained that the optimum conditions for working Sn:TiO₂ as a DSSCs are 5%Sn doping ratio, N_3 dye solution and pH = 3. EIS measurements were used to quantify the kinetics of interfacial charge transfer, such as chemical capacitance, electron recombination lifespan, charge transfer resistance, charge collection efficiency, and charge transfer resistance. Enhanced power conversion equals 12.32% for %5Sn:TiO₂/based N₃ dye/GO at pH =3 by using solar simulator (100 mW/cm^2).

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1. Introduction

The greatest method to tackle the global energy dilemma is to use ecologically friendly renewable energy instead of polluting fossil energy. There are different sources of clean energy such as wind, hydrogen, tidal and geothermal energy but, the solar energy appears to be a good choice to be the next generation energy source because the energy provided by sun irradiation to the globe exceeds world energy consumption. The conversion of solar energy into a useful form is a critical topic for all solar energy researchers. The solar cell, which is based on photovoltaic technology, is a well-known method for converting sun irradiation energy to electrical energy [1,2]. Grätzel and his collaborators created the first photochemical dye sensitized solar cells (DSSCs), which drew a lot of interest due to their low cost, ease of manufacture, and environmental friendliness [3]. DSSCs have a lower conversion solar irradiation to electric energy efficiency than silicon-based solar cells, but they are still a key component for providing electricity with higher conversion [4-7]. DSSCs are typically made up of two conducting glasses sandwiched together. After immersing in electrolyte solution, one of these glasses is covered by a monolayer of dye molecules on the metal oxide surface and functions as a photoanode, while the other glass is covered with metal, such as silver or graphene oxide, and the two conductor glasses are connected by clips [8]. Much effort has been focused on the modification or preparation of new dyes [9], new

^{*} Corresponding author: zaidhameed_91@yahoo.com

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electrolytes and counter electrodes, as well as the photoanode, which plays a critical role in the operation of dye sanitized solar cells. As a result, new photoanodes must be developed to improve power conversion efficiency [10,11]. Many oxides materials such as ZnO [12], In_2O_3 [13], SnO_2 [14] and TiO₂ have been examined for use as photoanodes in DSSCs [15]. TiO₂ was chosen as a photoanode by the researchers because of its excellent chemical and physical properties, including an appropriate energy band structure for charge injection from dye molecules, a proper point of isoelectic for dye adsorption, and a suitable orbit for decreasing recombination of photogenerated charges [16-19]. Generally, the tetragonal structure anatase phase of TiO_2 is more applied as a photoanode in DSSCs. The lower mobility of electrons leads to large density of states near the band of conduction, which supplies effective electron transfer channels to provide much faster in DSSCs [20]. The anode electrode of DSSCs must have a large surface area, a fast rate of charge mobility, and a porous structure in order to adsorb a significant amount of dye. The problem of surface area is overcome by nanoscale preparation of materials, but there is another issue that arises from the usage of these materials, which is represented by grain boundaries, which act as an electron trap and reduce the efficiency of DSSCs [21-23]. Extension attempts to overcome this problem have been focused on making 1D nanoparticles and doping them with other elements [24]. The doping procedure is an experimental method for improving TiO_2 nanoparticles by lowering the rate of photolysis-induced carrier recombination and boosting the rate of electron transport, but the appropriate choice of doping elements still reigns supreme [25]. Cr⁺³ [26], Mn⁺² [27], Zn⁺² [28], and Fe⁺³ [29] are some of the ions that doped TiO₂. However, Sn-TiO₂ based dve sanitized solar cells (DSSCs) have not been explored under varied conditions. To improve efficiency, a different mole ratio of Sn⁺⁴ is a candidate for doping in the anatase phase crystal structure. Because the lattice constants and crystal structure of SnO₂ are almost identical to those of TiO₂, doping with Sn⁺⁴ would not cause any disadvantages in terms of trapping electrons. SnO₂ has a band gap of 3.8eV, which is greater than TiO₂'s band gap of 3.2eV [30]. At the interface of the anode and the electrolyte solution, enhancing electron mobility and minimizing the recombination process for photogenerated electrons were excluded. In this study, we used a new photolysis process to produce Sn-doped TiO_2 with varied mole ratios, and then built DSSCs using these anodes with iodine electrolyte and GO as counter electrode. Many parameters were investigated such as pH of dye, type of dyes $(D_{149} \text{ and } N_3)$ with theoretical study and different ratio of Sn doping TiO₂. The Sn ions was discovered to increase electron mobility and improve the efficiency of DSSCs.

2. Experimental procedure

All chemical materials were supplied from Sigma Aldrich Company and used without any future purification.

2.1. Materials

Reagent grade tin nitrate $[Sn(NO_3)_4]$, titanium iso-propoxide $(Ti[OCH(CH_3)_2]_4)$, ethylene glycol $(C_2H_6O_2)$ and indium tin oxide (ITO) were supplied from Sigma-Aldrich. Rhodamine B dye, ethanol (C_2H_6O) , potassium iodide (KI) and iodine (I_2) , graphite, potassium permanganate (KMnO₄) and hydrogen peroxide (H_2O_2) were purchased from Fisher scientist company. All materials were used with purity 98%.

2.2. Preparation of Sn-dpoed TiO₂

The photolysis approach was used to prepare pure and (1, 3 and 5%) mole ratio Sn doped TiO_2 by mixing equivalent quantities of $Sn(NO_3)_4$ and $Ti[OCH(CH_3)_2]_4$. Individually, each 200ml mixture was transferred to the irradiation system of 15W as shown in Fig. 1. The full procedure of irradiation system was reported by Zaid et al. [31]. The mixture was continuously irradiated for 1h under dropped 5ml ethylene glycol as surfactant and capping agent. The white powder was separated and cleaned with ethanol and deionized water many times. It was then dried for 6 hours at 80°C before being calcined for 2 hours at 400°C.



Fig. 1. Irradiation system with 15 watt power.

2.3. Preparation of graphene oxide (GO)

Hummer technique [32] was used to prepare graphene oxide (GO). To begin, 46ml sulfuric acid was mixed with (1, 2 and 6) gm graphite, sodium nitrate, and sodium permanganate in an ice bath for 2 hours. It was then transferred to a new 200ml beaker and kept at room temperature, stirring constantly. After diluting the mixture with 200mL distilled water, 10mL % H_2O_2 was added to convert KMnO₄ to manganese ions. Finally, the product was filtered and washed with 10ml acetone, ethanol, and deionized water before being dried at 50°C for 2 hours.

2.4. Assemble of DSSCs

Indium tin oxide (ITO, 80hm resistance, 83%)-coated glass substrate with $(3*4)cm^2$ dimension was immersed in ethanol bath and sonicated for 30min. The conductive glass was cleaned and then immersed in a 50mM titanium isoperoxide solution for 1 hour to create a blocking layer. An active area (2*2)cm² was defined by masking ITO substrate utilize tape of scotch. To make paste of photoanode, drop casting technique was used. Separately, 1gm of each photoanode compound (pure TiO₂ and (1, 3, 5 and 7%) mole Sn^{+4} -TiO₂) were mixed with 5ml absolute ethanol and sonicated for 10min. After that, some drops of paste were coated on the active side conductive using glass rode. The substrates were then sintered at 400°C for 1 hour. It was then dipped in a solution of N_3 and D_{149} dyes for 24 hours at room temperature. The photoanode substrate was then washed using ethanol to remove the molecules of anchored dye. By using profilometer SJ-210, the thickness of synthesized pure and Sn-doped TiO_2 were about 20 μ m. Coating prepared GO on the surface of an ITO substrate yielded counter electrodes. Finally, the anode and cathode electrodes were sandwiched between the 0.5M iodine electrolyte solution. The fabricated solar cells are characterized by recording the photocurrent-voltage curves (I-V) under irradiation halogen lamp with (100 mW/cm²). The principle work of DSSCs were showed in Fig. 2.



Fig. 2. Schematic diagram of working DSSCs.

Short circuit (Isc), open-circuit voltage (V_{oc}), and fill factor (FF) were used to compare the DSSCs, which were calculated as follows (Eq. 1): [33]

$$FF = \frac{I_{max} \times V_{max}}{V_{oc} \times I_{sc}}$$
(1)

where V_{max} and I_{max} represent the maximum output value of voltage and current respectively. The total conversion energy efficiency that defined as the ratio of the power output over input is estimated as follows (Eq. 2): [33]

$$n = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}}$$
(2)

where P_{in}: energy of incident energy.

2.5. Characterization and measurements

The structure of synthesized materials were investigated and recorded by Shimadzu x-ray diffraction using CuK α radiation and $\lambda = 1.5406$ A° with an accelerating voltage equal 30KV as well as, the diffractogram was displayed with the range of $2\theta = 10^{\circ}-80^{\circ}$. X-ray photoelectron microscopy (XPS) spectra was showed using spectrometer of a Kratos AXIS 165 with aluminum (Al) mono K-alpha X-ray to evaluate of chemical state. The morphology of synthesized materials were performed using field emission scanning electron microscope (ZEISS) and transmission electron microscope (JEOL JEM 2100). The spectra of Raman was done by microscope of laser Raman (Raman 11i) with wavelength of 525nm. Brunauer-Emmett-Teller (BET) was recorded to find the specific area of photoanodes materials utilizing micromeritics ASAP 2020 porosimeter. The spectral properties was evaluated using UV-VIS spectrophotometer (Jasco-V-650). The phenomena of interfacial charge transfer of the prepared dye sanitized solar cell (DSSC) was investigated using electrochemical impedance spectroscopy (EIS) utilizing Solarton gain phase analyzer. the current density-voltage (J-V) were measured by using the stander solar simulator with (AM 1.5G and 100mW/cm²).

3. Results and discussion

3.1. Structural study

X-ray diffraction (XRD) of Sn-doped TiO_2 with different mole ratio were illustrated at Fig. 3.



Fig. 3. XRD of doping different mole ratio of Sn:TiO₂.

The results demonstrate polycrystalline anatase phase TiO_2 with a tetragonal structure that is in good agreement with JCPDS (card no. 21-1272). The strength of the (101) diffraction peak rose as the mole ratio of Sn grew to 5%, showing that the anatase phase stabilized, which might be attributed to Sn incorporation in the anatase lattice [34]. Because the ionic radii and

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electronegativity of Sn^{+4} are close to or greater than Ti^{+4} and more than it, it is conceivable for tin ions to occupy or replace Ti^{+4} in the lattice of anatase [35], showing exceptionally excellent crystallinity compared to pure anatase [34]. As indicated in table 1, the greater radii of Sn^{+4} (0.69) compared to Ti^{+4} caused an expansion in the lattice parameters of Sn doped TiO₂ (0.68). As a result, the presence of 5% Sn⁺⁴ accelerates anatase peaks, indicating the optimum ratio doping. The crystallite size of pure and Sn doping TiO₂ samples were estimated by scherrer as in the following (Eq. 3): [36]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{3}$$

where 0.9 is the shape factor, λ is the wavelength of the X-ray source, and β is the full width at half maximum of the peak concerned.

Photocatalyst	2□ of crystal plane (101) of TiO ₂	Lattice parameter (A)	FWHM	D _(Scherrer) (nm)	D _{W-H} (nm)	Strain	Dye loading *10 ⁻⁴ (M/cm ²)
TiO ₂	25.46	a=b=3.78 c=9.5023	0.67036	12.92	23.25	0.00573	1.20
1%Sn:TiO ₂	25.39	a=b=3.78 c=9.5123	0.96305	8.31	17.90	0.00627	1.74
3%Sn:TiO ₂	25.31	a=b=3.78 c=9.5211	1.21004	6.59	16.75	0.00703	1.85
5%Sn:TiO ₂	25.25	a=b=3.78 c=9.5307	1.59307	4.99	16.48	0.00588	2.39

Table 1. Size of particles of TiO₂ and %Sn-doped TiO₂.

According to Table 1, increasing the Sn doping ratio causes a decrease in crystallite size, which could be attributed to Sn incorporation in the TiO₂ lattice and segregation of Sn⁺⁴ on the borders of TiO₂ particles, causing particle development to slow or become hampered [34]. Because of the increase in d-spacing that occurs from introducing dopant with bigger radii than central atoms, the dopant TiO₂ by Sn⁺⁴ plays a key role in pushing the peaks into low position. Furthermore, most of the literatures do on the analysis of XRD are limited to illustrate the crystallite size using broadening line profile of X-ray and neglecting likely contribution from strain. As here, in the equation of Scherrer, the size of crystallites are defined via supposing no distortion of lattice. To solve this problems, Williamson-Hall method is suggested [37]. It dose via considering that the existence of crystallographic distortions and the limited sizes of crystallite lead to distributions of Lorentzian intensity [38]. As appeared in Fig. 4, the plot contain ($\beta \cos\theta$) opposite (4sin θ) is called plot of Williamson-Hall deigns a strength line with slope corresponding to the microstrain value and y-intercept represent to inverse of the size of crystallite.



Fig. 4. Plot of Williamson-Hall of pure and Sn –doped TiO₂.

The y-intercept from Williamson-Hall plot can us to define a crystallite size mean value as well as, the plot obtains that slop values are quite small, which indicate that the synthesized material structure contains microstrain with a small amount. As shown in table. 1, it is seen that there is a difference between the crystallite size that got from Scherrer equation and Williamson-Hall plot and these which can be attributed to the presence of the strain. The XRD of Sn-doped TiO₂ demonstrated in Fig. 3, shows no characteristics peaks corresponding to Sn⁺⁴, implying that the Sn⁺⁴ is incorporated in the crystalline of anatase or is dispersed with values lower than the critical value of dispersion capacity, preventing the formation of a crystalline with separate phase.

The XRD patterns of GO prepared via modified Hummer's method is shown in Fig. 5. The results appear three diffraction peaks at 2 θ localized at (10.30°, 26.58 ° and 43.475 °) corresponding crystal plane (001), (002) and (100) and these results are in agreement with (JCPDS 41-1487). The diffraction peak at 10.30 corresponding to oxygenic groups of GO while, diffraction peak center at 26.58 back to residue of graphite that un-oxidize.



Fig. 5. XRD of GO.

3.2. Morphology study

Field emission-Scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) were utilized to investigate the morphology of Sn-doped TiO₂ as shown in Fig. 6a-d and Fig. 7 respectively. The results show agglomeration of spherical shape particles, which increased with Sn⁺⁴ content as well as interparticles mesoporous structure both of which could be attributed to small particle agglomeration. The agglomeration in particles were occurred because of interaction between the small particles [39]. When a different mole ratio of Sn is introduced, it decorates the TiO₂ nanoparticles, indicating that Sn was doped on the TiO₂ heterogeneous during synthesis (Fig. 6b-d). for more investigation about the agglomeration particles, the TEM measurements were carried out. As showing in (Fig. 7a-c), the particles have a spherical and

fusiform agglomeration with a dispersed distribution of the particle size approximately equal 20nm.



Fig. 6. FE-SEM of pure TiO₂ (A), %1Sn:TiO₂(B), %3Sn:TiO₂ (C), and %5Sn:TiO₂ (D).



Fig. 7. TEM of %1Sn:TiO₂ (A), %3Sn:TiO₂ (B) and %5Sn:TiO₂ (C).

The micro graph SEM images of graphene oxide (GO) are shown a sheet-like nanostructure (Fig. 8). As appear in images, it easily noted that the layer rolled as results presence oxygen groups in the edge of sheet as well as, many agglomeration of layers can also be seen. Therefore, some distortion on the surface of GO layers is shown may be back to oxidation method to transfer the graphite to graphene oxide.



Fig. 8. FESEM of GO.

3.3. Compositional study

3.3.1. Energy dispersive X-ray (EDX)

Energy dispersive x-ray (EDX) was used to analyze the elements of pure TiO_2 and $\%5Sn:TiO_2$ (Fig. 9a, b). The results corroborate the presence of only Ti and O, indicating a high-purity TiO₂, while the analysis shows a modest decrease in atomic ratio following doping with percent %5Sn and the presence of Sn, O, and Ti, as shown in Fig. 9b. The examined percentage of doping Sn is in a good agreement with practical calculation of doping 5% of SnO₂ with TiO₂, suggesting that the empirical formal of compound is Sn_{0.47}TiO₄.



Fig. 9. EDS spectrum of (A) TiO₂ and (B) %5Sn-TiO₂.

3.3.2. X-ray photoelectron spectroscopy (XPS)

Using an XPS spectrum, the chemical composition and bonding state of 1% Sn doped with TiO_2 were studied, and the results are given in (Fig 10a-d). As illustrated in Fig. 10d, two binding energies for pure anatase TiO_2 were found at 464.8 and 458.27 eV, corresponding to Ti $2p_{1/2}$ and

Ti $2p_{3/2}$. For doping 1%Sn, two bending energy appeared at 486.33eV and 495.22eV back to Sn $3d_{5/2}$ and Sn $3d_{3/2}$ as demonstrated in (Fig. 10c). Two bending energy centered at 458.09 and 458.46 back to coordinate Ti⁺⁴ with O⁻² and Sn⁺³ respectively and formation Ti-O-Sn linkage as well as, three binding energy found at 529.96eV, 529.99eV and 532eV corresponding to coordinate of O atoms with Ti, Sn and hydroxyl as shown in (Fig. 10b). As shown in Fig. 10a, the general XPS spectrum of 1%Sn:TiO₂ confirmed that the presence of Sn, Ti and O were detected in nanoparticles. In comparison to pure anatase TiO₂, the results show a positive shift toward high binding energy with a value of 0.1eV and a negative shift toward low binding energy with a value of 0.4eV for Ti 2p and Sn 3d. Due to the fact that Ti (1.54) has a lower electronegativity than Sn (1.96), the shifting in binding energy is attributed to Sn metallic ions in the anatase TiO₂ lattice, which attract deviating electrons from Ti metallic ions [40]. The minor shifts imply that Sn is being replaced by Ti, although it does not embed in the lattice gap, and these results are consistent with XRD.



Fig. 10. XPS spectrum of 1%Sn:TiO₂: survey spectrum (A), O 1s (B), Sn 3d (C), Ti 2p (D)

3.3.3. Raman spectrum

The analysis of variation bonds and particular uniformity were carried out using the Raman spectrum to characterize the effect of doping Sn in anatase TiO₂. Fig. 11 demonstrates the Raman spectrum of pure and %(1-5)Sn:TiO₂ in the range of 100-800cm⁻¹. According to [41], three vibration modes for pure anatase TiO₂ were shown at 144cm⁻¹, 195cm⁻¹, and 638 matching to Eg. Two vibration modes, 398cm⁻¹ and 518cm⁻¹, are assigned to B₁g, whereas the remaining vibration, centered at 513cm⁻¹, is assigned to A₁g. There are no peaks associated to SnO₂ in the results, indicating the development of uniform and uniform Sn doping. These vibrational modes corresponded to Ti-O bonds as well as changes in lattice characteristics caused by the opposing movement of oxygen atoms in the vicinity of O-Ti-O bonds. As illustrated in (Fig. 11), the position of anatae vibrational modes was shifted to a lower wavenumber with Sn doping, implying

that Sn doping causes higher internal strain and a reduced Hooke constant. Large constant parameters and weak Ti-O bonding are obtained as a result of these findings.



Fig. 11. Raman spectrum pure and different mole ratio Sn:TiO₂.

3.4. Spectrum properties 3.4.1. UV-Vis spectrum

The UV-Visible spectrum of pure and Sn-doped anatase TiO₂ was illustrated at Fig. 12.



Fig. 12. Transmittance spectra of pure TiO_2 and Sn-doped TiO_2 .

The results show that when % Sn is doped with anatase TiO_2 , the transmittance spectra reaches 80 %, indicating structural uniformity and excellent crystallization [42]. With a % mole ratio of Sn doping, the transmittance decreased, which might be attributed to an increase in photon scattering due to crystal defects as well as the adsorption of free carriers created by doping [43]. Tauc relation was used to calculate the band gap of pure anatase TiO_2 and Sn doped TiO_2 : (Equation 4) [44].

$$(\alpha h v)^2 = A(h v - E_q) \tag{4}$$

 E_g represents the optical band gap, v represents the frequency of incident photons, h is the Planck's constant, and A is a constant called the band tailing parameter. The bands gap of prepared samples were demonstrated at Fig. 13.



Fig. 13. Energy gap of pure and Sn doped TiO_2 .

According to the findings, the energy gap of TiO_2 narrowed as the doping ratio of Sn increased, owing to an increase in the minimum energy required for exciting electrons from the valance band (VB) to the conduction band (CB) [44], as well as the doping of Sn forming a dopant level of energy in the band gap of TiO_2 located below the conduction band of TiO_2 . As a result, the red shift observed when doping TiO_2 nanoparticles could be caused by an electron transitioning from valance band to valance energy level.

3.4. Photovoltaic characterization

Many parameters were tested in our research to find the best conditions for using the prepared doping TiO2 as DSSCs. The parameters are illustrated as follows:

3.4.1. Effect the ratio Sn doping

The J-V curves of TiO_2 and Sn-doping TiO_2 nanoparticles based DSSCs with indoline dye are shown in Fig. 14.



Fig. 14. J-V plot of pure and Sn-doped TiO₂ with indoline dye.

Table 2 summarizes the DSSCs fabricated parameters (J_{sc} , V_{oc} , I_{max} , V_{max} , FF and η). The results reveal that all Sn doping improves the efficiency of DSSCs when compared to pure TiO₂, which is related to a lower rate of recombination electrons-holes. The PL spectrum was used to analyze the issue, and the results are shown in Fig.15.



Fig. 15. PL spectrum of pure and Sn-doped TiO₂.

The PL intensity of produced nanoparticles dropped when the concentration of SnO_2 was increased, showing a delay or friction in electron-hole recombination due to effective charges transfer as the doping ratio was increased. When comparing pure TiO₂ based DSSCs to Sn-TiO₂ based DSSCs, the J_{sc} and V^{oc} parameters improve, which could be due to two factors: The first is the amount of dye on the photoanode's surface and the rate at which electrons are injected at photoanodes/dye. The adsorbed amount of dye was increased with increasing the surface area as shown in BET analysis appeared in Fig. 16 and the strong interaction between Sn in the surface of TiO₂ and hydroxyl groups in the dye.



Fig. 16. BET of pure and Sn-doped TiO₂.

The amount of adsorbed D_{149} dye per unit area is investigated using UV-VIS spectrum and given in Table 1. The results obtained that the Sn:TiO₂ has dye loading behavior compared to pure TiO₂ due to the strong interaction between Sn ions and hydroxyl anchoring group in the dye, as well as, the surface area of doping sample, specially, %5Sn:TiO₂. Furthermore, the formed Ti⁺³ ions from doping Sn play an important role in inhibiting recombination and promoting high electron injection, all of which contribute to an increase in short circuit current density (J_{sc}), while increasing the concentration of Sn causes an increase in electron concentration, which leads to a slight rise in Fermi level and, as a result, an increase in V_{oc} [45].

No.	Anode J_{sc} mA/cm ²		V _{oc} V	I _{max} mA/cm ²	V _{max} V	FF	% η
1	TiO ₂	6.05	0.6	5.5	0.44	0.66	2.44
2	1%Sn:TiO ₂	10.96	0.54	9.69	0.42	0.685	4.05
3	3%Sn:TiO ₂	13.38	0.58	10.55	0.48	0.652	5.05
4	5%Sn:TiO ₂	14.58	0.59	12.24	0.48	0.682	5.86

Table 2. DSSCs parameters with different ratio Sn doping TiO₂.

3.4.2. Effect of Dyes

Fig. 17 shows the J-V curves of %5Sn-doping TiO₂ and %5Sn:TiO₂ nanoparticles based DSSCs with indoline (D₁₄₉) and Ruthenium dye (N₃) respectively.



Fig. 17. J-V plot of Sn-doped TiO₂ photoanode based N_3 and D_{149} .

Because of the band gap, adsorbed quantity, and structures, the results show that DSSCsbased N_3 dye is more efficient than D_{149} dye. Density functional theory (DFT) at the b3lyp/lanl2dz level using Gaussian 03 package was used to investigate the effect of dye structure on efficiency, as shown in Fig. 18.



Fig. 18 the structure of N3 and D149 at b3lyp/lanl2dz level using Gaussian 03 package.

The LUMO of indoline dye is centered on the rings of benzene surrounding cylcopentane and positioned at the substituents of the basic core of structure, whereas the LUMO of N_3 dye is centered on the bipyridyl where carboxylic groups are present. The distance between proton carboxylic groups of N_3 and D_{149} and nearest LUMO are 0.9839 and 5.0121A respectively. The

probability density of LUMO near carboxylic group of N3 dye is larger compared to D_{149} dye. Based on the aforementioned theoretical data, it is predicted that DSSCs produced with N₃ dye will be more efficient than DSSCs fabricated with D_{149} dye. The photovoltaic parameters (J_{sc}, V_{oc}, I_{max}, V_{max}, and FF) of percent 5%Sn:TiO₂ DSSCs were summarized in Table 3. As predicted from the close surface of LUMO to the anchoring group, the results show consistency between theoretical and experimental data. According to De Angelis et al., [46], the high J_{sc} observed in % 5Sn:TiO₂ DSSCs-based N₃ dye is due to the mechanism of adiabatic injection, in which the change in electronic states from N₃ dye to %5Sn-TiO₂ causes strong electronic coupling and result increasing the J_{sc} as well as the strength the electronic coupling depending on the position of LUMO of dye and anchoring group. In the case of N₃ dye, the LUMO is placed on the anchoring group, causing an increase in coupling and then J_{sc}, however in D₁₄₉, the anchoring proton is located far away from the nearest LUMO site, resulting in a considerable distance between the anchoring proton and nearest LUMO site [47-49].

Table 3. Photovoltaic parameters of 5%Sn:TiO₂ photoanode with different dyes.

No.	Anode	J _{sc} mA/cm ²	V _{oc} V	I _{max} mA/cm ²	V _{max} V	FF	% ղ
1	5% Sn:TiO ₂ /based D ₁₄₉	14.58	0.59	12.24	0.48	0.682	5.86
2	5%Sn:TiO ₂ /based N ₃	17.22	0.68	15.48	0.52	0.687	8.04

3.4.3. Effect of pH

In addition to the aforementioned alterations, the pH of the DSSCs cell can have a significant impact on its efficiency. UV-Vis for solution dye at varied pH with range 3-10 were measured at 500nm wavelength to determine the quantity of dye loaded on the surface of $\%5Sn-TiO_2/N_3$ dye/GO, as shown in Fig.19.



Fig. 19. UV-VIS spectrum of N_3 dye solution at different pH remain after immersion photoanode 24h.

After immersing the photoanode in acid, the intensity of peaks dye reduced with lowering pH, indicating that the loaded amount of N_3 dye increased with decreasing pH. The findings show that the amount of dye adsorbed in acidic medium is higher than in other media, resulting in increased light gathering in DSSCs. The DSSCs fabricated with photoanode of %5Sn-TiO2/N₃dye that dealt with different pH were examined under sun illumination (100mW/cm²). The parameters summarized in Table 4. The results reveal that decreasing the pH of the dye increases the efficiency of DSSCs while keeping the V_{oc} nearly constant for all produced cells since the Fermi level does not change with pH treatment. With decreasing pH, the hydrophilic characteristics of

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the samples increased, implying that the surface of OH is greater in acidic medium and binds with carboxylic groups more easily, resulting in higher dye loading efficiency on the photoanode [50,51].

рН	Anode	$J_{\rm sc}$ mA/cm ²	V _{oc} V	I _{max} mA/cm ²	V _{max} V	FF	%η
3	5%Sn:TiO ₂ /based N ₃ dye/GO	21.82	0.778	20.91	0.59	0.726	12.32
5		20.91	0.77	18.7	0.62	0.720	11.59
7		17.22	0.68	15.48	0.52	0.687	8.04
10		16.16	0.66	14.42	0.53	0.716	7.636

Table 4. Photovoltaic parameters of 5%Sn:TiO₂/based N₃ dye/GO at different pH.

3.5. Mechanism of interfacial charge transfer

To examine the interfacial charge transfer in fabricated DSSCs based pure and different doping ratio of $Sn-TiO_2$, electrochemical impedance spectr al (EIS) was used in frequency range of 1MHz to 1Hz and the results were plotted in Fig. 20.



Fig. 20. EIS-Nyquist plot of pure and Sn doped TiO₂.

Three semicircles were showed from Nyquist plot of fabricated DSSCs at high, mid and low frequency and it represented to redox reaction in electrolyte/GO interface (R_{cl}), charge transfer at the Sn-TiO₂/N₃/electrolyte interface (Rrec) and third correspond to the resistance of Warburg diffusion (R_w) of electrolyte solution. The Nyquist plot in Fig. 20 shows double semicircles behavior, with the low frequency response for Warburg diffusion resistance (Rw) being very low, and the contribution of it being combined with recombination resistance (Rrec), as well as the diameter of semicircles increasing with doping Sn compared to pure TiO₂, indicating that the recombination resistance of TiO₂ with Sn doping is larger than pure TiO₂ based device. The doping of Sn provides the direct bonding Sn-Ti as well as stimulates the excess of electrons to formation Ti⁺³ ions trap state which is proper to transfer electrons for long distances with reduced diffusive obstruction in DSSCs. Also, the interconnection of Sn with TiO₂ nanoparticles can provide more electrons of conduction pathway which can properly improve charge injection. The doping Sn gives a large surface area and improves N₃ loading, which increases the excitation process and supports high charge carrier separation, resulting in reduced electron recombination in manufactured DSSCs and increased recombination resistance. As shown in Table 5, the % 5Sn:TiO₂ based DSSCs appear to have higher recombination resistance than pure and (% 1, 3) Sn-doped TiO₂ based DSSCs due to the larger surface area and ability to adsorbed more N_3 dye.

Sample	R _s (Ω)	R_{ct} (Ω)	$egin{array}{c} {\sf R}_{ m rec} \ (\Omega) \end{array}$	$C_{\mu}(\mu F)$	$ au_e \ (ms)$	$ au_t$ (ms)	D _e	L _n	φ_c
TiO ₂	14.09	21.32	35.98	3.05	0.109	0.065	7.446	28.48	40.36
1%Sn:TiO ₂	15.13	20.94	81.21	4.063	0.329	0.085	5.694	43.28	74.16
3%Sn:TiO ₂	16.02	41.08	186.87	4.12	0.769	0.169	2.863	44.97	78.02
5%Sn:TiO ₂	12.54	20.01	295.86	5.954	1.218	0.119	4.067	70.38	90.22

Table 5. Electrochemical parameters and kinetic of charge transport of pure and 5%Sn:TiO₂.

Fig. 21 illustrates the plot of Bode phase for the spectra of EIS which shows two frequencies – phase angle shifts correspond to process of charge transfer GO/electrolyte and TiO_2/N_3 dye/ electrolyte interfaces respectively.



*Fig. 21. EIS-Bode phase plot of pure and Sn doped TiO*₂*.*

According to the plot, the maximum frequency for the region of mid frequency of pure anatase phase of TiO₂ and %1, 3 and 5 Sn:TiO₂ based DSSCs are found to be 1995.26Hz, 691Hz, 602Hz and 199.52Hz respectively. As shown in Table 5, the peak frequency of Sn- doped TiO₂ shifted to a lower frequency due to the longer life time of electrons compared to pure TiO₂ due to its higher recombination resistance and chemical capacitance, as calculated by the following equation (Eq. 5):

$$\tau_e = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} \tag{5}$$

where: τ_e : lifetime recombination electron, f_{max} : maximum peak frequency at mid frequency. Increases in τ_e can hold back reaction electrons injected with iodide ions in the electrolyte, resulting in higher DSSC efficiency [52]. From experimental EIS data, the transport time of electrons τ_t and diffusion coefficient of electrons (De) calculated as follows: (Eq. 6 and 7) [53]

$$\tau_t = R_{ct} \times C_\mu \tag{6}$$

$$D_e = \frac{L^2}{R_{ct} \times C_{\mu}} \tag{7}$$

where: R_{ct} is charge transfer resistance, L^2 : thickness of nanoparticles film. The results demonstrate that the calculated transport lifetime of electrons of DSSCs was less than recombination lifetime of electrons which shows rapid transportation of electron with less recombination time [54]

To describe the dynamic competition between recombination process and electron transport, the charge collection efficiency and electron diffusion length were calculated by using following (Eq. 8 and 9) [55] and summarized in Table 5:

$$\varphi_c = 1 - \left(\frac{\tau_t}{\tau_e}\right) \tag{8}$$

$$L_n = \left(D_e \tau_e\right)^{\frac{1}{2}} \tag{9}$$

The results reveal that the diffusion length of produced DSSCs is longer than the thickness of their films, implying that electron transportation is efficient during the promoted diffusion process. The manufactured DSSCs based on 5% $Sn:TiO_2$ appear to have a longer diffusion length (70.38), resulting in good charge collecting efficiency (90.22).

4. Conclusion

In summary, the pure and $Sn:TiO_2$ were successfully synthesized by using low temperature photolysis method and their structure is confirmed by XRD. XPS confirms the formation of a Ti-Sn bond in the presence of a Ti⁺³ trap state. The spherical agglomeration nanoparticles with mesoporous structure were visible in the FE-SEM images. The empirical formula $Sn_{0.05}TiO_4$ was calculated from EDX spectrum data to make a 5% $Sn:TiO_2$ solution. According to BET analysis, an increased loading of dye by 5% $Sn:TiO_2$ with high surface was reported in an adsorption-desorption investigation of N₃ dye. EIS experiments show that the Ti-Sn direct bond inhibits recombination and increases electron lifespan and charge transfer.

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