Influence of Tin Doped TiO$_2$ Nanorods on Dye Sensitized Solar Cells

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Abstract: The one-step hydrothermal method was used to synthesize Sn-doped TiO$_2$ (Sn-TiO$_2$) thin films, in which the variation in Sn content ranged from 0 to 7-wt % and, further, its influence on the performance of a dye-sensitized solar cell (DSSC) photoanode was studied. The deposited samples were analyzed by X-ray diffraction (XRD) and Raman spectroscopy, which confirmed the existence of the rutile phase of the synthesized samples with crystallite size ranges in between 20.1 to 22.3 nm. In addition, the bare and Sn-TiO$_2$ thin films showed nanorod morphology. A reduction in the optical band gap from 2.78 to 2.62 eV was observed with increasing Sn content. The X-ray photoelectron spectroscopy (XPS) analysis confirmed Sn$^{4+}$ was successfully replaced at the Ti$^{4+}$ site. Thin films showed nanorod morphology. A reduction in the optical band gap from 2.78 to 2.62 eV was observed with increasing Sn content. The X-ray photoelectron spectroscopy (XPS) analysis confirmed Sn$^{4+}$ was successfully replaced at the Ti$^{4+}$ site. The 3-wt % Sn-TiO$_2$ based DSSC showed the optimum efficiency of 4.01%, which was superior to 0.87% of bare and other doping concentrations of Sn-TiO$_2$ based DSSCs. The present work reflects Sn-TiO$_2$ as an advancing material with excellent capabilities, which can be used in photovoltaic energy conversion devices.

Keywords: Sn-doped TiO$_2$; Hydrothermal method; X-ray diffraction; photoelectrode; dye-sensitized solar cells

1. Introduction

Nanostructured, nanoporous semiconducting metal oxides with large surface areas and high diffusion rates are exclusively utilized as photoanode materials in dye-sensitized solar cells (DSSCs) [1]. Due to their cost-effectiveness, ease of manufacturing, and higher light conversion efficiency, DSSCs have become important alternatives to traditional silicon solar cells [2,3]. Various metal oxide semiconductors, such as ZnO, TiO$_2$, Nb$_2$O$_5$, and SnO$_2$, have been explored as photoanode materials for the development of high-performance DSSCs [4–7]. The contributing factors that establish the TiO$_2$ semiconductor electrodes as the best photoanodes are their charge transport capability and chemical stability. TiO$_2$ plays a very important role in DSSCs as it provides a high surface for adsorption of...
dye, acquiring electrons from the excited dye state, and quickly transferring to fluorine-
doped tin oxide (FTO). Since TiO$_2$ possesses a large bandgap of about 3.2 eV, it cannot be
efficiently used in the visible light region but is more sensitive to the ultraviolet region.
Hence, different research groups have synthesized TiO$_2$ by various methods to improve
the edge of absorption, mostly in the visible region. Doping of different elements in TiO$_2$
is one of the best ways to reduce the bandgap and change the electronic structure, as well as
to minimize the recombination rate and promote visible light absorption. All the above
parameters could help to improve the charge transfer rate, high open-circuit voltage ($V_{oc}$),
and will be beneficial to enhance the DSSCs’ efficiency [8,9].

Suitable metal ions doping in the TiO$_2$ can cover up the grain boundaries, which will
generate oxygen vacancies and can improve the photoelectrochemical properties of the
photoanodes. Many metals are used for doping in the TiO$_2$ host lattice, but Sn is the most
influential because of the close ionic radius of Ti$^{4+}$ = 0.60 Å and Sn$^{4+}$ = 0.69 Å, which helps
to suitably replace Ti$^{4+}$ in TiO$_2$ with Sn$^{4+}$ ions to generate a homogenous mixture [10].
The Sn doping enhances the charge transport, photon absorption, and improves the surface
quantum-dots loading density of TiO$_2$, which results in high photoelectrochemical efficiency
[11,12]. Xiang et al. prepared Ta added TiO$_2$, which shifts the potential negatively and
raises the concentration of electrons of the TiO$_2$ electrode, resulting in the reduction of
the electron recombination rate and electron transport by Ta doping [13]. Su et al. reported
improvement in the short circuit current density ($J_{sc}$) by Nb doping in TiO$_2$. The enhance-
ment in the $J_{sc}$ is attributed to variation in the conduction band minimum (CBM), which
facilitates electron transport and enhances the conductivity [14,15]. Different investigations
have been done on doping TiO$_2$ for the improvement of $V_{oc}$ and $J_{sc}$.

Different approaches have been used to synthesize Sn-doped TiO$_2$ thin films which include
spray pyrolysis [16,17], a microwave-assisted method [18], sol-gel [19–21], chemical
cooprecipitation [22], atomic layer deposition [23], a gas-phase oxidation method [24], and
spin coating [25,26]. The Sn-doped TiO$_2$ thin films have previously been used for different
applications such as photocatalysis [27,28], gas sensing [29,30], lithium-ion batteries [31,32],
and DSSCs [33,34]. Out of different synthesis processes available for the synthesis of TiO$_2$
thin films, the hydrothermal method offers certain advantages such as the synthesis of
rutile and anatase crystalline forms of TiO$_2$ at relatively low temperatures, fine-tuning of
morphology, and uniform coating onto the substrates [35].

In the present work, the hydrothermal method has been applied for the synthesis of
Sn-doped TiO$_2$ thin films using an acid catalyst. The Sn-TiO$_2$ thin films are systematically
synthesized by varying Sn concentration. The influence of Sn-doping concentration on
structural, optical, morphological, and photoelectrical properties of Sn-TiO$_2$ thin films has
been examined. Improved photovoltaic performance is observed for the DSSCs fabricated
with Sn-TiO$_2$. Further, the Sn-doped TiO$_2$ thin films have been successfully employed as
photoelectrodes in DSSCs, which suggests a positive effect on its photovoltaic performance.

2. Methods
2.1. Synthesis of Sn-Doped TiO$_2$ Films

Sn-doped TiO$_2$ thin films were prepared by a single-step hydrothermal route by
varying the Sn concentration in TiO$_2$. FTO substrates were washed for 15 min by ultrasonic
stirring using equal amounts of isopropyl alcohol, acetone, and deionized water (DIW)
followed by drying in an N$_2$ atmosphere. An equivalent volume of DIW and concentrated
HCl was mixed and stirred for 10 min. In the aforementioned solution, 0.5 mL of titanium
butoxide was mixed dropwise and constantly stirred for the next 30 min. The desired
amount of tin (IV) chloride was poured into the aforesaid solution and stirred for the next
30 min until the solution becomes clear and homogeneous. The solution was then poured
into the Teflon vessel and the ultrasonically cleaned FTO substrate was dipped in solution.
The FTO substrate was kept inclined to the wall of the Teflon vessel with the conducting
side facing upwards. The Teflon vessel was then fitted in the autoclave and heated for 3 h at
180 °C in a furnace. The autoclave was then allowed to cool naturally to room temperature.
The FTO substrate coated with the desired material was then rinsed with DIW and dried at room temperature. The prepared films were finally annealed at 450 °C for 1 h. Sn-TiO₂ thin films with different Sn concentrations (3, 5, and 7-wt %) were also prepared by the same procedure. Undoped TiO₂ thin film was synthesized by the same procedure without the addition of the Sn precursor.

2.2. Cell Fabrication and Photovoltaic Measurements

Hydrothermally synthesized bare and Sn-doped TiO₂ films with different concentrations of Sn were soaked in ethanolic 0.5 mM N719 dye (cisbis(isothiocyanato) bis(2,2′-bipyridyl-4,4′dicarboxylato) ruthenium (II) bis-tetrabutylammonium, (Greatcell, Queensland, Australia) solution for 24 h. After completion of the dye loading process, sensitized photoelectrodes were rinsed in acetonitrile and dried in air. DSSCs were fabricated by a two-electrode configuration comprising a working electrode and counter electrode. Dye-loaded bare TiO₂ and Sn-TiO₂ on FTO act as working electrodes, whereas platinum-coated FTO (Pt: FTO) acts as a counter electrode. Both these electrodes were sealed using polyacrylamide 1 mm spacers. The Pt: FTO electrodes were freshly prepared by drop-casting 0.5 mM hexachloroplatinic acid (H₂PtCl₆) dissolved in isopropanol solution onto FTO and heating at 400 °C for 20 min in air. The dye-loaded TiO₂ photoanodes and platinum counter electrodes were closed with Surlyn thermoplastic (SX-1170-25, Solaronix, Aubonne, Switzerland) at specific temperatures and pressure. The electrolyte iodolyte AN-50 was introduced through a pre-drilled Pt: FTO electrode opening. The system was eventually sealed with thermoplastics. The photovoltaic measurements were carried out at room temperature.

2.3. Characterizations

Rigaku Ultima X-ray diffractometer (Tokyo, Japan) with Cu Kα radiation, λ = 1.54 Å was used to investigate the structural characteristics. The WITec ALPHA 300 M Raman microscope was used to obtain the Raman spectra (excitation at 532 nm, 2.33 eV, Ulm, Germany). The chemical bonding of bare and doped TiO₂ was examined using Fourier transform infrared spectroscopy (FTIR; Perkin Elmer 1760X spectrophotometer, Waltham, MA, USA) at wavelengths ranging from 400 cm⁻¹ to 4000 cm⁻¹. The surface morphologies were studied by using a field emission scanning electron microscope (FE-SEM, JSM-7001F, JEOL, Tokyo, Japan). The particle size was determined by using a JEM-2100F (JEOL, Tokyo, Japan) transmission electron microscope with an acceleration voltage of 125 kV. The Brunauer Emmett Teller (BET) N₂ adsorption and desorption analyses were carried out by Quantachrome Instruments v10.0 (Florida, USA) to determine the surface area, pore size, and volume. The elemental composition of samples was analyzed using an X-ray photoelectron spectrometer (XPS, Thermo Scientific Inc., East Grinstead, UK) focused with Al (Kα) monochromator (1486.6 eV) and the spot size was variable (30–400 µm in 5 µm steps). The absorbance spectra were obtained by Jasco spectrophotometer (Jasco V-770, Tokyo, Japan) with a wavelength ranging from 200 to 800 nm. The photovoltaic measurements were carried out with a solar simulator (McScience K201 LAB50, Suwon, Korea) for 10 s with AM 1.5 G with 1 sun (100 mW cm⁻²) illumination intensity. An NREL-calibrated Si solar cell with a KG-5 filter was used as a reference cell.

3. Results and Discussion

The X-ray diffraction (XRD) patterns of bare and Sn-TiO₂ thin films are shown in Figure 1a. The Sn-TiO₂ thin films have a tetragonal rutile crystal structure, which is the same as bare TiO₂ (JCPDS No. 21-1276). Sn doping slightly affects the rutile TiO₂ crystal structure. The (002) reflection of the Sn-TiO₂ film is slightly displaced to a higher 2θ value and its intensity has decreased, as the concentration of Sn doping has increased from 1 to 7-wt %. The Sn doping has increased the intensity of (110) reflection. Due to Sn doping, only a slight variation in the lattice constants of bare-TiO₂ thin films is observed, signifying the partial replacement of Ti⁴⁺ sites by Sn⁴⁺ cations due to their close ionic radii. The relevant crystal structure parameters, like the crystallite size, lattice constant, and cell
volume, are shown in Table S1. The average crystallite size for the bare, 1, 3, 5, and 7-wt % Sn-TiO₂ is determined as 20.1, 20.7, 21.2, 21.7, and 22.3 nm, respectively. This implies that with increasing Sn content, the average crystallite size of the samples increases. In all the samples, the rutile phase is the dominating phase, as shown in Figure 1a.

Figure 1. (a) XRD patterns, (b) Raman spectra, and (c) FT-IR spectra of hydrothermally synthesized bare TiO₂, 1-wt %, 3-wt %, 5-wt %, and 7-wt % Sn-TiO₂ thin films.

Figure 1b displays the Raman spectra of bare and Sn-TiO₂ thin films. The prominent reflections positioned at 144, 448, and 610 cm⁻¹ corresponding to the B₁g, E₉, and A₁g vibrational modes of the rutile phase, respectively. The intense reflections at 448 and 610 cm⁻¹ represent the O–Ti–O bending and Ti–O stretching vibrations of the rutile phase, respectively [36]. The stretching vibration at 233 cm⁻¹ can be assigned to compound vibration generated by a multi-phonon process, signifying the rutile phase of TiO₂ [37]. The absence of characteristic reflections for SnO₂ at 470 cm⁻¹, 574 cm⁻¹, 636 cm⁻¹, and 776 cm⁻¹ [38] confirms the non-existence of crystalline SnO₂ due to minimal Sn doping concentration.

Figure 1c represents the FT-IR spectra of bare and Sn-TiO₂ thin films in the 400–4000 cm⁻¹ range. The bands located at 1600 and 3400 cm⁻¹ can be assigned to the stretching and bending vibration of water molecules, respectively. In bare and Sn-TiO₂, the bands at 1632 cm⁻¹ represent the bending vibration of a water molecule and stretching vibration of O–H. The presence of a band over the range of 1022 to 1100 cm⁻¹ indicates the evidence of Ti–O–Ti vibrations in the films [39]. Peaks observed in the 400–800 cm⁻¹ range can be ascribed to vibration modes of Ti–O, Ti–O–Ti, Sn–O, and Ti–O–Sn bonds. The Sn doping
into TiO$_2$ results in a peak shift to a lower wavenumber observed in the FT-IR spectra of Sn-TiO$_2$ [40]. The shifting of the peak from 662 to 651 cm$^{-1}$ for Sn–TiO$_2$ films confirms the Ti–O–Sn bond formation [18]. The band at 1460 cm$^{-1}$ corresponds to the stretching vibration of the Ti–O–Ti, which has shifted to 1457 cm$^{-1}$ because of Sn$^{4+}$ doping [41]. The band observed at the low frequency region of FTIR spectra at 530 and 427 cm$^{-1}$ corresponds to bending vibrations of Ti–O and Ti–O–Ti bonds [42].

Figure 2a presents the UV-Visible spectra of bare and Sn-TiO$_2$ thin films with different Sn doping concentrations. A small redshift is observed for the thin films and absorption band edges have broadened to a visible region with the rise in Sn concentration. This effect is mainly caused by Sn$^{4+}$ doping, which generates a temporally indirect energy gap in the mid-gap zone of TiO$_2$, facilitating an electron excitation and lowering the energy barrier needed for electrons to be excited from the valence band (VB) to the conduction band (CB). In comparison with bare TiO$_2$, the absorption edge of Sn-doped TiO$_2$ thin films has slightly shifted to a longer wavelength. The desired doping concentration thus increases the efficiency of cells in the visible region [43]. Figure S1 shows the Tauc plots of bare and Sn-TiO$_2$ thin films, from which it is inferred that the bandgap has reduced from 2.78 to 2.62 eV with the increase in Sn content. The reduction in the bandgaps indicates that the minimum energy is required for the excitation of electrons. It facilitates the electron transfer from VB to CB.

In addition, the effect of Sn content on the surface morphology of the TiO$_2$ thin films was determined using the FE-SEM technique as presented in Figure 2b–f. The FE-SEM images at a magnification of ×50,000 are shown in Figure S2a–e. The surface morphology appeared in the form of 1D nanorods for the bare TiO$_2$, whereas for the Sn-TiO$_2$ thin films, 3D flower-like nanorods are noticed, as shown in Figures S2a and S3a,b, respectively. The detailed growth mechanism of TiO$_2$ nanorods has previously been explored [44]. The consistent growth of Sn-TiO$_2$ nanorods is observed. These nanorods are mixed and assisted together to offer more interspace. Each nanorod is composed of a set of thinner nanorods with square top facets. These nanorods are nearly uniform, well-aligned, and
uniformly distributed on the surface of the films. Nanorod morphology provides a larger surface area which enhances the efficiency of DSSCs by efficient transport of electrons. The whole surface of FTO is covered with well-aligned nanorods. The FTO substrate provides numerous nucleation centers which initiate the growth of the TiO$_2$ nanorods. As shown in Figure 2b–f and Figure S2, the nanorods appeared less normal to the substrate, which can be attributed to the decreased intensity of (002) reflections of Sn-TiO$_2$.

Figure 3a,b shows the cross-section of 3-wt % Sn-TiO$_2$ and 7-wt % Sn-TiO$_2$ thin films, respectively, which indicates the formation of well-aligned nanorods. The cross-sectional view of 3-wt % and 7-wt % Sn-TiO$_2$ thin films shows that the nanorods have grown almost perpendicular to the substrate. The average length and diameter of the nanorods are determined as 2.3 µm and 180 nm, respectively, for 3-wt % Sn-TiO$_2$. For 7-wt % Sn-TiO$_2$ thin films, the average length and diameter of the nanorods are estimated as 2.1 µm and 150 nm, respectively. The HR-TEM image of 7-wt % Sn-TiO$_2$ thin films is depicted in Figure 3c. It reveals that numerous nanorods come together and form a bundle of nanorods. These nanorods are moderately uniform, with an average length of nearly 2 µm, and an average diameter of nearly 150 to 250 nm. Figure 3d displays the HR-TEM image of 7-wt % Sn-TiO$_2$ thin films, in which lattice fringes of (110) reflection with interplanar spacing 0.33 nm are seen, which is a characteristic of rutile TiO$_2$.

The BET analyses of TiO$_2$ and Sn-TiO$_2$ samples are carried out to investigate the changes in the surface area and pore diameter raised due to Sn doping. Figure 3e exhibits the BET N$_2$ adsorption-desorption isotherms as representations of relative pressure (P/P$_0$) against a volume of gas adsorbed at equilibrium. The presence of mesopores in the bare and Sn-TiO$_2$ samples is confirmed by the presence of type IV isotherms with a significant hysteresis loop. The average specific surface areas of the polycrystalline bare-TiO$_2$, 1, 3, 5, and 7-wt % Sn-TiO$_2$ samples are determined as 80.69, 84.11, 107.57, 88.88, and 92.30 m$^2$ g$^{-1}$, respectively. The average pore volumes and mean pore diameters of bare-TiO$_2$, 1, 3, 5, and 7-wt % Sn-TiO$_2$ samples are calculated as 0.146, 0.165, 0.166, 0.181, and 0.169 cm$^3$ g$^{-1}$, and 7.25, 7.86, 6.20, 8.16, and 7.33 nm, respectively. It is observed that the surface area (S$_{BET}$), pore-volume, and pore diameter of the bare and Sn-TiO$_2$ thin films vary with Sn content. The 3-wt % Sn-TiO$_2$ has the highest S$_{BET}$ value, suitable for effective dye adsorption. The values of specific surface area, pore-volume, and mean pore diameter of bare-TiO$_2$ and Sn-TiO$_2$ samples have been illustrated in Table 1.

| Samples     | Surface Area (m$^2$ g$^{-1}$) | Total Pore Volume (cm$^3$ g$^{-1}$) | Mean Pore Diameter (nm) |
|-------------|-------------------------------|-----------------------------------|--------------------------|
| Bare TiO$_2$| 80.69                         | 0.146                             | 7.25                     |
| Sn-TiO$_2$ (1-wt %)| 84.11               | 0.165                             | 7.86                     |
| Sn-TiO$_2$ (3-wt %)| 107.57             | 0.166                             | 6.20                     |
| Sn-TiO$_2$ (5-wt %)| 88.88               | 0.181                             | 8.16                     |
| Sn-TiO$_2$ (7-wt %)| 92.30               | 0.169                             | 7.33                     |
Figure 3. SEM cross-section of (a) 3-wt % (b) 7-wt % Sn-TiO$_2$ thin films. HR-TEM image of 7-wt % Sn-TiO$_2$ (c) Bundles of nanorods and (d) Lattice fringes with interplanar spacing of (110) reflection. (e) The N$_2$ adsorption-desorption isotherms of the bare TiO$_2$ and Sn-TiO$_2$ thin films with varying Sn concentration.

The XPS technique is used to assess the chemical states and elemental composition of the prepared films. Figure S4 shows the survey spectrum of 7-wt % Sn-TiO$_2$ thin film, which confirms the existence of titanium, tin, and oxygen elements in the synthesized film. The Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ peaks are detected for Sn-TiO$_2$ thin films and are shown in the inset of Figure S4. Figure 4a displays the deconvoluted XPS spectra of Ti 2p of bare TiO$_2$ and 7-wt % Sn-TiO$_2$ thin films.
The binding energy for Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} for bare TiO\textsubscript{2} is found to be 457.87 and 463.53 eV, respectively, whereas for Sn-TiO\textsubscript{2}, it is found to be 458.02 and 463.72 eV, respectively. When compared to the spectra of bare-TiO\textsubscript{2}, the two peaks of the Ti 2p spectra of 7-wt % Sn-TiO\textsubscript{2} show a slight positive shift, which is most likely due to the interaction between Ti, O, and Sn atoms. It reveals that Sn doping induces a peak shift of Ti 2p to higher binding energy and indicates the +4 oxidation state of titanium [45]. This positive shift implies that electron loss from Ti\textsuperscript{4+} in the oxide is due to the existence of Sn\textsuperscript{4+} with considering their electronegativity difference (Ti = 1.54 and Sn = 1.96) [46]. The deconvoluted narrow scan XPS spectrum of Sn 3d is shown in Figure 4b. The binding energy 485.69 and 495.48 eV corresponds to Sn 3d\textsubscript{5/2} and Sn 3d\textsubscript{3/2} and confirms that Sn\textsuperscript{4+} is incorporated into the TiO\textsubscript{2} lattice. Also, the deconvoluted Sn3d\textsubscript{5/2} reflects two additional peaks at 483.62 and 488.43 eV, which are attributed to presence of Sn\textsuperscript{2+} and Sn\textsuperscript{4+} oxidation states, respectively [47,48]. Figure 4c represents the deconvoluted O 1s spectra of Sn-TiO\textsubscript{2} and 7-wt % Sn-TiO\textsubscript{2} thin films. The intense peaks observed at 529.10 eV and 529.23 eV are due to lattice oxygen (Ti–O) and the less intense peaks at 531.14 eV and 531.18 eV correspond to adsorbed hydroxyl (–OH) group in the bare-TiO\textsubscript{2} and Sn-TiO\textsubscript{2} thin films, respectively. The peak shifting to higher binding energy due to Sn doping is observed for...
Sn-TiO₂ thin films. These findings support the existence of the Ti–O–Sn bond in Sn-doped films because of the replacement of Ti⁴⁺ by Sn⁴⁺.

The graphical view of 1D and 3D Sn-TiO₂ nanorods for the application of DSSCs is depicted in Figure 5a. The 3D Sn-TiO₂ flower-like morphology comprises single-crystalline nanorods, which enhance electron mobility and photon harvesting through light scattering (Figure S5). Furthermore, the flower-like morphology provides a higher surface area for dye loading, and thus more absorption takes place towards the visible region.

Figure 5b represents the J–V curves of the DSSCs constructed using bare-TiO₂ and 1, 3, 5, and 7-wt % Sn-TiO₂ thin films sensitized with ruthenium dye N719. Table 2 summarizes the different DSSCs performance parameters of bare-TiO₂ and 1, 3, 5, and 7-wt % Sn-TiO₂ thin films. The cell configurations employed to measure J–V characteristics were FTO/TiO₂/N719 Dye/I−-I₃−/Pt: FTO and FTO/Sn-TiO₂/N719 dye/I−-I₃−/Pt: FTO.

Figure 5. (a) The graphical view of 1D and 3D Sn-TiO₂ nanorods based DSSCs (b) The Photocurrent density–photovoltage (J–V) curves of dye-sensitized bare TiO₂ and Sn-TiO₂ photoelectrodes with different Sn concentrations.

Table 2. Performance characteristics of DSSCs based on the bare-TiO₂ and Sn-TiO₂ photoelectrodes with varying Sn concentrations.

| DSSCs          | Jsc (mA cm⁻²) | Voc (V) | FF (%) | Rsh (Ω) | Rs (Ω) | η (%) |
|----------------|---------------|---------|--------|---------|--------|-------|
| Bare TiO₂      | 1.65          | 0.68    | 77.70  | 355881  | 168.6  | 0.87  |
| Sn-TiO₂ (1-wt %) | 5.35          | 0.63    | 66.43  | 11760   | 86.6   | 2.26  |
| Sn-TiO₂ (3-wt %) | 9.49          | 0.64    | 65.29  | 8769    | 56.2   | 4.01  |
| Sn-TiO₂ (5-wt %) | 6.66          | 0.64    | 68.17  | 12518   | 57.4   | 2.93  |
| Sn-TiO₂ (7-wt %) | 7.08          | 0.64    | 65.64  | 10212   | 56.6   | 3.00  |

The magnitude of the Jsc observed is 1.65 mA cm⁻² for the bare-TiO₂ and 5.35, 9.49, 6.66, and 7.08 mA cm⁻² for 1, 3, 5, and 7-wt % Sn-TiO₂ thin films, respectively. The DSSCs with bare TiO₂ thin films provided power conversion efficiency (PCE) of 0.87% with a fill factor (FF) of 77.70%. It is observed that the variation in the Jsc values is governed by variation in the Sn concentration. As compared to bare TiO₂, the enhancement in the PCE of Sn-TiO₂ based DSSCs is observed. The possible reason for the enhancement in the PCE of Sn-TiO₂ is ascribed to the large surface area of vertically grown nanorods that may enhance the output photocurrent. Moreover, the morphology observed for 3-wt % Sn-TiO₂ thin films is a uniformly distributed, well-aligned bundle of nanorods (Figure S3a), which offers a greater surface area for dye loading and facilitates the transport of electrons.
the DSSCs fabricated with 3-wt % Sn-TiO$_2$ thin films, the highest $J_{sc}$ of 9.49 mA cm$^{-2}$ is observed with $V_{oc}$ of 0.64 V, and it has provided the highest PCE of 4.01%.

The Sn-TiO$_2$ nanorods are found to be capable of enhancing the efficiency of DSSCs by providing a confined path for the transport of charge carriers with redox electrolyte and rapid charge separation. The PCE of Sn-TiO$_2$ photoelectrode is marginally higher than bare TiO$_2$ photoelectrodes due to a modest rise in defect states, leading to less recombination in the trapped sites. The interaction of Sn with the TiO$_2$ lattice generates a shift in the Fermi level of TiO$_2$. Consequently, the Sn captures the electron within the conduction band of TiO$_2$. In the meantime, the equilibrium of the Fermi level is achieved [49]. Electron capture by Sn extends the lifespan of holes and reduces hole–electron recombination. Hence, noticeable improvement in the $J_{sc}$ and $V_{oc}$ is observed. Doped photoelectrode cells have a much higher performance than pure photoelectrode cells due to enhanced chemisorptions onto doped TiO$_2$ [50]. The substitution of Sn causes distortion in the TiO$_2$ lattice, creates oxygen vacancies, and contributes to enhanced photo activity. The improvement of the Sn-doped photoelectrode-based cell implies that doping may generate a donor level, leading to a greater concentration of the carrier with a decrease in film resistance [51]. For ideal DSSCs, the $R_s$ (series resistance) should be low, and $R_{sh}$ (shunt resistance) should be a maximum. The current-voltage characteristics depends upon $R_s$ and $R_{sh}$ resistance. A lower $R_s$ enhances current flow in the circuit, and high $R_{sh}$ provides fewer shorts or leaks in the device. In an ideal cell, the $R_s$ value is close to zero, and $R_{sh}$ approaches infinity. The $R_s$ and $R_{sh}$ are measured by the J–V curve and can be determined by Equations (1) and (2).

$$\left(\frac{dI}{dV}\right)_{V=0} = \left(\frac{1}{R_s}\right)$$

$$\left(\frac{dI}{dV}\right)_{I=0} = \left(\frac{1}{R_{sh}}\right)$$

The bare-TiO$_2$ showed the lowest efficiency with a high $R_s$ value of 168.66 Ω, whereas the 3-wt % Sn-TiO$_2$ films exhibited higher efficiency with a low $R_s$ value of 56.2 Ω. These findings confirmed that low $R_s$ and high $R_{sh}$ determine the PCE of the DSSCs.

The tin doping reduces the band gap of TiO$_2$. The charge transfer from the bulk to the surface of nanorods reduces the bandgap and facilitates the photogeneration process. The concentration of impurities increases with dopant concentration. Such impurities act as charge trapping sites for hole–electron recombination. If a doping content is more or less than 3-wt %, the recombination rate is more severe and results in a reduction in $V_{oc}$ and $J_{sc}$ and thus affects the PCE. Therefore, 3-wt % Sn-TiO$_2$ thin films showed the optimum quantity of dopant, which gives better PCE.

4. Conclusions

We have designed Sn-TiO$_2$ nanorod morphology-based DSSCs using a simple, low temperature, and low-cost hydrothermal method. The synthesized bare and Sn-TiO$_2$ thin films with nanorod morphology have been successfully sensitized with N719 dye using the piranha solution etching process. The Sn-doped TiO$_2$ facilitates the rutile phase formation at a certain annealing temperature and reduces the band gap of TiO$_2$. The 3-wt % Sn-TiO$_2$ showed a specifically large surface area of about $107.57 \text{ m}^2 \text{ g}^{-1}$ which adsorbs more dye and thereby improves the performance of DSSCs. Photovoltaic studies showed considerable enhancement in PCE for the 3-wt % sample with a maximum $J_{sc}$ of 9.49 mA cm$^{-2}$ with a $V_{oc}$ of 0.64 V and a PCE of 4.01%. Hence, Sn-TiO$_2$ photoelectrodes will be promising photoelectrode materials for the development of highly efficient DSSCs.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/ma14216282/s1, Figure S1: Tauc plots showing bandgap of synthesized thin films having a different concentration of Sn; Figure S2: FE-SEM images of (a) bare TiO$_2$, (b) 1-wt %, (c) 3-wt %, (d) 5-wt % and (e) 7-wt % Sn-TiO$_2$ thin films with magnification of $\times 50,000$; Figure S3: FE-SEM images of (a) 3-wt % Sn-TiO$_2$ and (b) 7-wt % Sn-TiO$_2$ showing epitaxial growth of nanorods forming flower-
like morphology; Figure S4: XPS survey spectrum of 7-wt % Sn-TiO2; Figure S5: Morphological variation from nanorods to nano-flower; Table S1: Crystal structure parameters of bare-TiO2 and Sn-TiO2 thin films.

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