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Enhanced Charge Transfer of TiO_2 Photoanode for Low Temperature Dye Sensitized Solar Cell via Tin Sintering Aid Integration

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The charge transfer of electrons is an important process in the dye sensitized solar cell (DSSC) photoanode. However, the low temperature for the sintering of flexible DSSC photoanode caused low interparticle connectivity and poor charge transfer in titanium dioxide (TiO_2)-based photoanode. Therefore, this study aimed to integrate tin (Sn) as sintering aid to TiO_2 photoanode at 150 °C as an effort to resolve the issue. Morphological analysis found that there were necks forming at the TiO_2-Sn interface. These necks helped to enhance the interparticle connection in the photoanode. The improvement was further proved from the electron transfer analysis which showed lower charge transfer and series resistance values by 86% when Sn sintering aid was integrated. The resistance values were also found to be lower than commercially prepared TiO_2 photoanode prepared at 450 °C. Hence, Sn metal was found to a suitable sintering to produce high performing DSSC photoanode component. Flexible DSSC with high performance and efficiency could be fabricated from the low temperature process used in the research.

Keywords: DSSC; TiO_2; tin; low temperature; photoanode

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In recent years, third-generation solar cells such as perovskite solar cells, organic solar cells and dye sensitized solar cells (DSSCs) have been the emerging trend in photovoltaic technology [1]. Among those, DSSC have been a promising solar cell technology because of the low-cost and simple fabrication process, potential for wide range of applications and capable of operating under low light or indoor light condition [2]. DSSC structure is generally consist of components including photoanode, substrates, counter electrode, electrolytes and sensitizers [3]. Photoanode, is an important component in DSSC and the photoanode material require large specific surface area to permit dye absorption for light harvesting and enabling efficient electron or charge transfer [4]. Thus, semi-conductor material such as titanium dioxide (TiO_2) has been commonly implemented as photoanode material due to their large surface area with wide energy bandgap of 3.2 eV, low photo-corrosion and exceptional optoelectronic properties [5]. Besides, the low cost of TiO_2, along with their stable and non-toxic nature were other determining factors TiO_2 was generally chosen in DSSC fabrication [6].

DSSC could also be manufactured as flexible solar cell with the use of polymer substrates including polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) [7]. Flexible DSSCs with high flexibility, lightweight, with ease of implementation and low cost were developed for a wide range of application [8]. However, low thermal stability of polymer substrates means that the processing temperature of flexible TiO_2-based DSSC can only be done at low temperature around 150 °C [9]. This was significantly lower than the general 450 °C sintering temperature used when preparing TiO_2 photoanode for rigid glass-based DSSCs to remove organic contaminants and improve the connectivity between the nanoparticles [10]. Hence, flexible DSSCs have produced low power conversion efficiency (PCE) of around 8%, compared to glass-based DSSC with up to 15% efficiency [11]. Therefore, researchers have performed various studies to improve the charge transfer in TiO_2 photoanode at low temperature that could be used to develop highly efficient flexible DSSC.

One example was by utilising metallic nano-particles to dope TiO_2 photoanode and tune the energy

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bandgap, enhance the optical and electrical properties for better light absorption properties [12]. Magnesium [12], zirconium [13], and nickel [14] were some examples of metals used as dopants in TiO_2 photoanode fabrication for DSSCs. Besides, metal nanoparticles were also utilised as sintering aid to TiO_2 photoanode for enhancing the photoanode sintering process. Zinc (Zn) nanoparticles were implemented as sintering aid to fabricate TiO_2-Zn-based photoanode at 200 °C that produced DSSC with PCE of 4.92% in a study by Ahmad et. al [15]. The value was 15% higher than DSSC fabricated with pure TiO_2 photoanode prepared at 450 °C due to the enhanced connection in the photoanode nanoparticles from the necking at TiO_2-Zn interface. Meanwhile, our previous research [16] was able to develop DSSC at 250 °C that yielded high PCE of 8.73% from the addition of lead (Pb) nanoparticles in the TiO_2 photoanode that acts as sintering aid. The Pb sintering aid caused necking at the TiO_2-Pb interface from the liquid phase sintering phenomena that enhance the photoanode's interparticle connectivity [17]. This then eventually improved the charge transfer for better overall efficiency. By using bismuth (Bi) nanoparticles with melting point of 271.5 °C, we have also managed to fabricate DSSC with high efficiency of 7.93% at even lower temperature of 200 °C [18]. Liquid phase sintering was said to occur at 2/3 of a metal's melting point, thus, by adding metals with lower melting point as sintering aid, the sintering temperature could be lowered even more [17].

Tin (Sn) is a non-toxic and cheap metal, with excellent optical and electrical properties which made the metal suitable for solar cell application [19]. Several studies have been conducted to use Sn metal as doping material in TiO_2 photoanode for DSSC fabrication. Ni et. al [20] doped TiO_2 photoanode with Sn to produce DSSC with good PCE (9.43%) because of the enhanced electron mobility as well as reduced recombination reaction at the photoanode interface. Meanwhile, Mahmoud et. al [21] developed DSSC via the doping of TiO_2 photoanode with Sn that improved the photoanode surface for better dye loading. DSSC with better light harvesting, reduced recombination reactions, enhanced electron lifetime and improved charge transfer for high PCE of 12.32% was developed. Thus, Sn metal, with low melting point of 232 °C, looked to be a good sintering aid to be integrated to TiO_2 photoanode even at low temperature. Therefore, the aim of the research was to develop TiO_2 photoanode with better charge transfer at 150 °C from the integration of Sn metal as sintering aid. Low sintering temperature of 150 °C was used in the research to ensure that the method used could be implemented in flexible plastic-based DSSC fabrication with potentially high performance and efficiency.

EXPERIMENTAL

Materials

Titania (TiO_2) paste acquired from Sigma-Aldrich, Sn powder (100 mesh) acquired from ThermoFisher Scientific, fluorine-doped tin oxide (FTO) coated glass acquired from Sigma-Aldrich, ethanol acquired from ThermoFisher Scientific and binder clips.

Preparation and Fabrication of Photoanode Specimens

Firstly, Sn powder was wet grinded in a planetary ball mill machine from Fritsch. Zirconia balls with 5 mm diameter was deposited in the jar followed by 20 g of as received Sn powder and small amount of distilled water. The milling process was then conducted for 15 minutes at 500 rpm and the grinded Sn powder was collected before placed in a dry oven at 70 °C overnight. The grinded and dried Sn powder with sizes around 800 – 900 nm was then kept for further use.

Then, suitable amount of TiO_2 paste and grinded Sn powder was collected and weighed to prepare the TiO_2-4 wt.% Sn and TiO_2-7 wt.% Sn specimens. The TiO_2 paste and grinded Sn powder was then mechanically mixed before they were coated onto clean FTO glass via doctor blade technique. The coating was performed on the FTO glass surface with coating area of 1 cm^2 and left to dry at room temperature for 1 h. Meanwhile, pure TiO_2 specimen was also prepared by coating the as received TiO_2 paste on the FTO glass with similar process. Laboratory hotplate was then used to sinter the prepared specimens at 150 °C for 3 h. After that, the specimens were carefully kept for the characterization studies.

Characterization of Specimens

There were several characterization studies conducted for the specimens including morphological studies, light absorption studies and electron transfer studies. Morphological studies of TiO_2, Sn and TiO_2-Sn specimens were conducted via characterisation equipment including TESCAN's scanning electron microscope (SEM) and Hitachi's transmission electron microscope (TEM). Meanwhile, x-ray diffractometer (XRD) from Rigaku was used for the phase identification of the crystal structure for the specimens. UV-vis spectrophotometer from PerkinElmer was used to measure the light absorbance for the specimens dissolved in ethanol solution. Finally, electron transfer studies were conducted using a Gamry potentiostat, where electrochemical impedance spectroscopy (EIS) analysis was run. Each prepared photoanode specimen was clipped with a clean FTO glass to perform the EIS tests with voltage supply was set at 10 mV for each analysis.

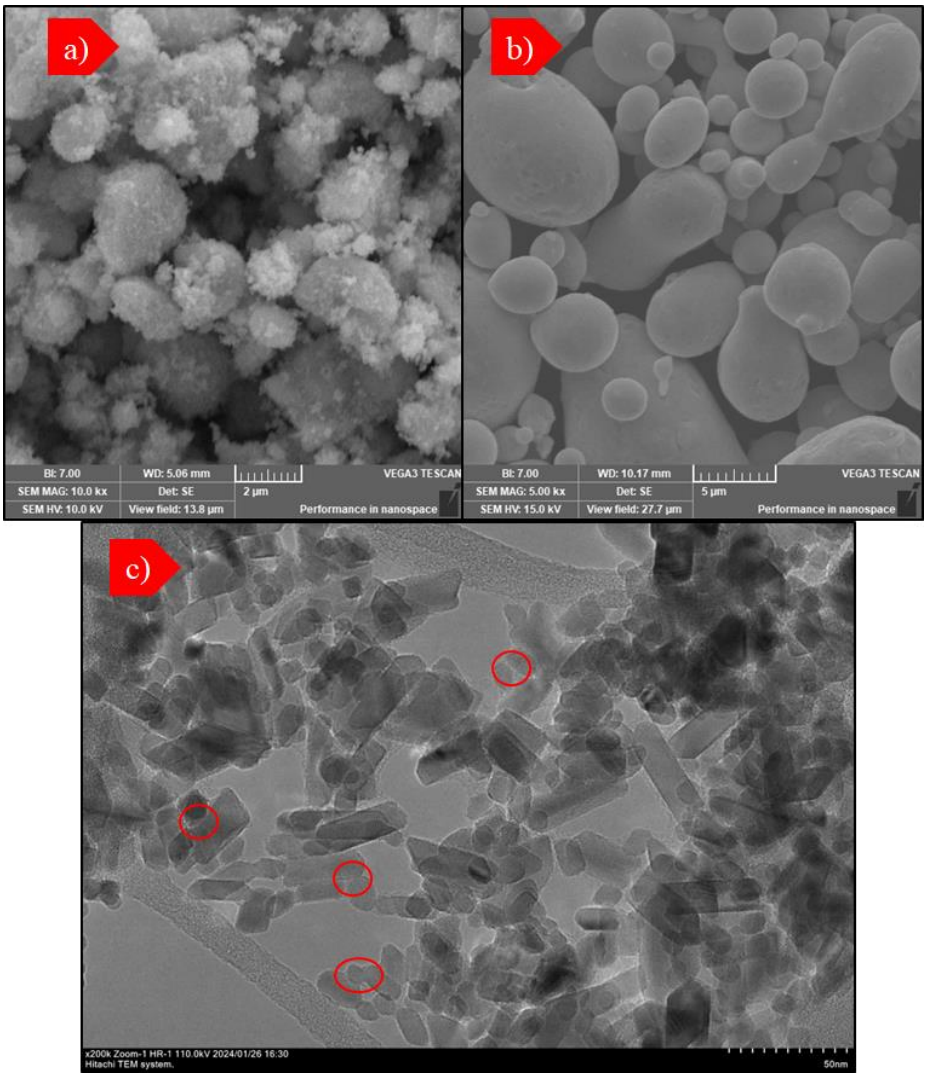

Figure 1. a) SEM image of TiO_2 specimen b) SEM image of Sn specimen c) TEM image of TiO_2-Sn specimen.

RESULTS AND DISCUSSION

Morphological Studies

SEM images shown in Figure 1a and 1b showed different structures and surfaces for both TiO_2 and Sn specimens. The TiO_2 specimen was showing rough surfaces with large specific surface that would be advantageous for dye absorption in DSSC process. Meanwhile, Sn specimen showed smoother surface which could be beneficial for the necking process during the liquid phase sintering [17]. This was then shown in the TEM image highlighted in Figure 1c where there were necking occurring at TiO_2-Sn interface of the prepared TiO_2-Sn specimen. Due to the low melting point of Sn at 232 °C, surface diffusion of Sn occurred during sintering at 150 °C which led to the necking phenomena. These necks would enhance the connectivity in the TiO_2 nano-particles that would lead to better charge transfer and reduced recombination of the photoanode.

Phase analysis via XRD was also conducted for the specimens to investigate the crystal structures present in the as received specimens and prepared specimen. XRD spectra in Figure 2 below showed that the TiO_2 used in the research was the anatase TiO_2. This crystal structure was generally preferred for DSSC photoanode application due to their superior photocatalytic activity. Anatase TiO_2 has a larger specific surface area, extra active sites and longer charge carrier lifetime compared to other TiO_2 crystal structure including rutile and brookite [22]. From the XRD spectra, it was observed that the prepared TiO_2-Sn specimen have managed to retain the anatase TiO_2 crystal structure even after sintering at 150 °C and with the addition of Sn sintering aid. This was evident with formation of peaks at 2θ positions of 25.31°, 37.79° and 48.05° with miller indices of (101), (004) and (200) planes respectively. These findings were matching with the XRD spectra of pure TiO_2 specimen. Meanwhile, Figure 2 also showed peaks formation at 2θ positions of 30.65°,

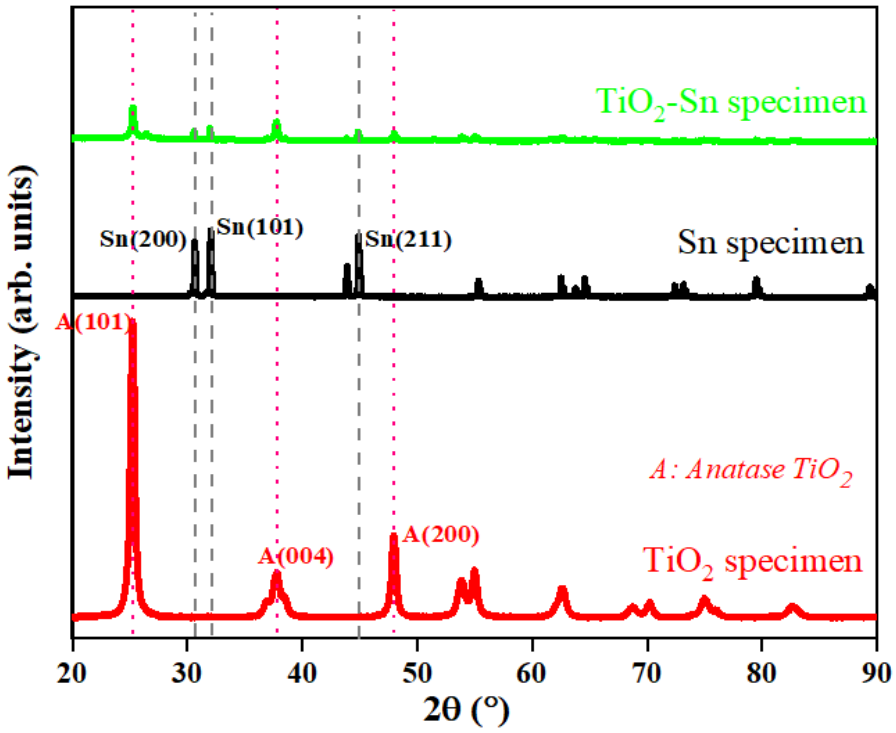

Figure 2. XRD spectra of TiO_2, Sn and TiO_2-Sn specimens.

32.02° and 44.90° with miller indices of (200), (101) and (211) planes respectively. The same peaks were formed on XRD spectra for both pure Sn specimen and TiO_2-Sn specimen which showed that Sn sintering aid was integrated in the photoanode specimen. The findings also showed that Sn have remained the same crystal structure without being oxidised during the fabrication process. Hence, the phase analysis showed the fabrication process did not cause changes to the crystal structure of the materials and was only affecting the surface morphology.

Light Absorption Studies

Ethanol was used as solvent for the specimens while pure ethanol solution as reference in the UV-vis. The result obtained was presented in the absorbance spectra shown in Figure 3 below. Absorbance spectra showed TiO_2 specimen formed absorbance peak at around the 324 nm wavelength range, in the UV region which was common for TiO_2 particles [23]. The absorbance was then found to be reduced beyond the UV region, meaning light absorption did not occur in the visible and infrared region for TiO_2 specimen. Meanwhile, Sn specimen displayed peak absorbance at 351 nm wavelength range which was also in the UV region. Another absorbance peak was also observed in the infrared region at wavelength range of 867 nm. Thus, showing that Sn has light absorption beyond the UV region. Figure 3 also showed that both the TiO_2-Sn specimens displayed absorbance peak at wavelength of 405 nm, which was just in the visible region. Thus, indicating that integration of Sn sintering aid has extended the light absorption of TiO_2-Sn specimen beyond the UV region. Therefore, the integration of Sn as sintering aid would eventually improve the light harvesting capability of the TiO_2-Sn photoanode over pure TiO_2-based photoanode. Increasing the Sn loading in the specimen also led to higher absorbance from the increased surface density of Sn which caused higher optical absorption activity.

Electron Transfer Studies

EIS analysis was an important process to evaluate and analyse the electron transfer mechanism in the DSSC system including the photoanode film, as well as the recombination in the photoanode interface [24]. From the EIS response obtained in the analysis, both Nyquist and Bode plot was plotted along alongside a suitable circuit model. From the Nyquist plot, charge transfer resistance (R_{CT}) and series resistance (R_S) of the photoanode specimens was obtained. Meanwhile, Bode plot allowed for the calculation of electron lifetime (t) via the following equation [25]:

$$t = \frac{1}{2\pi f_{max}} \quad (1)$$

Where f_{max} = maximum peak frequency from Bode plot.

For comparison, commercially prepared TiO_2 photoanode specimen at 450 °C from Solaronix was included in the EIS analysis to further analyse the

impact of Sn sintering aid in the research. Nyquist plot in Figure 4a, showed that both the charge transfer and series resistance was reduced with the integration of Sn sintering aid from the smaller curve observed in the plot. The TiO_2 photoanode was found to yield higher R_{CT} of 27.69 kΩ•cm^2 and R_S of 55.92 kΩ•cm2, while photoanode specimen with TiO_2-4 wt.% Sn yielded significantly lower resistance values (R_{CT} = 5.02 kΩ•cm^2 and R_S = 10.13 kΩ•cm^2). The reduction in resistance proved the improvement in the charge transfer of the photoanode due to the enhanced connectivity in the photoanode nanoparticles caused by the necking phenomena at the TiO_2-Sn interface as discussed beforehand. The findings were further proven by the longer electron carrier lifetime of 2.5 x 10^{-4} ms to 3.8 x 10^{-4} ms for the TiO_2 photoanode and TiO_2-4 wt% Sn photoanode respectively. A longer *t* value also indicated reduced recombination reactions in the photoanode.

Figure 4a also displayed that the TiO_2-7 wt.% Sn photoanode produced lower R_{CT} of 3.91 kΩ•cm^2 and R_S of 7.91 kΩ•cm^2, than the commercially prepared TiO_2 photoanode with sintering temperature of 450 °C (R_{CT} = 4.48 kΩ•cm^2 and R_S = 9.19 kΩ•cm^2). Thus, the integration of Sn sintering aid was able to significantly improve the charge transfer of TiO_2 photoanode even at 150 °C that could match the high temperature prepared photoanode. The low melting point of Sn at only 232 °C was an important factor that allowed for the surface diffusion of Sn and liquid phase sintering process to occur at 150 °C. This process eventually helped in enhancing the interparticle connection and improved the photoanode charge transfer. Therefore, it can be concluded that Sn metal was a very suitable sintering aid for TiO_2 photoanode for sintering at low temperature. With the sintering temperature of 150 °C, the process could be applied for the fabrication of flexible plastic-based DSSC devices with improved performance.

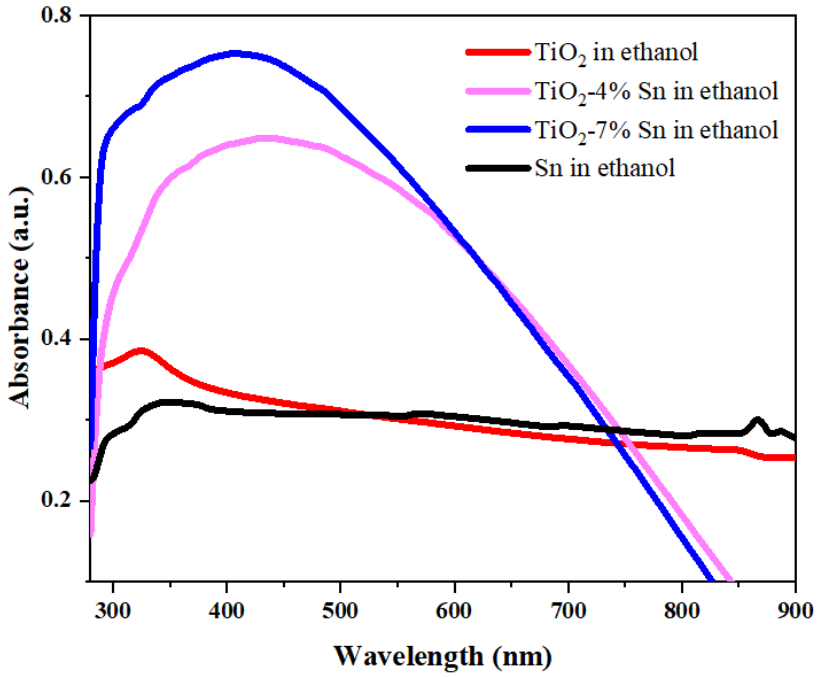

Figure 3. Absorbance spectra for various specimens in ethanol solution.

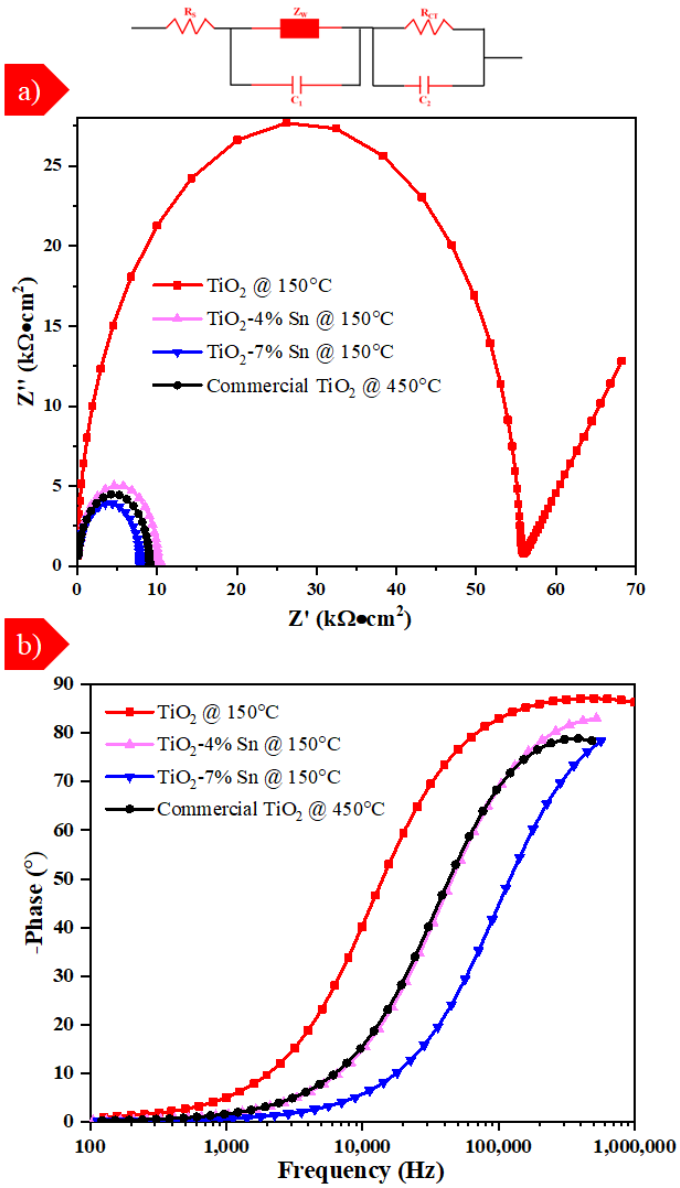

Figure 4. EIS response from EIS analysis a) Nyquist plot for TiO_2, Sn and TiO_2-Sn photoanode specimens with circuit model b) Bode plot for TiO_2, Sn and TiO_2-Sn photoanode specimens.

Table 1. Values of R_{CT}, R_S and *t* for different specimens obtained from EIS response.

Specimens	Sintering temperature (°C)	R_{CT} (kΩ•cm²)	R_S (kΩ•cm²)	*t* (ms)
TiO_2	150	27.69	55.92	2.5×10^{-4}
TiO_2-4 wt.% Sn	150	5.02	10.13	3.8×10^{-4}
TiO_2-7 wt.% Sn	150	3.91	7.91	3.5×10^{-4}
Commercial TiO_2	450	4.48	9.19	4.1×10^{-4}

CONCLUSION

Sn nanoparticles with melting point of 232 °C was integrated as sintering aid to the TiO_2 photoanode to enhance connection of photoanode nanoparticles and improve the charge transport at 150 °C. Morphological studies found that necks were forming at TiO_2-Sn interface from the surface diffusion of Sn. Phase analysis found that the prepared TiO_2-Sn specimen was able to retain the desirable anatase TiO_2 crystal structure after the fabrication process. Meanwhile, light absorption analysis showed that the integration of Sn sintering aid has enhanced the light absorption capability of TiO_2-Sn specimen beyond the UV spectrum. Electron transfer studies demonstrated the increased charge transfer activities of the TiO_2-Sn photoanode specimens with reduced R_{CT} and R_S values with electron carrier lifetime. Hence, further proving the enhancement of the photoanode's interparticle connectivity. The charge transfer of the TiO_2-Sn photoanodes was also found to be comparable with lower resistance values than the commercially prepared TiO_2 photoanode at 450 °C. Thus, the next step would be to fabricate complete DSSC devices with the use of prepared photoanode specimens to prove that the integration of Sn sintering aid could produce superior DSSC devices at low temperature. Due to the low temperature nature of the sintering and fabrication process in the research, the method implemented in the research is expected to be suitable in fabricating low temperature flexible TiO_2-based DSSC with high efficiency and performance. Further research on other type of metals with low melting point could be conducted to determine optimal sintering aid metals. However, it is also important to consider other determining factors such as cost of materials, ease of process and safety or environmental impact in using suitable metals as sintering aid.

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