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# Effect of lead sintering aid to $TiO_2$ photoanode for flexible dye sensitized solar cell

**H Khir[1], A K Pandey[1,2], R Saidur[1,6], M S Ahmad[3], M Dewika[4], M Samykano[5]**

[1] Research Centre for Nanomaterials and Energy Technology (RCNMET), School of Engineering & Technology, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, Petaling Jaya, 47500 Selangor Darul Ehsan, Malaysia
[2] Sunway Materials Smart Science and Engineering (SMS2E) Research Cluster, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, Petaling Jaya 47500, Selangor, Malaysia
[3] Higher Institution Centre of Excellence (HICoE), UM Power Energy Dedicated Advanced Centre (UMPEDAC), Level 4, Wisma R&D, University of Malaya, Jalan Pantai Baharu, 59990 Kuala Lumpur, Malaysia
[4] Centre of American Education, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, Petaling Jaya, 47500 Selangor Darul Ehsan, Malaysia
[5] College of Engineering, University Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia
[6] School of Engineering, Lancaster University, LA1 4YW, United Kingdom

Email: adarshp@sunway.edu.my

**Abstract.** The commercial application of flexible dye sensitized solar cells (DSSCs) is somewhat limited due to the devices' low conversion efficiency. The low sintering temperature in preparing the photoanode has caused poor interparticle contact, low charge transfer and low efficiency. Hence, this research aims to improve the interparticle contact of titanium dioxide ($TiO_2$) photoanode with the novel use of lead (Pb) nanoparticles as sintering aid at low temperature. $TiO_2$-Pb composite photoanode was prepared with different composition of Pb including 4% and 7% sintered at low temperature of 250°C. The research discovered that $TiO_2$ photoanode mixed with 4% Pb composition showed the lowest charge transfer resistance ($R_{CT}$) even at low sintering temperature. The $R_{CT}$ value was even lower than a commercial $TiO_2$ photoanode sample that was sintered at 450°C. The addition of Pb sintering aid has improved interparticle contact in the photoanode via the neck formation at the $TiO_2$-Pb interface and enhanced charge transfer despite the low temperature. The prepared photoanode samples displayed potential in developing highly efficient flexible DSSC.

## 1. Introduction

The high emissions of greenhouse gases such as carbon dioxide ($CO_2$) have encouraged the use of sustainable energy such as solar energy. Hence, solar cells such as dye sensitized solar cell (DSSC) have been developed as an alternative in converting solar energy into electricity via the photovoltaic effect [1]. DSSC is typically made up of photoanode (titanium dioxide ($TiO_2$)), counter electrode, conductive substrate, sensitizer and electrolyte [2]. DSSC has the advantage of being low cost, easy to fabricate with optimum efficiency that can even be developed into flexible DSSC using plastic substrate [3]. Flexible DSSCs are portable, easily shaped for building implementation and cost lower from roll-to-roll production [4]. However, flexible DSSC suffers from low efficiency with the highest recorded efficiency is at 10.28% [4], compared to the typical rigid DSSC with efficiency of 14.2% [1]. The low sintering temperature for flexible DSSC caused poor interparticle contact in the photoanode and low charge transfer, leading to low efficiency [5].

Metallic cations such as copper and manganese have been used as dopants to $TiO_2$ photoanode, increasing DSSC efficiency by 6.7% and 2.1% respectively [6]. The plasmon resonance effect present in the metallic dopants tuned the $TiO_2$ bandgap and improved the efficiency [7]. Meanwhile, nickel-doped $TiO_2$ photoanode was found to exhibit low resistance and better charge transfer despite the low sintering temperature of 150°C, suitable for flexible DSSC fabrication [8]. Metallic nanoparticles have also been used as sintering aid to improve $TiO_2$ interparticle contact using the plasmon resonance effect and metallurgical sintering concept. Germanium nanoparticles sintering aid formed necks with $TiO_2$ nanoparticles, improve interparticle contact, enhance electron transfer and light harvesting capability [9]. Meanwhile, zinc nanoparticles sintering aid with low melting point of 419.5°C, has improved the DSSC efficiency by 15% despite low sintering temperature of 200°C [10].

This research aims to improve the interparticle contact of $TiO_2$ photoanode and increase charge transfer with the novel use of lead (Pb) nanoparticles as sintering aid. The low melting point (327.5°C) properties of Pb would make the metal a suitable sintering aid even at low sintering temperature of 250°C for flexible DSSC application.

## 2. Methodology

Pb powder (Sigma-Aldrich,100 mesh) was grinded in a planetary ball mill (Fritsch Pulverisette 5) until nanoparticle size of around 500 nm was obtained. Appropriate amount of grinded Pb nanopowder and $TiO_2$ paste (Sigma-Aldrich) was weighed on a weighing scale and was then mechanically mixed together and stirred. Nanocomposite paste of $TiO_2$-4% Pb and $TiO_2$-7% Pb was prepared. Few amounts of the nanocomposite paste were deposited and coated onto a clean fluorine tin oxide (FTO) glass (Sigma-Aldrich) via the doctor blade technique. Photoanode samples with a coating dimension of 1cm x 1cm were obtained and left to dry at room temperature for 1 hour. The dried photoanode samples were then placed on a hotplate and sintered at 250°C for 3 hours. Similar process was also repeated for photoanode sample with pure $TiO_2$ paste with similar steps as shown in Figure 1. Scanning electron microscope (SEM) (TESCAN VEGA3), x-ray diffraction (XRD) (Rigaku Miniflex 600) analysis and UV-visible spectroscopy (Perkin Elmer Lambda 750) was used to analyse the photoanode materials. Electrochemical impedance spectroscopy (EIS) analysis was then conducted for the prepared photoanode samples using a Gamry Interface 1010E Potentiostat at frequency of 0.1 Hz - 1 MHz and AC voltage of 10 mV.

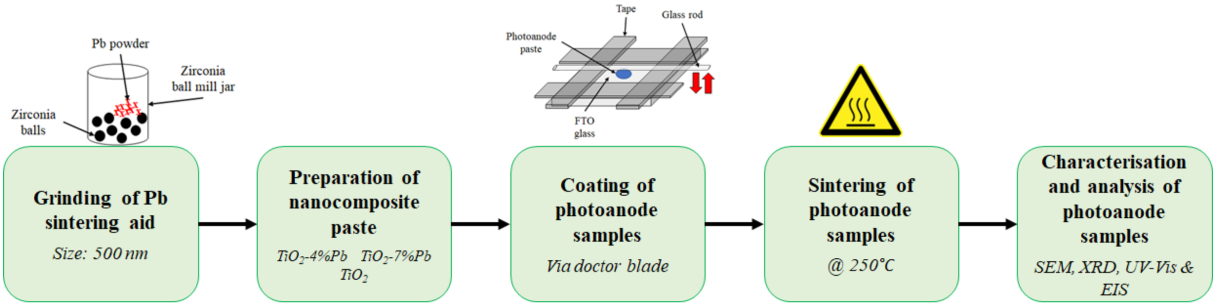

**Figure 1.** Methodology flowchart.

## 3. Results and discussion

### 3.1. *Morphological studies*

Scanning electron microscope (SEM) have been used to analyse the morphology of pure $TiO_2$ and Pb powders before they were coated and sintered onto FTO glass. Figures 2a and 2b showed that $TiO_2$ and Pb particles have irregular shapes with $TiO_2$ nanoparticles showing smaller size (100 nm) than Pb.

The small size of both these raw materials would encourage the joining of these nanoparticles during the sintering process to improve the interparticle contact of photoanode materials. The presence of these materials can be seen in the XRD spectra from the XRD analysis of the photoanode sample. The XRD spectra displayed peaks that indicates the presence of the more desirable $TiO_2$ anatase phase with larger bandgap, lower recombination and better photovoltaic activity [11]. $TiO_2$ anatase phase can be observed at 2θ positions of 18.6°, 39.5° and 49.5° while rutile phase was found at 20.4°. The presence of Pb sintering aid was also indicated in the spectra at 2θ position of 27.0° and it did not cause any changes to the $TiO_2$ phase, with anatase phase more dominant than the less desirable rutile phase. Thus, highlighting the benefit of implementing Pb sintering aid in this research.

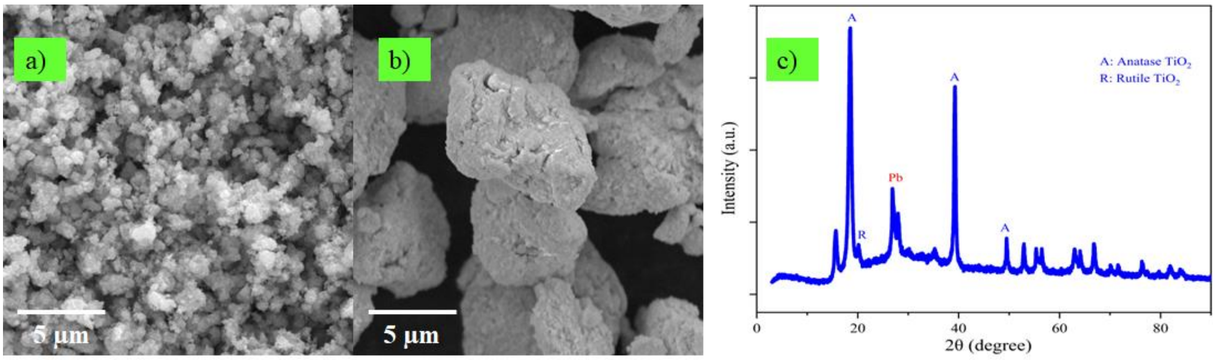

**Figure 2.** a) SEM images of pure $TiO_2$ nanoparticles b) SEM images of pure Pb particles c) XRD spectra of $TiO_2$-Pb photoanode sample

### 3.2. *Light absorption studies*

Pure $TiO_2$ and Pb powders was dissolved into ethanol solution and sonicated for 30 minutes before they were placed in the UV-visible spectroscopy. Pure ethanol solution was also used as reference for the light absorption analysis. Figure 3 showed that $TiO_2$ showed absorption in the UV region with the formation of peaks at around the 200-400 nm wavelength. Pb meanwhile showed the formation of few peaks in the infrared region of around 750 nm and 850 nm. Thus, indicating that the implementation of Pb could push the absorption for $TiO_2$ photoanode to move towards the visible region as well. This will then further enhance the light absorption of the photoanode when the composite materials were used.

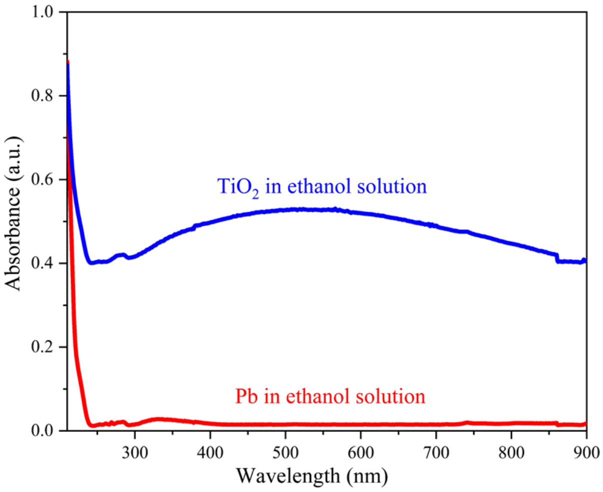

**Figure 3.** UV-visible spectra of $TiO_2$ and Pb in ethanol solution.

### *3.3. Electron transfer*

EIS analysis has been conducted for all the prepared photoanode samples as well as with one as received commercial $TiO_2$ photoanode sample (Solaronix), sintered at 450°C, as comparison and reference. A clean FTO glass was used as the second surface to complete the circuit with frequency range set at 0.1 Hz – 1 MHz and AC voltage of 10 mV. Nyquist plot and Bode plot was plotted based on the data obtained in the EIS response shown in Figure 4.

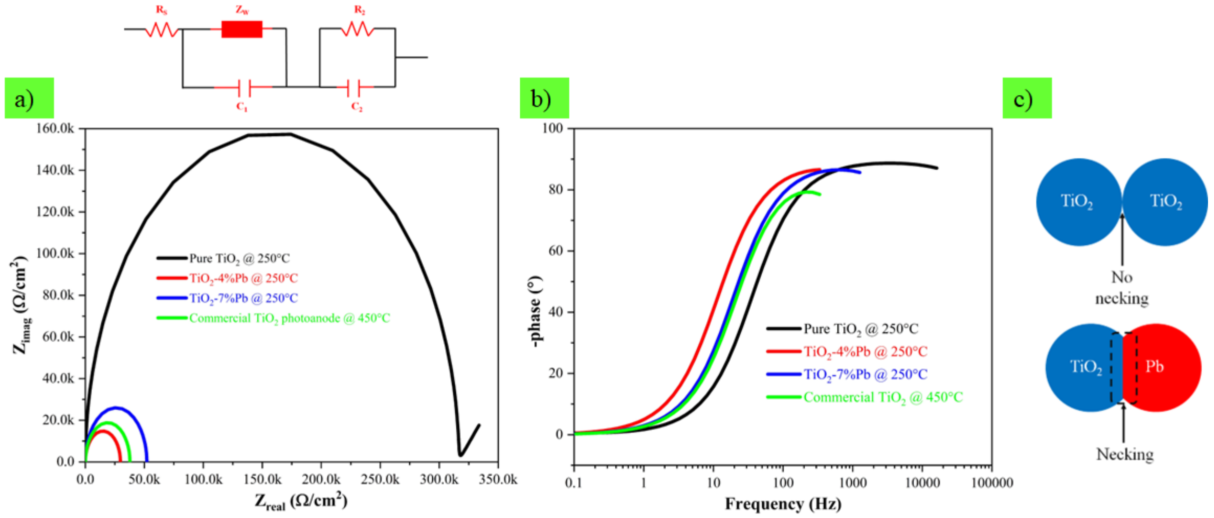

**Figure 4.** EIS response with respective circuit a) Nyquist plot for photoanode samples b) Bode plot for photoanode samples c) Schematic diagram of neck formation at the $TiO_2$-Pb interface

The charge transfer resistance ($R_{CT}$) of the photoanode samples can be determined by the Nyquist plot shown in Figure 4a. Figure 4a showed that the $R_{CT}$ decreases when Pb sintering aid was implemented. Pure $TiO_2$ photoanode sintered at 250°C showed $R_{CT}$ value of 157.30 kΩ/cm$^2$ while $TiO_2$-4% Pb photoanode showed $R_{CT}$ value of 14.78 kΩ/cm$^2$. Lower $R_{CT}$ values was highly desirable as this indicates lower resistance, increasing the charge transfer that would eventually lead to improved efficiency for the DSSC being developed. The lowering of the $R_{CT}$ values were due to the improved interparticle contact in the photoanode samples. During the sintering process, $TiO_2$ nanoparticles and Pb nanoparticles formed necks that increased the interparticle contact as shown in Figure 4c. The electron transfer has been increased, lowering the resistance. However, when the composition of Pb reaches 7%, the $R_{CT}$ showed the higher value (26.01 kΩ/cm$^2$) due to the presence of impurities that became surface defects and electron trapping sites [10]. These have then led to poor interparticle contact, increasing the resistance and recombination even further. Hence, it is important that suitable Pb composition was implemented in order to improve the performance of photoanode.

Figure 4a also showed that the $R_{cT}$ value for $TiO_2$-4% Pb photoanode sample was even lower than the $R_{CT}$ value for commercially prepared $TiO_2$ photoanode that was sintered at high temperature of 450°C. The commercially prepared $TiO_2$ photoanode yielded $R_{CT}$ value of 18.81 kΩ/cm$^2$, 21.42% higher than the $TiO_2$-4% Pb photoanode sample. The concept of metallurgical sintering states that the sintering temperature of metallic nanoparticles was around 2/3 of the metal's melting point [12]. Since Pb has a melting point of 327.5°C, it has managed to undergone sintering even at low sintering temperature of 250°C. The sintering of Pb nanoparticles formed necks at the $TiO_2$-Pb interface that led to improved interparticle contact, lower resistance and better charge transfer. Thus, highlighting why the method of implementing Pb as sintering aid could help enhance the performance of DSSC photoanode at low temperature over the typical $TiO_2$ photoanode sintered at high temperature.

Besides Nyquist plot, Bode plot has also been plotted for the photoanode samples in order to determine their electron lifetime ($t$) using Equation (1)[6]:

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

Where, $f_{max}$ = maximum frequency from the Bode plot (Hz)
The *t* value was important to determine the electron lifetime of photoanode that will determine the possibilities of recombination reactions in the photoanode. Longer electron lifetime value was desirable in order to lower the recombination reactions and eventually improving the performance of DSSC photoanode. The addition of Pb sintering aid has managed to enhance the electron lifetime of photoanode as the *t* value was increased from 0.049 ms for pure $TiO_2$ photoanode to 0.601 ms and 0.317 ms for $TiO_2$-4% Pb and $TiO_2$-7% Pb respectively. Thus, further support the effectiveness of adding Pb sintering aid in improving the performance of DSSC photoanode. Similarly, 4% Pb loading has been discovered to have shown longer *t* value as opposed to 7% Pb and should be considered as suitable Pb composition for future research. EIS results have shown that the addition of Pb as sintering aid improved the interparticle contact of photoanode, improve charge transfer, lowers resistance, enhance electron lifetime and reduce recombination reactions. $TiO_2$-4% Pb photoanode sintered at 250°C was also discovered to be a very suitable photoanode in developing highly efficient DSSC device that could even rival DSSC based on $TiO_2$ photoanode sintered at high temperature. Due to the low temperature requirement in this approach, it could be applicable for fabricating highly efficient flexible DSSC devices as well. The data obtained in the EIS analysis have been presented in Table 1 below for observation.

**Table 1.** EIS results for each photoanode samples.

| Photoanode samples | Sintering temperature (°C) | $R_{CT}$ ($k\Omega/cm^2$) | *t* (ms) |
|---|---|---|---|
| **Pure $TiO_2$** | 250 | 157.30 | 0.049 |
| **$TiO_2$-4% Pb** | 250 | 14.78 | 0.601 |
| **$TiO_2$-7% Pb** | 250 | 26.01 | 0.317 |
| **Commercial $TiO_2$** | 450 | 18.81 | 0.733 |

## 4. Conclusion

The research has implemented Pb as sintering to $TiO_2$ photoanode to improve the interparticle contact of the photoanode at low temperature of 250°C. The research discovered that Pb sintering aid has managed to enhance the interparticle contact, lower the resistance and recombination reactions as well as improving the charge transfer from the neck formation at the $TiO_2$-Pb interface. Pb composition of 4% have shown lowest $R_{CT}$ value with long electron lifetime while higher Pb composition of 7% was not desirable due to the presence of impurities and surface defects. $TiO_2$-4% Pb photoanode has even managed to rival the commercially prepared $TiO_2$ photoanode sintered at 450°C despite their low temperature of 250°C. Thus, highlighting their potential in developing highly efficient DSSC devices. The low sintering temperature used in this research also meant that this particular approach in adding Pb sintering aid could also be applicable in fabricating flexible DSSCs. Further research can be conducted in implementing different Pb composition or sintering temperature to study their effectiveness in developing flexible DSSC devices.

## 5. Author Contributions

H Khir: writing – original draft, methodology, formal analysis, data curation, investigation, visualization. A K Pandey: Writing – review and editing, supervision, methodology, funding acquisition, conceptualization. R Saidur: Writing – review and editing, supervision. M S Ahmad: Writing – review and editing, supervision, investigation. M Dewika: writing – review and editing. M Samykano: Writing – review and editing, resources.

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