



# Study on Dye-Sensitized Solar Cells Based on TiO<sub>2</sub> Composite Nanomaterials

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## ABSTRACT

With the continuous development of nanomaterials, how to improve the conversion efficiency of DSSCs has been the focus of scholars. Nano-TiO<sub>2</sub> material is a wide bandgap semiconductor with a bandgap of 3.2eV. It exhibits good performance in dye adsorption, charge separation, electron transport, etc., and has good chemical stability and strong acid and alkali resistance. Therefore, it was always the material of choice for the preparation of photoanodes. In this paper, different thicknesses of TiO<sub>2</sub> NRs barrier layers were prepared on FTO substrates by solvothermal method and two-step spin coating method, and their electrochemical and photoelectric properties were tested by using relevant test instruments. The effects of barrier layers with different thicknesses of TiO<sub>2</sub> NRs on the performance of DSSCs were analysed. The anatase TiO<sub>2</sub> NRs with an average length of 28±10nm and a diameter of 2±1nm were obtained. The concentration of TiO<sub>2</sub> NRs was 0.245mol·L<sup>-1</sup> (TiO<sub>2</sub> NRs-12). When the thickness is 88.58nm, DSSCs exhibit the best photoelectric performance.

## INTRODUCTION

Since 1991, Grätzel first proposed the development of dye-sensitized solar cells (DSSCs), improving the conversion efficiency of DSSCs has been the focus of scholars. After a lot of theoretical and experimental explorations, it is found that due to the poor adhesion between the photoanode and the conductive substrate, I<sup>3-</sup> in the electrolyte and D<sup>+</sup> in the dye easily diffuse onto the conductive substrate, thereby recombining with the photogenerated electrons to form a dark current. Therefore, in the photoanode, the interface between the conductive substrate and the semiconductor material is regulated, and the photoelectric conversion efficiency of the DSSCs is effectively improved (Hu et al. 2016). Generally, a dense barrier layer can be constructed between the interfaces to passivate the surface of the transparent conductive material, and a potential barrier is directly generated between the semiconductor and the conductive glass, which can effectively suppress the electronic recombination at the interface and improve the performance of the DSSCs.

Nano-TiO<sub>2</sub> material is a wide bandgap semiconductor with a band gap of 3.2eV. It exhibits good performance in dye adsorption, charge separation, electron transport, etc., and has good chemical stability and strong acid and alkali resistance. Therefore, it has always been the material of choice for the preparation of photoanodes (Lee et al. 2016).

In this paper, TiO<sub>2</sub> NRs barrier layers with different thicknesses were prepared on the FTO substrate by solvothermal method and two-step spin coating method, and their

electrochemical and photoelectric properties were tested by using relevant test instruments, the effects of barrier layers with different thicknesses of TiO<sub>2</sub>NRs on the performance of DSSCs were analysed.

## EARLIER STUDIES

A recent study conducted detailed research on various components constituting dye-sensitized solar cells, and achieved phased results, which promoted the development and practical application of dye-sensitized solar cells (Hu et al. 2016). The TiO<sub>2</sub>/CeO<sub>2</sub> composite photoanode is taken as an example to illustrate the development of photoanode film materials for dye-sensitized solar cells, and summarized the light scattering effect, up-conversion properties, specific surface area, the impact of optical responsiveness and electronic transmission performance on overall battery performance optimization (Lee et al. 2016). Saini et al. (2016) prepared a POM@TiO<sub>2</sub> composite photoanode by a sol-gel method in which a sandwich type polyacid compound K15{K3[(A-PW9O34)2Fe2(C2O4)2]}·29H2O having intramolecular electron transfer characteristics was combined with TiO<sub>2</sub>. Previous research studied the effects of TiO<sub>2</sub> nanoparticles, one-dimensional TiO<sub>2</sub> nanorod arrays and nano-forest structures on the performance of photoanodes and DSSCs (Ran et al. 2017). The experimental results show that the TiO<sub>2</sub> nano-forest structure can improve the utilization of incident and scattered light by photoanodes and the collection and transmission rate of photo generated carriers. A study pre-

pared TiO<sub>2</sub> photoanodes with different morphologies and used the solar simulator to test the photoelectric properties of four different photoanode dye-sensitized solar cells. The results show that under the same illumination conditions, the photoelectric performance of the dye-sensitized nanocrystalline solar cell with composite three-layer photoanode is optimal (Feng et al. 2016).

## MATERIALS AND METHODS

### Preparation of TiO<sub>2</sub> NRs Barrier Layer

**FTO conductive glass treatment:** The FTO substrate was cut into a specific size (1.5cm × 1.5cm), then immersed in detergent, acetone, isopropanol, absolute ethanol, ultrasonically in an ultrasonic cleaner for 30 min, and finally placed in absolute ethanol. When using, dry the surface anhydrous ethanol, wipe the FTO surface with a clean cotton swab dipped in absolute ethanol, and then place it in a plasma cleaner for 20 minutes.

**Preparation of different concentrations of TiO<sub>2</sub> NRs solution:** Different concentrations of TiO<sub>2</sub> NRs in toluene solution were prepared, which were 0.49mol·L<sup>-1</sup>, 0.245mol·L<sup>-1</sup>, 0.163mol·L<sup>-1</sup> TiO<sub>2</sub> NRs toluene solution. Specific steps: 20mL of cyclohexane and 7mL of oleic acid were poured into a 200mL beaker and stirred. 1g of tetrabutyl titanate was slowly added dropwise to the mixed solution, which immediately turned bright yellow and stirred at room temperature for 30 min. Then, 5mL of triethylamine was added dropwise to the former solution twice, stirred at room temperature for 30 min, stirred uniformly, poured into a 50mL reaction kettle, placed in an electric blast drying oven, and reacted at 180°. 24h, after the reaction is finished, the electric blast drying oven is cooled to room temperature, the reaction product is taken out, poured into a 200mL beaker, and then poured into about 75mL of ethanol, allowed to stand for 3h, and allowed to layer, and the upper layer is light yellow. The solution was poured off, leaving the lower layer of yellowish floc, which was centrifuged 2 to 3 times (10000 r·min<sup>-1</sup>, 10 min) with ethanol under a bench-top high-speed centrifuge, and

the resulting pale-yellow lower layer precipitate was dried. Then dissolved in toluene to obtain different concentrations of TiO<sub>2</sub> NRs in toluene solution (Rho et al. 2017).

### Preparation of TiO<sub>2</sub> Nanocrystalline Colloid

5mL of tetrabutyl titanate was slowly added dropwise to 50mL of deionized water, stirred at room temperature for 30 min to form a white precipitate, which was suction filtered with a sand core funnel and washed several times with deionized water to remove by-products. The obtained white powder is added to 75mL of water and stirred, and then 5mL of acetic acid and 0.5mL of nitric acid are sequentially added thereto, and the mixture is heated and stirred at 80°C until the blue colour is transparent. 0.2g of P25 is weighed and added to the blue transparent solution. After stirring evenly, ultrasonic for 30 min, stirring for 30 min, the obtained solution was poured into a high-pressure reaction kettle, placed in an electric blast drying oven, and reacted at 200°C for 12h. After the reaction was completed, it was cooled to room temperature, and the upper layer was clarified after being taken out. The solution was poured off to obtain a white powder precipitate, which was poured into a beaker, and 0.4g of polyethylene glycol 20,000 (PEG 20000) and 3-4 drops of Triton X-100 were added thereto at 80 to 100°C. The mixture was concentrated by heating to a certain concentration to obtain a TiO<sub>2</sub> colloid (Jiang et al. 2017).

## RESULTS AND DISCUSSION

Fig. 1 (a), (b) and (c) show the FESEM cross-section of TiO<sub>2</sub> NRs barrier layer prepared with three different concentrations (0.49mol·L<sup>-1</sup>, 0.245mol·L<sup>-1</sup>, 0.163mol·L<sup>-1</sup>). The TiO<sub>2</sub> NRs barrier layers with different thicknesses of about 138.89nm, 88.58nm and 46.72nm were obtained by different concentrations of TiO<sub>2</sub> NRs in toluene solution.

**Electron transport composite dynamics of DSSCs:** The DSSC's Jsc is effective in improving the electron transport properties of the TiO<sub>2</sub> NRs barrier layer. Dynamic intensity modulated photocurrent spectroscopy (IMPS) and dynamic

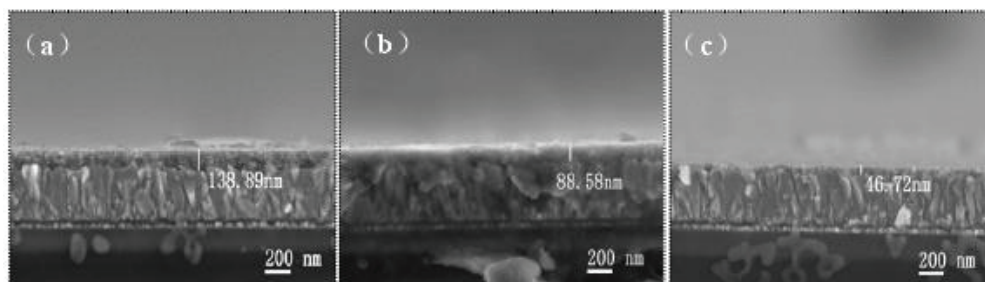


Fig.1: Cross section of TiO<sub>2</sub> NRs barrier layer with different thickness FESEM: (a)TiO<sub>2</sub> NRs-6; (b)TiO<sub>2</sub> NRs-12; (c)TiO<sub>2</sub> NRs-18

Table 1: EIS values of assembled DSSCs with different thickness TiO<sub>2</sub> NRs barrier layers.

Photoanode	Rs ( $\Omega \cdot \text{cm}^2$ )	R1 ( $\Omega \cdot \text{cm}^2$ )	R2 ( $\Omega \cdot \text{cm}^2$ )
TiO <sub>2</sub> NRs-0	2.79	2.57	6.52
TiO <sub>2</sub> NRs-6	2.84	1.87	4.26
TiO <sub>2</sub> NRs -12	2.84	1.13	4.07
TiO <sub>2</sub> NRs -18	2.83	1.91	4.42

intensity modulated photovoltage spectroscopy (IMVS) were used to test electron transport and recombination kinetics in the cell. The time constants in Figs. 1(a) and (b) include electron transit time ( $\tau_d$ , IMPS) and electron lifetime ( $\tau_n$ , IMVS), calculated by the formula:

$$\tau_d = (2\pi f_d)^{-1} \quad (2) \quad \tau_n = (2\pi f_n)^{-1} \quad (3) \quad \eta_e = 1 / (1 + \tau_d / \tau_n) \quad \dots(1)$$

Where,  $f_d$  and  $f_n$  are the characteristic frequency values of the lowest point of the imaginary part of the curve obtained by IMPS and IMVS respectively. As shown in Fig. 1(a), there is a linear relationship between the electron transit time  $\tau_d$  and the illumination intensity. Compared with DSSCs photoanodes without TiO<sub>2</sub>NRs, the TiO<sub>2</sub>NRs barrier layer reduces the electron transport time of DSSC under the same light intensity, which means that the introduction of TiO<sub>2</sub>NRs barrier layer accelerates the electron transport rate, further illustrating that the TiO<sub>2</sub>NRs barrier layer is electronic. Transmission provides an efficient channel that speeds up the transmission of electrons in DSSCs and reduces the recombination of electrons. Similarly, Fig. 1(b) shows the relationship between the electron lifetime  $\tau_n$  and the illumination intensity, and there is a linear relationship. The introduction of the TiO<sub>2</sub>NRs barrier layer increases the electron lifetime in DSSCs, indicating that the electron recombination is slow. Especially in the DSSCs battery assembly of TiO<sub>2</sub>NRs-12 photoanode, showing shorter electron transport time ( $\tau_d$ ) and longer electron lifetime ( $\tau_n$ ) under the same conditions, indicating that DSSCs photoanode electron transfer rate is fast and complex. slow.

After DSSCs were assembled by spin coating different thicknesses of TiO<sub>2</sub> NRs, electrochemical impedance spectroscopy (EIS) was performed to better understand the charge transfer and recombination kinetics in DSSCs. Fig. 2 shows the Nyquist of the EIS of DSSCs assembled with different thicknesses of TiO<sub>2</sub> NRs under different conditions in the DSSCs photoanode under the optical conditions (100mW·cm<sup>-2</sup>) and the applied open circuit voltage. The relevant parameter values are recorded in Table 1 respectively. Rs, R<sub>1</sub> and R<sub>2</sub> represent the surface resistance of the counter electrode and the wire, the electrolyte charge transfer resistance, and the TiO<sub>2</sub>/dye/electrolyte surface composite resistance, respectively. In this paper, the Pt counter elec-

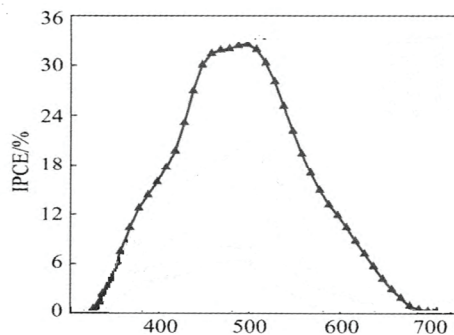


Fig. 2: The incident photon to current conversion efficiency (IPCE).

trode, the prepared TiO<sub>2</sub>, FTO substrate and so on are the same, so the Rs value is relatively close, corresponding to the intercept generated by the intersection of the left semicircle of the high frequency region of the Nyquist graph and the X axis. R<sub>1</sub> is mainly due to the charge transport resistance generated by the mesoporous layer TiO<sub>2</sub> film/FTO substrate and the Pt counter electrode/electrolyte I<sub>3</sub><sup>-</sup>/interface. DSSCs spin-coated with TiO<sub>2</sub> NRs barrier on the photoanode exhibited lower R<sub>1</sub> values than DSSCs without TiO<sub>2</sub>NRs. This indicates that the interface between the TiO<sub>2</sub> mesoporous layer and the FTO substrate is improved after the addition of a barrier layer of TiO<sub>2</sub>NRs in the DSSCs, and the TiO<sub>2</sub>NRs barrier layer has better electron transport channels, fewer defects and recombination. The final resistive element of R<sub>2</sub> fitted by the large semicircle in the low frequency region is primarily determined by the charge transfer resistance at the dye coated TiO<sub>2</sub>/electrolyte interface. The R<sub>2</sub> value is different from the R<sub>1</sub> value but has the same tendency, mainly because the spin-coated TiO<sub>2</sub>NRs barrier layer in the DSSCs photoanode improves the adhesion between the FTO substrate and the mesoporous TiO<sub>2</sub> film.

**IPCE spectrum of DSSCs:** Fig. 2 shows the incident photon to current conversion efficiency (IPCE) spectra after assembly of DSSCs with different thicknesses of TiO<sub>2</sub>NRs barrier. It can be seen from Fig. 2 that the IPCE value is increased due to the introduction of the TiO<sub>2</sub> NRs barrier layer. In particular, TiO<sub>2</sub>NRs-12 barrier layer assembled DSSCs have the largest IPCE value. Since the IPCE is proportional to the photocurrent density J<sub>sc</sub>, the IPCE test is consistent with the

IV test results. The IPCE value is related to light trapping efficiency, electron injection efficiency, and electron collection efficiency. The electron injection efficiency is related to the electron transport and electron recombination. DSSCs reduce the electron transport time and electron recombination due to the introduction of the TiO<sub>2</sub>NRs barrier layer, thereby improving the electron collection efficiency, corresponding to the IMVS and IMPS test results, and further increasing the IPCE value.

## CONCLUSION

After a lot of theoretical and experimental explorations, it is found that due to the poor adhesion between the photoanode and the conductive substrate, I<sub>3</sub><sup>-</sup> in the electrolyte and D<sup>+</sup> in the dye easily diffuse onto the conductive substrate, thereby recombining with the photogenerated electrons to form a dark current. Anatase TiO<sub>2</sub>NRs with an average length of 28±10nm and a diameter of 2±1nm were successfully synthesized by one-pot solvothermal method. With the concentration of TiO<sub>2</sub>NRs as 0.245mol·L<sup>-1</sup> (TiO<sub>2</sub>NRs-12) and the thickness as 88.58nm, DSSCs showed the best photoelectric performance. The PCE of the DSSCs was 8.44%, the Voc was 0.79 V, the Jsc was 16.1 mA·cm<sup>-2</sup>, and the FF was 66%.

The TiO<sub>2</sub> NR barrier layer has good electron transport channels and less electron recombination, which helps to improve electron transport rate, electron lifetime, charge collection efficiency and electronic recombination reaction, and it is beneficial to improve the photoelectric conversion performance of DSSCs.

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## REFERENCES

- Feng, Y., Chen, J., Huang, X., Liu, W., Zhu, Y. and Qin, W. 2016. A ZnO/TiO<sub>2</sub> composite nanorods photoanode with improved performance for dye-sensitized solar cells. *Crystal Research and Technology*, 51(10): 548-553.
- Hu, J., Cheng, J., Tong, S., Li, Z., Duan, J. and Yang, Y. 2016. Dye-sensitized solar cells based on p25 nanoparticles/TiO<sub>2</sub> nanotube arrays/hollow TiO<sub>2</sub> boxes three-layer composite film. *Journal of Materials Science Materials in Electronics*, 27(5): 1-9.
- Jiang, L., Sun, L., Yang, D., Zhang, J., Li, Y. J., and Deng, W.Q. 2017. Niobium-doped (001) dominated anatase TiO<sub>2</sub> nanosheets as photoelectrode for efficient dye-sensitized solar cells. *ACS Appl. Mater. Interfaces*, 9(11): 9576.
- Lee, K.W., Kim, M., Kim, J.M., Kim, J.J. and Lee, I.H. 2016. Enhanced photovoltaic performance of back-illuminated dye-sensitized solar cell based on TiO<sub>2</sub> nanoparticle/nanowire composite film in cobalt redox system. *Journal of Alloys and Compounds*, 656: 568-572.
- Ran, H., Fan, J., Zhang, X., Jing, M., and Shao, G. 2017. Enhanced performances of dye-sensitized solar cells based on Au-TiO<sub>2</sub> and Ag-TiO<sub>2</sub> plasmonic hybrid nanocomposites. *Applied Surface Science*, 430.
- Rho, W. Y., Da, H. S., Sang, H. L. and Jun, B. H. 2017. Enhanced efficiency in dye-sensitized solar cells by electron transport and light scattering on freestanding TiO<sub>2</sub> nanotube arrays. *Nanomaterials*, 7(10): 345.
- Saini, R.K., Singh, D., Bhagwan, S., Sonika, Singh, I. and Kadyan, P.S. 2016. Photovoltaic characterization of dye sensitized solar cells based on tio2 nanoparticles using triarylmethane dyes as photosensitizers. *Journal of Nanoelectronics and Optoelectronics*, 11(2): 175-182.
- Wei, L., Chen, S., Yang, Y., Dong, Y., Song, W. and Fan, R. 2018. Effect of graphene/TiO<sub>2</sub> composite layer on the performance of dye-sensitized solar cells. *Journal of Nanoscience and Nanotechnology*, 18(2): 973-978.