12-2019

Study on Dye-Sensitized Solar Cells Based on TiO2 Composite Nanomaterials

Cuiping Kang
Baoji University of Arts and Sciences

Muhammad Aqeel Ashraf
China University of Geosciences

Yung-Tse Hung
Cleveland State University, y.hung@csuohio.edu

Nature Environment and Pollution Technology
An International Quarterly Scientific Journal
p-ISSN: 0972-6268
e-ISSN: 2395-3454
Vol. 18
No. 5 (Special Issue)
pp. 1701-1704
2019

Original Research Paper
Open Access

Study on Dye-Sensitized Solar Cells Based on TiO_2 Composite Nanomaterials

Cuiping Kang*, Muhammad Aqeel Ashraf and Yung-Tse Hung*****
*Baoji University of Arts and Sciences, Baoji, Shaanxi Province, China
** School of Environmental Studies, China University of Geosciences, Wuhan, China
***Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, Ohio, 44115 USA

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 03-08-2019
Accepted: 30-10-2019

Key Words:
Dye-sensitized solar cell
TiO_2 nanomaterial
Photoanode
Dye adsoption

ABSTRACT

With the continuous development of nanomaterials, how to improve the conversion efficiency of DSSCs has been the focus of scholars. Nano-TiO_2 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_2 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_2 NRs on the performance of DSSCs were analysed. The anatase TiO_2 NRs with an average length of 28±10nm and a diameter of 2±1nm were obtained. The concentration of TiO_2 NRs was 0.245mol·L^{-1} (TiO_2 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, $I3^-$ in the electrolyte and D^+ 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_2 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_2 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_2NRs 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_2/CeO2 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_2 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_2. Previous research studied the effects of TiO_2 nanoparticles, one-dimensional TiO_2 nanorod arrays and nano-forest structures on the performance of photoanodes and DSSCs (Ran et al. 2017). The experimental results show that the TiO_2 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 prepared TiO_2 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_2 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_2NRs solution: Different concentrations of TiO_2NRs in toluene solution were prepared, which were 0.49mol·L^{-1}, 0.245mol·L^{-1}, 0.163mol·L^{-1} TiO_2NRs 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^{-1}, 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_2 NRs in toluene solution (Rho et al. 2017).

Preparation of TiO_2 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_2 colloid (Jiang et al. 2017).

RESULTS AND DISCUSSION

Fig. 1 (a), (b) and (c) show the FESEM cross-section of TiO_2NRs barrier layer prepared with three different concentrations (0.49mol·L^{-1}, 0.245mol·L^{-1}, 0.163mol·L^{-1}). The TiO_2NRs barrier layers with different thicknesses of about 138.89nm, 88.58nm and 46.72nm were obtained by different concentrations of TiO_2NRs in toluene solution.

Electron transport composite dynamics of DSSCs: The DSSC's Jsc is effective in improving the electron transport properties of the TiO_2NRs barrier layer. Dynamic intensity modulated photocurrent spectroscopy (IMPS) and dynamic

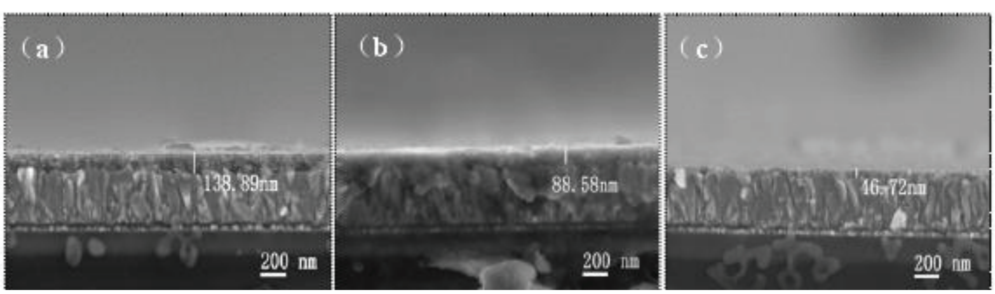

Fig.1: Cross section of TiO_2NRs barrier layer with different thickness FESEM: (a)TiO_2NRs-6; (b)TiO_2NRs-12; (c)TiO_2NRs-18

Table 1: EIS values of assembled DSSCs with different thicknessTiO_2 NRs barrier layers.

Photoanode	Rs ($\Omega \cdot cm^2$)	R1 ($\Omega \cdot cm^2$)	R2 ($\Omega \cdot cm^2$)
TiO_2NRs-0	2.79	2.57	6.52
TiO_2 NRs-6	2.84	1.87	4.26
TiO_2NRs -12	2.84	1.13	4.07
TiO_2NRs -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 (τ_d, IMPS) and electron lifetime (τ_n, IMVS), calculated by the formula:

$$\tau_d = (2\pi f_d)^{-1} (2)\, \tau_n = (2\pi f_n)^{-1} (3)\, \eta_c = 1(1 + \tau_d / \tau_n) \qquad \ldots(1)$$

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 τ_d and the illumination intensity. Compared with DSSCs photoanodes without TiO_2NRs, the TiO2NRs barrier layer reduces the electron transport time of DSSC under the same light intensity, which means that the introduction of TiO_2NRs barrier layer accelerates the electron transport rate, further illustrating that the TiO_2NRs 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 τ_n and the illumination intensity, and there is a linear relationship. The introduction of the TiO_2NRs barrier layer increases the electron lifetime in DSSCs, indicating that the electron recombination is slow. Especially in the DSSCs battery assembly of TiO_2NRs-12 photoanode, showing shorter electron transport time (τ_d) and longer electron lifetime (τ_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_2 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_2 NRs under different conditions in the DSSCs photoanode under the optical conditions ($100mW \cdot cm^{-2}$) and the applied open circuit voltage. The relevant parameter values are recorded in Table 1 respectively. Rs, R_1 and R_2 represent the surface resistance of the counter electrode and the wire, the electrolyte charge transfer resistance, and the TiO_2/dye/electrolyte surface composite resistance, respectively. In this paper, the Pt counter electrode, the prepared TiO_2, 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. R1 is mainly due to the charge transport resistance generated by the mesoporous layer TiO_2 film/FTO substrate and the Pt counter electrode/electrolyte I3-/interface. DSSCs spin-coated with TiO_2 NRs barrier on the photoanode exhibited lower R1 values than DSSCs without TiO_2NRs. This indicates that the interface between the TiO_2 mesoporous layer and the FTO substrate is improved after the addition of a barrier layer of TiO_2NRs in the DSSCs, and the TiO_2NRs barrier layer has better electron transport channels, fewer defects and recombination. The final resistive element of R2 fitted by the large semicircle in the low frequency region is primarily determined by the charge transfer resistance at the dye coated TiO_2/electrolyte interface. The R2 value is different from the R1 value but has the same tendency, mainly because the spin-coated TiO_2NRs barrier layer in the DSSCs photoanode improves the adhesion between the FTO substrate and the mesoporous TiO_2 film.

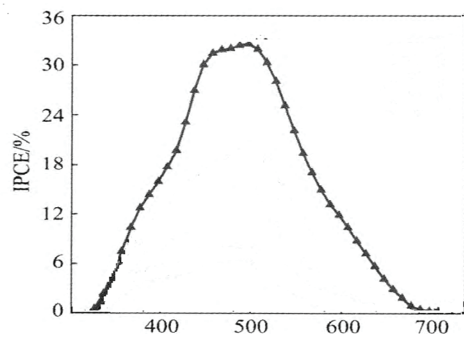

Fig. 2: The incident photon to current conversion efficiency (IPCE).

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_2NRs barrier. It can be seen from Fig. 2 that the IPCE value is increased due to the introduction of the TiO_2 NRs barrier layer. In particular, TiO_2 NRs-12 barrier layer assembled DSSCs have the largest IPCE value. Since the IPCE is proportional to the photocurrent density Jsc, 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_2NRs 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, $I3^-$ in the electrolyte and D^+ in the dye easily diffuse onto the conductive substrate, thereby recombining with the photogenerated electrons to form a dark current. Anatase TiO_2NRs 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_2NRs as 0.245mol·L^{-1} (TiO2NRs-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 m A·cm^{-2}, and the FF was 66%.

The TiO_2 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.

ACKNOWLEDGEMENT

Scientific research plan projects of Education Department of Shaanxi province of China (Grant No. 12JK0983) Natural Science Basic Research plan in Shaanxi Province of China (Grant No. 2012JQ1011) and Key project of Baoji university of arts and science (Grant No. ZK2017036).

REFERENCES

Feng, Y., Chen, J., Huang, X., Liu, W., Zhu, Y. and Qin, W. 2016. A ZnO/TiO2 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_2 nanotube arrays/hollow TiO_2 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_2 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_2 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-TiO2 and Ag-TiO2 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_2 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_2 composite layer on the performance of dye-sensitized solar cells. Journal of Nanoscience and Nanotechnology, 18(2): 973-978.