TiO$_2$ Nanowire dye-sensitized solar cells Fabricated by Hydrothermal Method

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Abstract. TiO$_2$ nanowire dye-sensitized solar cells were fabricated by using hydrothermal method. The synthesizing of TiO$_2$ nanowire/nanorod arrays directly on FTO substrate would cause a high conducting loss to solar cells. Through laminating a compact layer between FTO substrate and photonic anode layer, the conducting loss could be effectively prevented. Results indicated that using different concentration of titanium tetrabutoxide would affect the photoelectric conversion efficiency and different producing methods of the compact layer also played an important role to the conversion efficiency.

1. Introduction
Nowadays, energy crisis and environmental pollution are two major challenges in 21st century. Developing renewable green energy, especially solar cells, has become major issues of human society facing. Up to now, the highest efficiency of the solar cells prepared by single crystal silicon or polycrystalline silicon films could be up to 20% or more, but the cost was too expensive. Developing low-cost photovoltaic active materials as well as fabrication process are important. Currently ZnO, CdS, CdSe, CdTe, Fe$_2$O$_3$, SnO$_2$, TiO$_2$ and many other compounds have been used for dye-sensitized solar cells (DSCs)[1-4]. Although CdSe, CdTe and other solar cells have some advantages, they are highly toxic and harmful to environment. Dye-sensitized TiO$_2$ powder cell possessed the advantages of both low cost and simple fabrication process, it propels great amount of investigation all over the world and becomes the forefront of chemistry and material science fields. Up to now, the highest photoelectric conversion efficiency of TiO$_2$ DSC surpassed 10% and further improvement is also underway to reach the theoretical prediction. However, the lastest theoretical analysis indicated that TiO$_2$ powder had a lower photoelectric conversion efficiency compared with that of TiO$_2$ nanowire[5, 6].

The typical composition of a TiO$_2$ DSC included the dye-sensitized semiconductor anode, the electrolyte and the counterpart electrode. The TiO$_2$ photonic anode was produced by absorbing the photosensitizers on the surface of TiO$_2$ nanowire, the counterpart electrode was produced by sputtering a certain thickness Pt thin film on FTO substrate and the electrolyte was permeated in between. The dye molecular can absorb the visible photo energy and transit from groud state to excited state. Due to the unstable of excited state, the electronic will fast return to the lower energy conducting band of TiO$_2$ through the interaction of dye molecular and the TiO$_2$ suface. And subsequently the electronic will inject into the FTO conducting thin film and finally generate photoelectric current through outside circuit. The oxided dye molecular will be reduced by the electrolyte, which will then diffuse to the counterpart electrode to be charged. The complete circulation could be described as[7-10]:

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Ground state Dye molecular (S) + hv $\rightarrow$ Excited dye molecular (S\text{3})
Excited dye molecular (S\text{3}) + TiO\text{2} $\rightarrow$ e- (conducting band of TiO\text{2}) + oxidized dye molecular (S\text{+})
(generating photoelectric current)
Oxidized dye molecular (S\text{+}) + reduced electrolyte (R\text{-}) $\rightarrow$ Ground State dye (S) + Oxidized electrolyte (R) (Dye reduction)
Oxidized electrolyte (R\text{+}) + e- (cathode) $\rightarrow$ Reduced electrolyte (R\text{-}) (electrolyte reduction)
Oxidized electrolyte (R\text{+}) + e- (TiO\text{2} conducting band) $\rightarrow$ Reduced electrolyte (R\text{-}) (Dark current)

In present paper, well-aligned TiO\text{2} nanowire arrays were successfully prepared on the FTO substrate by hydrothermal method with different amount of titanium tetrabutoxide (Ti(OC\text{4}H\text{9})\text{4}) in starting materials. The as-prepared TiO\text{2} nanowire arrays with a rutile structure were about 10\text{μm} in length and 200nm in width. The photoelectric conversion efficiency of the DSCs fabricated by the as-synthesized TiO\text{2} nanowire arrays was detailed investigated.

2. Experiment

The TiO\text{2} nanowire/nanorod arrays were synthesized by hydrothermal method. The FTO conducting glass was cleaned by soaking in the deionized water for 20min as well as by ultrasonic cleaning for 20min. The titanium tetrabutoxide, high concentration hydrochloric acid and deionized water were chosen as the precursors, which were hydrothermally synthesized in the reaction kettle at 150°C for 20hrs. The TiO\text{2} photonic anodes were then soaked in the N97 dye for 12hrs before the final encapsulation.

3. Results and discussion

Fig. 1 illustrated the J-V curve of TiO\text{2} DSC as a function of concentration of titanium tetrabutoxide. As the concentration of titanium tetrabutoxide increased, the conversion efficiency increased firstly and when the concentration reached 0.75 M, the photoelectric conversion efficiency became the highest of 0.31%, with the current density and short circuit voltage being 3.27mA/cm\text{2} and 0.465 mV respectively. As the concentration further increased to 1.0M the conversion efficiency decreased instead.

![Fig. 1](image)

Fig. 1 The photoelectric conversion efficiency of TiO\text{2} DSC as a function of concentration of titanium tetrabutoxide. Fig. 2 XRD patterns of TiO\text{2} photonic anode varied with concentration of titanium tetrabutoxide.

Fig. 2 illustrated the as-prepared XRD patterns of TiO\text{2} photonic anode varied with concentration of titanium tetrabutoxide. The diffraction peaks could be indexed based on rutile TiO\text{2} phase (JCPDF card file No. 881175) with tetragonal P4_3/mnm (No.136) space group, which indicated TiO\text{2} composition was successfully synthesized under present parameters. And the higher the concentration of titanium tetrabutoxide was, the stronger the diffraction peaks of TiO\text{2} phase exhibited. The lower concentration samples also exhibited some diffraction peaks of FTO substrate, which might be arose
from the thin size of the TiO$_2$ layer or the very loose surface structure of TiO$_2$ layer under the low concentration.

Fig. 3 indicated the SEM photos of the DSC with different concentration of titanium tetrabutoxide. As could be seen, the concentration affected the density of the nanowire arrays. As the concentration increased, the nanoarray became denser and the distribution of TiO$_2$ nanowire became more uniform. The density had a close relationship to the surface area of the photonic anode, and the photoelectric conversion efficiency increased with the increase of surface area and reached the maximum when the concentration was 0.75M. The cross section photograph (d) indicated a thickness of about 10 microns TiO$_2$ photonic anode layer.

Fig. 3 SEM photographs of the TiO$_2$ photonic anode fabricated with the titanium tetrabutoxide concentration being (a) 0.5 M titanium, (b) 0.75M and (c) 1.0 M. (d) was the cross section of picture b.

SEM pictures also indicated that there existed some area without the growth of TiO$_2$ nanowire, where became the place of current leakage in DSCs, and thus lowered the photoelectric conversion efficiency. In order to avoid this problem, we employed a buffer layer between FTO substrate and TiO$_2$ photonic anode to improve the efficiency. The buffer layer was produced by the following two methods: rotary gelatinizing method using titanium tetrabutoxide and directly deposited TiO$_2$ buffer layer on FTO by magnetron sputtering method, using sputtering time to control the film thickness.
Fig. 4  SEM cross-section images of the buffer layer produced by (a) rotary gelatinizing method, (b) magnetron sputtering method, (c) J-V curves of the three type battery with titanium tetrabutoxide being the same concentration of 0.75 M, (1 was the DSC without buffer layer, 2 represented the DSC with magnetron sputtered buffer layer, 3 was the DSC with rotary gelatinized buffer layer).

Fig4 illustrated the cross-section SEM images of the DSCs produced with buffer layer. The buffer layer could be clearly observed between FTO substrate and TiO$_2$ photonic anode. The one produced by rotary gelatinizing method was about 15um thickness, while that produced by magnetron sputtering method was about 18 um. Fig4(c) indicated that among the three DSCs, the one with buffer layer produced by rotary gelatinizing method possessed the highest cell efficiency. The open circuit voltage and fill factor were improved by about and respectively, compared with the DSC without buffer layer. However, when the buffer layer was produced by magnetron sputtering method, the short-circuit current decreased. The possible reasons for this phenomenon lied in that the crystallization in the buffer layer made by magnetron sputtering method was worse than that in and the lattice defects inside acted as traps for electronic transmission and lowered the short-circuit current. Moreover, one could expect a higher conversion efficiency in DSC-3 if the gap existed beween the buffer layer and conductive glass could be eliminated.
Fig. 5 J-V curves of the DSCs with (a) the buffer layer produced by magnetron sputtering for 10 minutes, (b) different thickness of buffer layer fabricated by different sputtering time.

Fig. 5(a) illustrated the J-V curves of DSCs with the buffer layer produced by magnetron sputtering for 20 minutes. The highest conversion efficiency was still obtained in the 0.75M sample, which corresponded very well with the conclusion in Fig 1, however, the efficiency was improved because of the buffer layer. The thickness of the buffer layer prepared by magnetron sputtering also had a significant influence on the photoelectric conversion efficiency of DSCs. As could be seen in Fig 5(b), when the sputtering time was two minutes for the DSC produced with 0.75M titanium tetrabutoxide, the highest conversion efficiency of 0.43% was obtained, with the current density and open circuit voltage being 0.83mA/cm² and 0.58mV respectively.

4. Conclusions

TiO₂ nanowire/rod array DSCs were prepared by hydrothermal method in the present research, results showed that:

1. The concentration of tetrabutyl titanate played an important role on the conversion efficiency of the DSCs. The highest conversion efficiency of 0.31% was obtained when the concentration of tetrabutyl titanate was 0.75M, with the current density and open-circuit voltage being 3.27mA/cm² and 0.47mV respectively.

2. Using buffer layer between FTO substrate and TiO₂ photonic anode could effectively improve the conversion efficiency. When the rotary gelatinizing method prepared buffer layer had a higher conversion efficiency than the magnetron sputtering prepared one. When the concentration of tetrabutyl titanate was 0.75M, the conversion efficiency of the former was improved to 0.71%, with the current density and open-circuit voltage being 1.36mA/cm² and 0.63mV respectively.

3. The thickness of the buffer layer also affected the battery conversion efficiency. When magnetron sputtering time was 2 minutes, the conversion efficiency of DSC reached the highest of 0.43%, with the current density and open-circuit voltage being 0.83mA/cm² and respectively 0.58mV respectively.

The optimal photoelectric conversion property was obtained when the amount of Ti(OC₄H₉)₄ was 0.75M. The open-circuit voltage and short circuit current density were 0.47 V and 3.27 mA/cm², respectively. The photoelectric conversion efficiency was about 0.31%. However, when the TiO₂ buffer layer were prepared on the FTO substrate by spin coating before hydrothermal treatment, the open circuit voltage was improved to 0.63V and the current density was 1.32mA/cm². The conversion efficiency was increased to 0.7%.

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