Study of Different TiO$_2$ Electrode Structures on Dye-Sensitized Solar Cell

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Abstract In this research, applications of different TiO$_2$ electrode structures on Dye-Sensitized Solar Cell were investigated. The different TiO$_2$ electrode structures include: (1) synthesis of TiO$_2$ nano-particles and TiO$_2$ film electrode by sol-gel and spin-coating method; (2) fabrication of the TiO$_2$ film electrode by RF Sputtering; (3) fabrication of the rod TiO$_2$ electrode by photo lithography. X-ray diffraction patterns show that the best sintering temperature of nano-TiO$_2$ thin film is 500 °C, at which TiO$_2$ anatase phase forms best and the smallest particle-size (8-10 nm) can be obtained. Ultraviolet-visible absorption spectra reveal that the rod TiO$_2$ electrode with TCPP sensitizer adsorbed on has the best optical absorption from 400 nm to 700 nm. The results of current-voltage analyses reveal that the solar cell with rod TiO$_2$ electrode has higher conversion efficiency than the others. This result also provides clear evidence for the contact area between TiO$_2$ electrode and TCPP sensitizer plays an important role on the efficiency of dye-sensitized solar cell.

Introduction

Dye-sensitized solar cell (DSSC) has become an alternative photovoltaic device, which provides a more technical and economical light-to-electric converting mode than that based on p-n junction [1-3]. Nowadays, this kind of solar cell reaches a photoelectric conversion efficiency exceeding 10 % under sunlight irradiation [4-5], which shows a good prospect for application in solar conversion. The DSSC consists of sensitizing dye, TiO$_2$ porous film (anode electrode), electrolyte and opposite electrode (cathode electrode). When DSSC is irradiated by sunlight, the electrons of dye are excited from ground state to excited state by adsorbing photons. The excited electrons are injected to the conductive band of TiO$_2$ porous film, and then transfer to the conducting glass through the porous TiO$_2$ film. Since TiO$_2$ porous film plays a key role in the enhancement of photoelectric conversion efficiency of DSSC, many scientists focus their researches on it [6-8]. Chemical and physical treatment methods are usually used to improve the surface state and performance of TiO$_2$ porous film.

However, the randomly porous structure of TiO$_2$ electrode gives rise to several undesired characteristics. These include low conductivity, which is due to the film consists of tiny crystals measuring 10–30nm in diameter [9]. The small size of the crystals does not support the formation of space charge region. This is thought to enhance the recombination rate of photo-injected electrons due to absence of an energy barrier at the electrode/electrolyte interface [10]. Another detrimental characteristic of the sol–gel produced TiO$_2$ electrode is the random porous network, which limit to access the entire film surface [11-14]. Thus, techniques for fabricating large surface area TiO$_2$ with
good conductivity and a higher degree of order within the porous network are interest to DSSC. Recently, DC magnetron sputtering technique has been used to deposit porous TiO₂ thin films with large surface area in this type of solar cell. The sputtered films yielded a higher photocurrent and conversion efficiency than sol–gel produced films of similar thickness when incorporated into DSSC configuration [15]. In this work we report on assembling and performance of and dye-sensitized solar cell using sol-gel method, RF sputtering method, and photolithography. We also discuss and compare these different TiO₂ electrode structures to investigate the effects of contact area between TiO₂ electrode and TCPP sensitizer on photocurrent and conversion efficiency of DSSC.

Experiments

In this study, we use sol-gel method, RF sputtering method, and photolithography to prepare different TiO₂ electrodes and discuss the influence of the application on dye-sensitized solar cells.

**Spin-coating method.** The nano-TiO₂ electrode were prepared from Ti(OC₄H₉) and C₂H₅OH as the starting precursors using sol-gel, by adding HCL solution to control the hydrolysis reaction. The purpose of adding H₂O (DI water) was to speed up the reaction process. The samples were baked in over at 100 °C for 10 mins, and then sintered at 600 °C for 30 mins in air. The preparation of nano-TiO₂ electrode on ITO conductive glass was finished.

**RF Sputtering method.** We prepared TiO₂ film using Ti as target in RF sputtering and stick ITO conductive glass to holder with heat-resisting adhesive tape. We abstracted 5×10⁻⁶ torr air out until vacuum and then hit plasma. The TiO₂ film was annealed at 600 °C for 30 mins in air. Finally we finished the preparation of TiO₂ film electrode.

**Rod TiO₂ electrode by photolithography process.** The steps of making photolithography are following. At the beginning, we washed TiO₂ film that we had sputtered down with acetone. The samples were baked at 50 °C for 10 mins and then coated with negative photo-resister until the thickness is about 4µm. We put it in photo-mask to expose and baked for 5mins, and then took out sample and put developer to make development. We adopted wet etching to get rid of TiO₂ film and then use the acetone to get rid of photo-resister on TiO₂ film. Finally we finished the preparation of TiO₂ electrode.

**Assembling the dye-sensitized solar cell.** The TiO₂ electrode layer was treated with the TCPP dye, (Tetrakis (4-carboxyphenyl) porphyrin), by immersing the electrode in 3×10⁻⁴ M ethanolic solution during 12h. The counter electrode was Pt film by Electron-beam Evaporation on ITO glass. The I⁻/I₃⁻ electrolyte consisted of a mixture of iodides and I₂ in acetonitrile. Finally, we put “ITO/TiO₂(Dye)/ [0.5M KI , 0.05M I₂ , CH₃CN ]/Pt/ITO” together to accomplish the fabricate of DSSC.

**Measurements of photo-electro characteristics.** We investigated these different TiO₂ electrode structures by X-ray diffraction, UV/Vis spectrophotometer, scanning electron microscopy (SEM), and current-voltage analyses. The surface morphology of the photolithography was observed using scanning electron microscopy (SEM). The current-voltage characteristics of samples were measured by Keithley 2400 source meter and determined under simulated sunlight with white light intensity equal to 25 mW/cm². All samples were illuminated by 150W lamp through an solar simulation (Newport Oriel Instruments).

Results and discussions

Fig. 1 is the XRD diffraction patterns that the nano-TiO₂ films sintered under the different temperature. We can find the crystallized direction intensity under different sintering temperature. When sintering temperature is 300 °C, it could discover that the anatase phase of nano-TiO₂ already
appeared. As increasing the sintering temperature to 600 °C, the best anatase phase of TiO$_2$ was obtained. If we increase the sintering temperature to 700 °C, the nano-TiO$_2$ film will turn to rutile phase. It indicates that the best sintering temperature of nano-TiO$_2$ film is 600 °C, at which the smallest particle-size 8–10 nm of TiO$_2$ can be obtained. Fig. 2 is XRD-diffracton patterns that the TiO$_2$ film prepared by RF sputtering annealed under the different temperature. By the figure we can find out before the film has not passed through the anneal processing, it presents amorphous. While the annealing temperature arrives to 500 °C, we could discover that the crystalized direction of anatase phase appeared. As increasing the sintering temperature to 600 °C, the best anatase phase of TiO$_2$ was obtained. If we increase the sintering temperature to 700 °C, the TiO$_2$ film will turn to rutile phase. This result is similar to those observed in nano-TiO$_2$ films.

Fig. 3 is the adsorption spectra of TCPP solution and TCPP stick on TiO$_2$ surface. It reveals that several absorption peaks for TCPP solution are observed at 428 nm for B band and at 512, 546, 588, and 644 nm for Q band, which are consistent with the values reported in the literature [16]. We can find that the absorption spectrum of TCPP/TiO$_2$ electrode from 400 nm to 700 nm is nearly invariant and is obviously greater than that of TCPP. These results indicate that TiO$_2$ electrodes of dye-sensitized solar cell can improve the absorption of visible light (400 nm ~700 nm). Fig. 4 is the front-view SEM of TiO$_2$ film after lithography. In the picture we can find its expose of distributing and each cylinder of size is about 20µm. The distance between the column is unanimous and the interval is about 20µm. Fig. 5 is the top-view of SEM after etching. Though the structure may not as well as we have expected but it still show the rod structure that we want to need.

Table 1 is the current-voltage characteristics parameters of different TiO$_2$ electrodes made by sol-gel method, sputter method, and photolithography manufacture. It reveals that the efficiency of rod TiO$_2$ electrode is higher than the others. It may be due to the rod TiO$_2$ electrode has better light-transmission and larger contact area with dye resulting in higher efficiency.

Conclusions.

In this work we report on assembling and performance of dye-sensitized solar cell using sol-gel method, RF sputtering method, and photolithography. X-ray diffraction patterns show that the best sintering temperature of nano-TiO$_2$ thin film is 500 °C, at which TiO$_2$ anatase phase forms best and the smallest particle-size (8-10 nm) can be obtained. Ultraviolet-visible absorption spectra reveal that the rod TiO$_2$ electrode with TCPP sensitizer adsorbed on has the best optical absorption from 400 nm to 700 nm. The results of current-voltage analyses reveal that the solar cell with rod TiO$_2$ electrode has higher conversion efficiency than the others. This result also provides clear evidence for the contact area between TiO$_2$ electrode and TCPP sensitizer plays an important role on the efficiency of dye-sensitized solar cell.

Acknowledgements

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References

Table 1. The current-voltage characteristics parameters of different TiO$_2$ electrodes made by sol-gel method, sputtering method, and photolithography manufacture.

<table>
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<tr>
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<th>Voc(V)</th>
<th>Isc(mA)</th>
<th>FF%</th>
<th>η%</th>
</tr>
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<tr>
<td>TCPP+nano-TiO$_2$ film by sol-gel $^*$</td>
<td>0.176</td>
<td>0.87</td>
<td>41</td>
<td>0.248</td>
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<td>TCPP+TiO$_2$ film by sputtering</td>
<td>0.426</td>
<td>1.83</td>
<td>53</td>
<td>1.652</td>
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<tr>
<td>TCPP+rod TiO$_2$ film</td>
<td>0.441</td>
<td>1.91</td>
<td>55</td>
<td>1.952</td>
</tr>
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Fig. 1 XRD diffraction patterns of the nano-TiO$_2$ films
sintered under different temperatures.

![Graph showing XRD diffraction patterns of TiO₂ films sintered under different temperatures.](image)

Fig. 2 XRD diffraction patterns of TiO₂ films sintered under the different temperatures.

![Graph showing adsorption spectra of TCPP solution and TCPP stick on TiO₂ surface.](image)

Fig. 3 The adsorption spectra of TCPP solution and TCPP stick on TiO₂ surface.

![Image showing the front view of SEM after lithography.](image)

Fig. 4 The front view of SEM after lithography.
Fig. 5 The top view of SEM after etching.