Application of TiO$_2$ nano-particles on the electrode of dye-sensitized solar cells

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**Article info**

**Abstract**

In this study, nano-TiO$_2$ thin film electrode and solar cell have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet–visible absorption spectra, contact angle, X-ray photoelectron spectroscopy (XPS), and current–voltage characteristics analyses. X-ray diffraction patterns show that the best sintering temperature of a nano-TiO$_2$ film is 600$^\circ$C, at which TiO$_2$ anatase phase forms best and the particle size of 8–10 nm can be obtained. The SEM images of a nano-TiO$_2$ thin film show that the surface of the film is smooth and porous, and the thickness of the nano-TiO$_2$ film is 4$\mu$m. The measurements of contact angle between nano-TiO$_2$ film and deionized water (DI water) reveal that the nano-TiO$_2$ film is super-hydrophilic when solarized under ultraviolet. The electrode of dye-sensitized solar cell is used as a free-base porphyrin with carboxyl group, 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP) as the sensitizer to adsorb onto the TiO$_2$ thin film. From the results of ultraviolet–visible absorption spectra and XPS analyses of the electrode, the effects of nano-TiO$_2$ particles’ addition to the electrode of dye-sensitized solar cell can improve the absorption of visible light (400–700 nm) and increase electrons transferred from TCPP to the conduction band of TiO$_2$, resulting in the enhancement of efficiency for dye-sensitized solar cells.

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1. Introduction

Recently, a new type of solar cell based on dye-sensitized nano-crystalline titanium dioxide has been developed by Regan and Grätzel [1]. Dye-sensitized solar cells (DSSCs) based on nano-crystalline TiO$_2$ electrodes are currently attracting widespread attention as a low-cost alternative to conventional inorganic photovoltaic devices [2–6]. The function of such devices is based upon the injection of an electron from a photo-excited state of the sensitizer dye into the conduction band of the semiconductor. Using the ruthenium bipyridyl complex as a sensitizer, high quantum efficiencies have been obtained and overall energy conversion efficiencies have been increased to 11% [7]. In addition, Grätzel et al. [8–11] used DSSCs sensitized with N3 (Ru$_{12}$(NC$_5$)$_2$L$_2$, L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) using guanidinium thiocyanate as self-assembly facilitating agent, leading to improvement in efficiency. Some of the cheaper dyes have also been used as sensitizers. Porphyrin species, such as the chlorophyll derivatives and zinc porphyrin complex, have been investigated. These dyes show an efficient sensitive effect due to their strong absorption in the visible region [12–14]. In this study, we synthesized TiO$_2$ nano-particles by the sol–gel method and used these particles to fabricate nano-TiO$_2$ thin films by spin-coating to apply on the electrode of dye-sensitized solar cells. Because ruthenium complex sensitizers are very expensive, we used a free-base porphyrin with carboxyl group, 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP) as the sensitizer of the solar cell. The price of TCPP is about 1/50 of the ruthenium-base sensitizers. The nano-TiO$_2$ thin film electrodes and solar cells were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), contact angle, ultraviolet–visible absorption spectra, X-ray photoelectron spectroscopy (XPS), and current–voltage characteristics analyses in order to investigate the effects of nano-TiO$_2$ particles addition in the electrode on the properties of dye-sensitized solar cells.

2. Experimental

The nano-TiO$_2$ thin films were prepared from Ti(OCl$_4$H$_4$) and C$_2$H$_4$OH as the starting precursors using the sol–gel spin-coating route, as shown in Fig. 1, by adding HCl solution to control the hydrolysis reaction. The purpose of adding deionized water...
(DI water) was to speed up the reaction process. For all samples discussed here, we used ITO-coated glass substrates with a resistivity of 30 $\Omega \cdot \text{cm}. After spin-coating TiO$_2$ onto the ITO glass, the samples were baked in an oven at 100 °C for 10 min and then sintered at 400–700 °C for 30 min in air. When cooling to room temperature, thin films with a TiO$_2$ anatase phase were formed and applied on the electrodes of dye-sensitized solar cells. TCPP was purchased from porphyrin products (Logan, UT) and used without further purification. Titanium tetrabutoxide, ethanol, potassium iodide, iodine, and platinum foil (99.99%) were all purchased from Aldrich. All the organic materials were burned off during this treatment and the electrode appeared pure white. The TCPP electrode was prepared by spin-coating TCPP solution (0.1 M) onto ITO glass and baked in an oven at 100 °C for 10 min. The thickness of the TCPP film is about 10 $\mu$m. The thickness of the TCPP electrode can affect the performance of the dye-sensitized solar cells because this TCPP electrode is without any TiO$_2$ added in and it is more difficult to transfer free electron from the TCPP dye to ITO glass than the TCPP/TiO$_2$ electrode. Indeed, we had tried 5, 8, 10, 12, and 15 $\mu$m and found that the optimal thickness of the TCPP electrode was 10 $\mu$m. To prepare TCPP/TiO$_2$ electrode, we soaked nano-TiO$_2$ films in ethanolic TCPP solution ($3 \times 10^{-4}$ M) for 6 h and baked in an oven at 100 °C for 10 min, and then the TCPP/TiO$_2$ electrode was fabricated. The dye-sensitized solar cell used for photovoltaic measurements consisted of a dye-coated TiO$_2$ electrode, a counter electrode, and an organic liquid electrolyte. The counter electrode was a Pt film sputtered on an ITO-coated glass plate. The I$_3^-$ electrolyte consisted of a mixture of 0.5 M iodides and 0.05 M I$_2$ (Wako Chemical) in acetonitrile (AN, Kanto Chemical) with and without 0.5 M 4-tert-butylpyridine (TBP, Aldrich). The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking. Structural analysis was carried out by powder X-ray diffraction. The surface morphology of the sample was observed using scanning electron microscopy. The contact angle between nano-TiO$_2$ film and DI water was measured by a contact angle measurement machine (VCA-Performa 200). The ultraviolet–visible absorption spectrum of the sample was observed by a UV–Vis spectrophotometer. In order to investigate the binding energy of TiO$_2$ with TCPP added in, X-ray photoelectron spectroscopy was used to observe the variations of the binding energy for TiO$_2$. The current–voltage characteristics of samples were measured by a Keithley 2400 source meter and determined under simulated sunlight with white light intensity $P_L = 25$ mW/cm$^2$. The size of the TiO$_2$ electrodes used was 1 cm$^2$ (1 cm $\times$ 1 cm).

3. Results and discussion

The surface morphology of the nano-TiO$_2$ electrodes was investigated using X-ray and SEM analyses. X-ray diffraction patterns of nano-TiO$_2$ films sintered at various temperatures are shown in Fig. 2. It is found that the TiO$_2$ anatase phase forms while the film is deposited. On increasing the sintering temperature to 600 °C (Fig. 2(d)), a small (110) peak of rutile phase can be observed at 2$\theta$~27.2°. If we increase the sintering temperature to 700 °C, the nano-TiO$_2$ film will turn to rutile phase completely. The best anatase phase of nano-TiO$_2$ can be observed in Fig. 2(d),

![Fig. 1. Sol–gel spin-coating process to prepare nano-TiO$_2$ thin films.](image1)

![Fig. 2. X-ray diffraction patterns of nano-TiO$_2$ films sintered at various temperatures (a) as deposited, (b) sintered at 400 °C, (c) sintered at 500 °C, (d) sintered at 600 °C and (e) sintered at 700 °C.](image2)
although there is a small rutile peak at 2θ ≈ 27.2°. It indicates that the best sintering temperature of the nano-TiO₂ film is 600 °C, at which the particle size 8–10 nm of TiO₂ can be determined by Debye–Scherrer’s equation [15]. The SEM images of the nano-TiO₂ film sintered at 600 °C are shown in Fig. 3. It reveals the highly porous nature of the film, which is consistent with that observed in similar preparations of nano-particulate TiO₂ electrodes [1]. Thickness of the TiO₂ film is about 4 μm, which is seen from Fig. 3 (b).

Fig. 3. SEM images of nano-TiO₂ films sintering at 600 °C (a) surface and (b) cross-section.

Fig. 4 (a) shows the contact angle between nano-TiO₂ films and DI water when solarized under ultraviolet (wavelength = 350 nm). It is found that the contact angle of the nano-TiO₂ film as deposited is ~63° and decreases to 25° while solarized under ultraviolet for 5 min. On increasing the solarized time to 10 min, the contact angle decreases to 5°. A similar result is also observed in the nano-TiO₂ films sintered at 500 and 600 °C. The contact angles decrease from 30° to 3° and from 25° to 3° for the nano-TiO₂ films sintered at 500 and 600 °C, respectively. However, the contact angle of the nano-TiO₂ films sintered at 700 °C is about 16°, and is nearly invariant when solarized under ultraviolet. Fig. 4 (b) shows the absorption spectra of TiO₂ anatase and rutile phases. As shown in Fig. 4 (b), the absorption of the TiO₂ anatase phase under ultraviolet (320–350 nm) is slightly higher than that of the rutile phase. The results of Figs. 4 (a) and (b) indicate that the TiO₂ anatase phase can absorb ultraviolet and turn to super-hydrophilic when solarized under ultraviolet. On the contrary, the contact angle of the film sintered at 700 °C (with TiO₂ rutile phase) is nearly invariant when solarized under ultraviolet. It is noted that the contact angle of the nano-TiO₂ film as deposited is ~63°, and decreases to 30°, 25°, and 16° on increasing the sintering temperature of nano-TiO₂ films to 500, 600, and 700 °C, respectively. This result reveals that heat treatment of the films affects their super-hydrophilicity significantly. It may be due to heat treatment, which changes the morphology of the films, resulting in different properties of films.

The ultraviolet–visible absorption spectrum of TCPP in solution is shown in Fig. 5. It reveals that several absorption peaks are observed at 428 nm for the B band and at 512, 546, 588, and 644 nm for the Q band, which are consistent with the values reported in the literature [16]. In order to prepare the electrode of the dye-sensitized solar cell, we soaked nano-TiO₂ film in TCPP.
solution for 6 h and baked in an oven at 100 °C for 10 min. The absorption spectrum of the TCPP/TiO₂ electrode is also shown in Fig. 5. We can find that the absorption spectrum of the TCPP/TiO₂ electrode from 400 to 700 nm is nearly invariant and is obviously greater than that of TCPP. These results indicate that the effects of nano-TiO₂ particles’ addition in the electrode of dye-sensitized solar cell can improve the absorption of visible light (400–700 nm) for the electrode of dye-sensitized solar cell. It is noted that the absorption spectra of nano-TiO₂ film are from 320 to 350 nm. The increase of absorption spectrum from 400 to 700 nm may be due to the change of energy level for the TCPP/TiO₂ electrode. Figs. 6 and 7 show the X-ray photoelectron spectra (XPS) of the TiO₂ and TCPP/TiO₂ for Ti(2P) and O(1S) regions. XPS is used to distinguish any changes in the binding energy of TiO₂ with TCPP adsorbed on. As XPS is a highly surface-selective technique, it is expected that different forms of surface could be distinguished. Parameters of the XPS peak obtained from the curve fits of Figs. 6 and 7 for Ti(2P₃/₂) and O(1S) are also listed in Table 1. The peaks of TCPP/TiO₂ are shifted to higher binding energies by 0.22 and 0.82 eV for Ti(2P₃/₂) and O(1S), respectively. Wei et al. [3] present that there is a substantial interaction between TCPP and TiO₂, resulting in the increase of electron transfer from TCPP to the conduction band of TiO₂. The increase of binding energy for Ti (2P₃/₂) and O (1S) while TCPP adsorbed on TiO₂ indicates the occurrence of binding or chelating between TCPP and nano-TiO₂, and also provides an evidence for Wei’s report.

The current–voltage characteristics of dye-sensitized solar cells with TCPP and TCPP/TiO₂ electrodes are shown in Fig. 8 and listed in Table 2. Dye-sensitized solar cells with TCPP consists of photo-electrode (TCPP and ITO), electrolyte and counter electrode (Pt coated on ITO). The current–voltage characteristics of samples were measured by a Keithley 2400 source meter and determined under simulated sunlight with white light intensity $P_L = 25 \text{ mW/cm}^2$. We can observe that the short-circuit current density ($I_{sc}$) is 1.91 mA/cm², the open circuit potential ($V_{oc}$) is 0.441 V, the fill factor is 55%, and the efficiency $\eta$ is 1.952% for the dye-sensitized solar cell with the TCPP/TiO₂ electrode. These values are obviously higher than those of the TCPP electrode. From the results of Figs. 5 and 8, and Table 2, the nano-TiO₂ particles’ addition in the electrode can improve the absorption of visible light (400–700 nm) and increase electrons transferred from TCPP to the conduction band of TiO₂, resulting in the enhancement of efficiency for dye-sensitized solar cells. In order to explain this point further, nano-TiO₂ with different particle sizes have been prepared to study the quantum size effect on the properties of the TCPP/TiO₂ electrode and the results will be published elsewhere.

### 4. Conclusions

In summary, we synthesized nano-TiO₂ thin films by spin coating to apply on the electrode of dye-sensitized solar cell and presented the results of X-ray diffraction, scanning electron microscopy, contact angle, ultraviolet–visible absorption spectra, X-ray photoelectron spectroscopy, and current–voltage characteristics analyses. It is noted that the absorption spectrum of TCPP/TiO₂ from 400 to 700 nm is nearly invariant and is obviously greater than that of TCPP. The results of XPS show that the peaks of TCPP/TiO₂ are shifted to higher binding energies by 0.22 and 0.82 eV for Ti(2P₃/₂) and O(1S), respectively.

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<tr>
<th>TiO₂</th>
<th>TCPP/TiO₂</th>
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<tr>
<td>Ti(2P₃/₂)</td>
<td>BE(eV)</td>
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<tr>
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<tr>
<td>O(1S)</td>
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FWHM is the full-width at half-maximum of the reflection.
0.82 eV for Ti(2P3/2) and O(1S), respectively. These results indicate that the effects of nano-TiO2 particles addition in the electrode of dye-sensitized solar cell can improve the absorption of visible light (400–700 nm) and increase electrons transferred from TCPP to the conduction band of TiO2, resulting in the enhancement of efficiency for dye-sensitized solar cell.

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References