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Thin TiO_2 Films Prepared via High-pressure Crystallization for Dye-sensitized Solar Cells

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Well-crystallized thin TiO_2 films were successfully prepared via high-pressure crystallization (HPC). The crystallization temperature of TiO_2 films was significantly decreased to 200 °C using the HPC route. The energy conversion efficiency of the dye-sensitized solar cells with the HPC-derived thin films was low because of the existence of organic residuals. Through UV-irradiation to remove the organic residuals, the energy conversion efficiency of the solar cells was significantly increased.

Dye-sensitized solar cells (DSSCs) composed of TiO_2 electrodes have attracted great attention.[1,2] Different synthesis methods such as sol–gel,[3] the hydrothermal,[4] and thermal hydrolysis routes[5] have been developed to prepare TiO_2 films with satisfactory properties. In the above processes, the prepared TiO_2 powders need to be heated at temperatures higher than 450 °C for obtaining crystallized films. On the other hand, the preparation of flexible DSSCs has become an important topic for new application. Metals and conducting polymers can be used as the substrates for flexible DSSCs.[6,7] The traditional heating processes for TiO_2 films at elevated temperatures are not suitable for flexible DSSCs on polymer substrates. This is because the high temperature will cause the thermal decomposition of polymer substrates.[8] In order to solve the problems for flexible DSSCs, developing a new heating process at low temperatures is necessary.

High-pressure crystallization has been applied to prepare different kinds of thin ceramic films.[9,10] However, there are no reports of using high-pressure crystallization techniques to develop DSSCs. In this study, a high-pressure crystallization (HPC) process was used to prepare crystallized thin TiO_2 films. DSSCs were assembled via adopting the HPC-derived thin films. The photovoltaic performance of the prepared thin films was investigated. The incident photo-to-current conversion efficiency (IPCE) of the HPC-derived films was also analyzed.

Titanium tetraisopropoxide (TTIP) was dissolved in prepared organic solvent composed of 1-pentanol and ethanol with a volume ratio of 10 to 1. The concentration of TTIP was set at 0.2 M. Fluorine-doped tin oxide (FTO) glass was used as the substrates. The substrates were cleaned with ethanol, deionized water, and acetone in series. The prepared solution was coated onto the cleaned substrates using the doctor-blading process, followed by drying at 70 °C for 10 min. The coating process was repeated five times to obtain the desired thickness of thin films. The prepared thin films were treated via HPC to improve the crystallinity of the thin films. Deionized water was used as the solvent in the process. The prepared thin films were loaded into an autoclave without immersion into the solvent. The reaction temperature was set to 200 °C, and the pressure was around 15.8 atm. The treatment duration was 5 h. After the process, the prepared samples were irradiated with ultraviolet (UV) for 10 h to remove residual organics. Films without the HPC treatment were also prepared to compare the results with those of the HPC-treated samples.

The crystallinity of the prepared thin films was examined via X-ray diffraction (XRD) using Cu Kα as the irradiation source. Grazing incident X-ray diffraction (GIXD) was used to study the crystallinity degree at different depths of the prepared thin TiO_2 films. To investigate the energy conversion efficiency of the HPC-derived thin films, the prepared TiO_2 films were immersed into N719 dye for 24 h at room temperature. The solar cells were fabricated by assembling the prepared thin TiO_2 films with the counter Pt electrodes. The electrolyte consisted of 0.5 M KI, 0.05 M I_2, and 0.05 M 4-*tert*-butylpyridine (TBP). The intensity of solar simulation was adjusted to 100 mW cm^{-2} using a standard Si diode. The photovoltaic performance of the prepared cells was measured via a source measure unit (Keithley Model-2400). The incident photo-to-current conversion efficiency (IPCE) was also measured for examining the light-harvesting effects of the prepared thin films.

The XRD pattern of the as-prepared thin films is illustrated in Figure 1a. The XRD peaks at 26.5, 33.8, and 37.8° were identified as the XRD peaks of the FTO substrates. No TiO_2

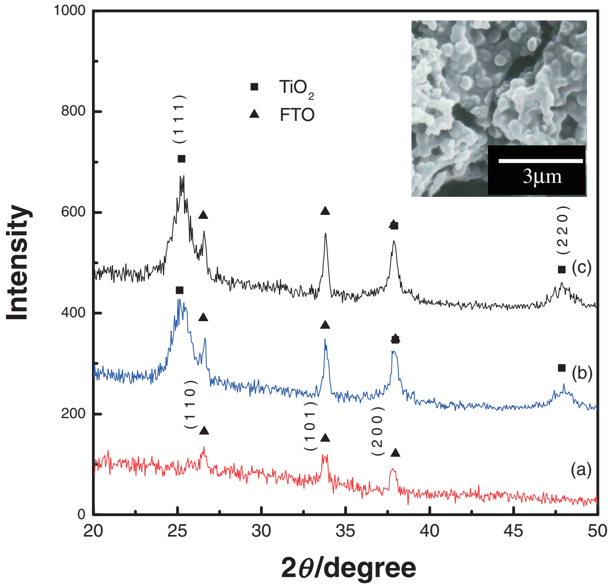

Figure 1. XRD patters of (a) as-prepared thin TiO_2 films, (b) HPC-derived thin TiO_2 films heated at 200 °C, and (c) HPC-derived thin films treated with UV-irradiation. The SEM image of HPC-derived thin TiO_2 films is shown in the inset.

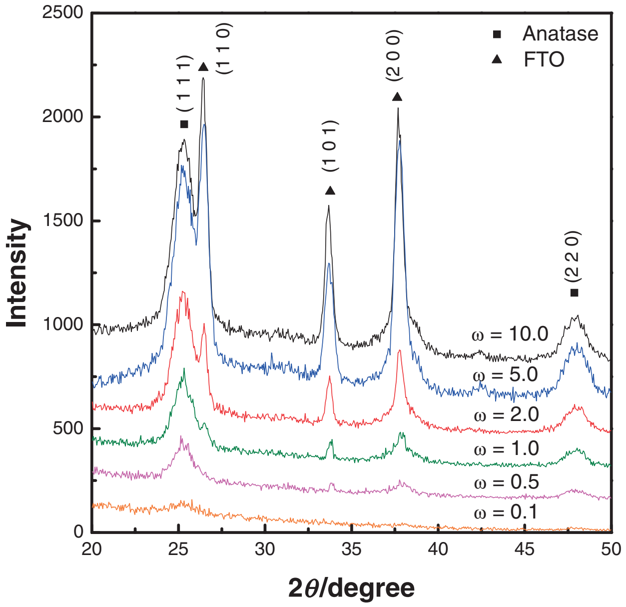

Figure 2. GIXD patterns of the HPC-treated thin TiO_2 films detected at incident angles ranging from 0.1 to 10°.

peaks were found, and this indicated that the as-prepared thin films were amorphous. Figure 1b shows the XRD pattern of the thin films prepared via the HPC process. After the HPC treatment, TiO_2 peaks belonging to the anatase phase were obtained. This reveals that the crystallized TiO_2 films were successfully prepared via the HPC process. The crystallization temperature of thin TiO_2 films prepared via HPC was merely 200 °C, which is much lower than that of thin TiO_2 films heated via traditional heating (around 450 °C). The *d* spacing of (101) was consistent with the data listed in ICDD# 21-1272. The crystal size of the prepared thin films was 1.1605 nm. The XRD pattern of the TiO_2 films treated with UV irradiation after HPC is shown in Figure 1c. The XRD peak intensity did not exhibit significant improvement, indicating that the UV treatment did not affect the crystallinity of the thin films. The SEM image of thin TiO_2 films prepared via HPC at 200 °C is shown in the inset in Figure 1.

Figure 2 illustrates the GIXD patterns of the thin films prepared via HPC at 200 °C. Different detection angles of the X-ray beam for GIXD resulted in different X-ray penetration depths in the prepared films. The X-ray penetration depths are calculated from the detection angles using the following equation[11]

$$D(\omega) = \frac{\mu}{\sin \omega} \qquad (1)$$

where $D(\omega)$ is the X-ray penetration depth, ω is the incident angle of the X-ray beam, and μ is the linear absorption coefficient. When the detection angle is increased, the X-ray penetration depth in the prepared thin TiO_2 films is increased. By varying the detection angles, the crystallinity degree at different depths of the prepared thin TiO_2 films can be examined. When the detection angle was 0.1° (depth: 0.028 µm), only the XRD peaks of TiO_2 belonging to the anatase phase were observed. By increasing the detection angle to 0.5° (depth: 0.141 µm), the XRD intensity of TiO_2 was significantly increased. The (101) peak of the FTO substrates was also found. As the detection angle was further increased, the XRD intensity of TiO_2 was significantly enhanced. This result indicates that the crystallinity on the surface of the HPC-derived thin films was lower than that of the sample near the substrates. During HPC, the organic residuals are evaporated from the surface of TiO_2 films. The evaporation of organic residuals will probably retard the crystallization of TiO_2 films on the film surface. Therefore, the crystallinity of TiO_2 changes along the depth of the films.

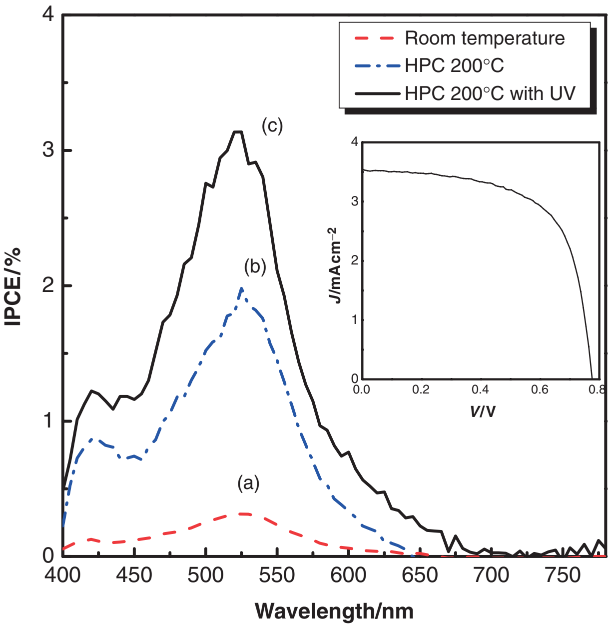

Figure 3. IPCE patterns of the dye-sensitized solar cells for (a) as-prepared thin TiO_2 films, (b) HPC-derived thin TiO_2 films heated at 200 °C, and (c) HPC-derived thin films treated with UV-irradiation. The *I–V* curve of the cells composed of HPC-derived thin TiO_2 films is illustrated in the inset.

Figure 3 depicts the IPCE curves for the thin films prepared under different reaction conditions. The as-prepared thin films had a maximum IPCE value at 525 nm. The IPCE value was zero at incident wavelengths above 650 nm. After HPC, the maximum IPCE was greatly increased by six times. This is because the treatment induced the crystallization of thin TiO_2 films, thereby increasing the electronic conductivity. With the UV-irradiation treatment, the IPCE values were further improved at 525 nm. At the red-light region ranging from 600 to 700 nm, the IPCE performance showed obvious enhancement. This resulted from the removal of organic residuals. The organic residuals show absorption in the red-light region, leading to a decrease in the IPCE performance in the long-wavelength region.[12] Under UV irradiation, the decomposition of organic residual occurred with the photocatalyst reaction of the anatase TiO_2. Hence, the IPCE showed an improvement in the red-light region, and the energy-conversion efficiency was increased. The photovoltaic characteristics of DSSCs for the HPC-treated thin TiO_2 films are shown in the inset in Figure 3. The cell performance was measured as $V_{oc} = 0.776\,V$, $J_{sc} = 3.547\,mA\,cm^{-2}$, and $FF = 0.641$.

In summary, well-crystallized thin TiO_2 films were successfully prepared via high-pressure crystallization (HPC). With the HPC process, the crystallization temperature for the thin TiO_2 films was significantly reduced to 200 °C. The IPCE curve of as-prepared thin films exhibited a maximum value at 525 nm. After the HPC treatment, the IPCE showed significant enhancement. With the UV-irradiation treatment, the IPCE values were further improved by 1.5 times. The cell performance for the HPC-derived thin films was measured as $V_{oc} = 0.776\,V$, $J_{sc} = 3.547\,mA\,cm^{-2}$, and $FF = 0.641$. This indicates that HPC can be applied effectively for preparing TiO_2 electrodes at relatively low temperatures.

References

1 B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
2 C. K. Xu, P. H. Shin, L. L. Cao, J. M. Wu, D. Gao, *Chem. Mater.* **2010**, *22*, 143.
3 S. Lee, I.-S. Cho, J. H. Lee, D. H. Kim, D. W. Kim, J. Y. Kim, H. Shin, J.-K. Lee, H. S. Jung, N.-G. Park, K. Kim, M. J. Ko, K. S. Hong, *Chem. Mater.* **2010**, *22*, 1958.
4 S. Pavasupree, J. Jitputti, S. Ngamsinlapasathian, S. Yoshikawa, *Mater. Res. Bull.* **2008**, *43*, 149.
5 M. Dürr, S. Rosselli, A. Yasuda, G. Nelles, *J. Phys. Chem. B* **2006**, *110*, 21899.
6 J. H. Park, Y. Jun, H.-G. Yun, S.-Y. Lee, M. G. Kang, *J. Electrochem. Soc.* **2008**, *155*, F145.
7 J. Nemoto, M. Sakata, T. Hoshi, H. Ueno, M. Kaneko, *J. Electroanal. Chem.* **2007**, *599*, 23.
8 K. Miettunen, J. Halme, P. Vahermaa, T. Saukkonen, M. Toivola, P. Lund, *J. Electrochem. Soc.* **2009**, *156*, B876.
9 C.-H. Lu, W.-H. Wu, R. B. Kale, *J. Hazard. Mater.* **2007**, *147*, 213.
10 C.-H. Wu, M. Qureshi, C.-H. Lu, *J. Phys. Chem. Solids* **2008**, *69*, 475.
11 T. C. Huang, in *Advances in X-ray Analysis*, ed. by C. S. Barrett, J. V. Gilfrich, T. C. Huang, R. Jenkins, P. K. Prdecki, Plenum Publishing, New York, **1990**, Vol. 33, p. 91.
12 C.-P. Chang, J.-N. Chen, M. C. Lu, *J. Chem. Technol. Biotechnol.* **2004**, *79*, 1293.