Research Article

Electrodeposition and Low-Temperature Post-Treatment of Nanocrystalline SnO₂ Films for Flexible Dye-Sensitized Solar Cells

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SnO₂ porous films were electrodeposited on Ti substrate using pulse-potential technique. These deposited films were dealt with different post-treatments. The effects of the post treatments were investigated through X-ray diffraction, FE-SEM, and Raman spectra. These investigations showed that crystal nanoporous SnO₂ films were obtained through low-temperature post-treatment process. The photoelectric conversion efficiency of the SnO₂ film treated with both the water vapour treatment and ultraviolet illumination was improved to be 0.35% which was comparable with the conversion efficiency of the film sintered at 550°C.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted great scientific and technological interests as photovoltaic devices for their utilization of nontoxic materials, simple preparation process, and high photoelectric conversion efficiency up to 11% [1, 2]. Conventionally, the working electrode was prepared based on the substrate of transparent conductive glass which cannot be bent and tends to be crashed. As a substitute, flexible substrate, such as poly(ethylene terephthalate) coated with indium-doped tin oxide (ITO/PET), has been adopted in the DSCs [3, 4]. The PET substrate is lightweight and flexible, but it cannot withstand the temperature above 150°C. To achieve high-quality nanoporous photoelectrode at low temperature, various methods have been developed, such as hydrothermal synthesis, chemical vapor deposition, physical vapor deposition, and electrodeposition [5–7]. In contrast with other techniques, the electrodeposition method shows many advantages, for example, it is usually carried out below 100°C and can give rigid control on film thickness and composition. The electrodeposited semiconductor oxides show high porosity and fine substrate adhesion. Various metal oxides, such as TiO₂, ZnO, In₂O₃, and ZrO₂, have been successfully electrodeposited [7–10]. During the electrodeposition process, the electrons keep flowing through the nanoporous film. So the electrodeposited film is expected to possess fine electron transport properties even without high-temperature sintering [8, 11].

SnO₂ has been extensively used in gas sensors and lithium ion batteries for its transparent property and high electronic mobility [12–15]. The application of SnO₂ in DSCs has also been reported [16–19]. Generally, the SnO₂ films show low photoelectric conversion efficiency because of the severe charge recombination and low conduction band edge [20, 21]. But these drawbacks could be overcome by the surface coating of other oxides, such as Al₂O₃, ZnO, and MgO [22, 23]. More importantly, highly crystallized SnO₂ could be obtained at low temperature, so SnO₂ should be a kind of suitable photoanode material for flexible DSCs. In this paper, we electrodeposited SnO₂ film and posttreated the film though various processes. Ti foil was selected to be the substrate of nanocrystalline SnO₂ films for the comparison of various post-treatment processes. After the water vapour treatment with HNO₃ and UV light irradiation, the photoelectric properties were comparable with that of the high-temperature-treated electrodes.
2. Experimental

2.1. Preparation and Characterization of SnO₂ Films. The preparation of nanocrystalline SnO₂ films was carried out with a simple three-electrode system. Ti sheet (thickness of 0.1 mm) and Pt sheet were used as working and counter electrode, respectively. The distance between the working electrode and the counter electrode was controlled to be about 3.5 cm. Ag/AgCl electrode with saturated potassium chloride aqueous solution worked as the reference electrode. The electrolyte consisted of 0.05 M SnCl₂·2H₂O and 0.1 M HNO₃. The deposition temperature was fixed at 75°C by an oil bath. The Ti sheet which was used as flexible metal substrate for nanocrystalline SnO₂ film was ultrasonically cleaned in detergent solution, acetone, and deionized water, sequentially. The exposed surface area of the working electrode was about 1.5 cm². Electrochemical deposition experiments were carried out with CHI660C electrochemical workstation (Shanghai Chen-Hua Instrument Co, China). Pulse-potential technique was adopted in the deposition process with a high potential of −0.1 V (versus Ag/AgCl) and a low potential of −0.6 V (versus Ag/AgCl). The pulse time was 10 s and deposition time was 2 h.

The as-grown SnO₂ films were yellow. The films were dried in air and treated as the following process: (1) water vapour treatment in an autoclave with 25 mL deionized water for 12 hours at 150°C (pure water vapour treatment), (2) water vapour treatment in an autoclave with 25 mL 0.3 M HNO₃ aqueous solution for 12 h at 150°C (HNO₃ treatment), (3) UV light irradiation treatment at 258 nm for 20 min after the water vapour treatment with HNO₃ solution (UV-treatment), and (4) sintering at 550°C for 1 h in air. After the post treatment, the electrodeposited SnO₂ films turned to be white.

The crystalline phase of the samples was characterized by X-PertPro X-ray diffractometer with a monochromatized Cu Ka irradiation (λ = 0.154145 nm) and morphologies were determined using HitachiS-4300F field emission scanning electron microscope (FE-SEM). The Raman spectra were measured by a laser Raman spectrometer (Renishaw-1000) at an output power of a 457.5 nm solid-state laser.

2.2. Fabrication and Characterization of Dye-Sensitized Solar Cells. For DSCs fabrication, the samples were immersed in a 5 × 10⁻⁴ mol L⁻¹ ethanol solution of N3 dye for 24 h. A transparent Pt counter electrode was prepared by spreading 5 m mol L⁻¹ H₂PtCl₆ aqueous solution on an FTO glass substrate and pyrolyzed at 390°C for 15 min. The mixture of 0.6 M dimethylpropylimidazolium iodide, 0.1 M iodine, 0.5 M 4-tertbutylpyridine, and 0.1 M lithium iodide in methoxy acetonitrile was selected to be the electrolyte of DSCs.

The photoelectrochemical characteristics of DSCs were measured by the photocurrent-voltage curve (I–V curves) measurement with CHI660C Electrochemical Workstation under the simulated solar light. A 500 W xenon lamp was used as the light source. The incident light intensity was 100 mW cm⁻² measured by a Radiation Meter (FZ-A, Beijing Normal University, China) and the active cell area was 0.25 cm². The electrochemical impedance spectra (EIS) were also carried out with CHI660C. The impedance measurement of DSC was recorded at the open circuit voltage under light illumination over a frequency range of 0.05–1 M Hz with ac amplitude of 10 mV.

3. Results and Discussion

The crystallinity of the SnO₂ film before and after post treatment was investigated by X-ray diffraction which is shown in Figure 1. The electrodeposited SnO₂ film without any post treatment already shows the property of crystalline (shown in Figure 1 curve a), but the reflect peaks are weak and broad. So, it is necessary to deal with the deposited films with post treatments. Here, four different post treatment processes were adopted: water vapour treatment with pure water at 150°C (curve b), water vapour treatment with 0.3 M HNO₃ solution at 150°C (curve c), water vapour treatment with 0.3 M HNO₃ solution at 150°C, and UV-treatment (258 nm) for 20 min (curve d), sintering at 550°C for 1 h (curve e). After water vapour treatment, the diffraction peak intensity of SnO₂ became stronger which indicated the enhancement of crystallinity degree. In addition, the diffraction peak intensity of electrodeposited SnO₂ films treated with HNO₃ treatment and UV-treatment was further improved.

Figure 2 shows FE-SEM images of the SnO₂ films obtained through different post-treatment processes. After pure water vapour treatment, crystal nanoporous SnO₂ film was obtained. But the SnO₂ particles exist in an agglomeration state. The particle size is as large as about 70–100 nm which is disadvantageous for the absorption of dye. With the addition of HNO₃ in the water vapour treatment process, more micropores were formed which facilitated the infiltration electrolyte. At the same time, the particle size of SnO₂ was decreased for the adsorption of more dye molecular. Comparing the FE-SEM images of the other three post-treatments, there was no obvious difference.
Table 1: Performance characteristics of DSCs based on the nanocrystalline SnO2 film under different post treatment processes.

<table>
<thead>
<tr>
<th>Post treatment conditions</th>
<th>J_sc (mA cm(^{-2}))</th>
<th>V_oc (mV)</th>
<th>FF</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water vapour treatment</td>
<td>0.60</td>
<td>329</td>
<td>0.48</td>
<td>0.09</td>
</tr>
<tr>
<td>HNO(_3) treatment</td>
<td>1.11</td>
<td>329</td>
<td>0.62</td>
<td>0.23</td>
</tr>
<tr>
<td>UV-treatment</td>
<td>1.65</td>
<td>340</td>
<td>0.63</td>
<td>0.35</td>
</tr>
<tr>
<td>Calcined at 550°C</td>
<td>4.22</td>
<td>334</td>
<td>0.37</td>
<td>0.52</td>
</tr>
</tbody>
</table>

In order to give more insight into the structural change of the SnO\(_2\) films obtained through different post treatments, Raman spectra are presented in Figure 3. The scattering peak at about 557 cm\(^{-1}\) of the low-temperature-treated films disappeared in the spectrum of the film sintered at 550°C which might be caused by the smaller particle size of the films without high-temperature crystallization process [24]. However, the SnO\(_2\) film treated with pure water vapour shows larger particle size in SEM spectra than that of the high-temperature sintered films. This phenomenon further suggested that the SnO\(_2\) existed as an agglomeration state though small SnO\(_2\) particles were electrodeposited from the electrolyte. The peak at 1600 cm\(^{-1}\) corresponded to the vibration of the OH units absorbed at the surface of SnO\(_2\) nanoparticles which facilitated the absorption of dye [24]. In addition, an extra peak was observed at the frequency of 1045 cm\(^{-1}\) after the HNO\(_3\) water vapour treatment. This new scattering peak should be associated with the interaction of the HNO\(_3\) and SnO\(_2\) nanoparticles. The addition of HNO\(_3\) had made some significant changes for the SnO\(_2\) films.

The SnO\(_2\) films obtained under different post treatment were sensitized with N3 dye and used to assemble DSCs. Figure 4 shows the current-voltage characteristics of the cells under simulated solar illumination (at 100 mW cm\(^{-2}\)) and Table 1 gives the characteristic parameters, that is, open circuit voltage (\(V_{oc}\)), short circuit current (\(J_{sc}\)), fill factor (FF), and overall light to electricity conversion efficiency (\(\eta\)). The SnO\(_2\) films treated with pure water vapour show low \(J_{sc}\) (0.60 mA cm\(^{-2}\)) and fill factor (0.48). With the addition of HNO\(_3\), the \(J_{sc}\) and fill factor were both enhanced to be 1.02 mA cm\(^{-2}\) and 0.64. The improvement of the short circuit might be caused by the increase of surface roughness.

![Figure 2: FE-SEM of the electrodeposited SnO\(_2\) films obtained at different conditions, (a) pure water vapour treatment, (b) HNO\(_3\) treatment, (c) UV-treatment, and (d) calcined at 550°C.](image)
(shown in Figure 3) which permitted more single molecular absorption on the SnO₂ film. The reason was that some SnO₂ nanoparticles might be etched away during the HNO₃ treatment. The enhancement of the fill factor should be related with the better crystallization and desorption of the surface-absorbed water. After the UV-treatment, the j_sc was significantly increased to be 1.65 mA cm⁻². The conversion efficiency was improved from 0.09% of the pure water treated SnO₂ film to 0.35% of the film after UV-treatment which was contributed to the enhancement of the crystallinity (shown in Figure 1). This conversion efficiency was expected to be further increased by the optimization of the water vapour and UV-treatment conditions, such as the water vapour pressure, the concentration of HNO₃, and UV-treatment time. It can be seen that the photoelectric properties of the SnO₂ films is possible to give a comparable performance with the films sintered at 550°C (0.56%) [25].

To further explore the effect of the post treatments on the electron transport performance, electrochemical impedance of these SnO₂ films was investigated. Impedance spectra of these DSCs are shown in Figure 5. Generally, the impedance spectrum of testing cells consisted of three main components, which were attributed to charge transfer at Pt/electrolyte (ω₁), TiO₂/electrolyte (ω₂), and diffusion impedance of I− in electrolyte (ω₃) [26, 27]. The characteristic frequency of (ω₂) could reflect the recombination lifetime (τₑ) of the injected electrons [28]. The characteristic frequencies (f_max) are 25.7, 3.7, 3.1, and 2.1 for the water vapour treatment, water vapour treatment with HNO₃, UV-treatment and high-temperature sintering, respectively. After the water vapour treatment of SnO₂ film in pure water, the electron lifetime should be much shorter than the high-temperature sintered films (according to τₑ = 1/2πfₚₐₓ). But the addition of HNO₃ during the water vapour treatment process improved the electron lifetime significantly. The results might be caused by the interaction of the NO₃⁻ and SnO₂ nanoparticles except for the better crystallization and desorption of

the surface-absorbed water. For the surface cleaning effect of UV-treatment, the electron lifetime was further improved to be almost the same as that of the high-temperature sintered film.

4. Conclusions

SnO₂ porous films were fabricated by electrodeposition at 75°C through pulse-potential technique. These deposited films proceeded with different post treatments. The effects of the post treatments on the SnO₂ film were investigated through X-ray diffraction, FTIR-absorption spectroscopy, FE-SEM, and Raman spectra. The water vapour treatment and UV-treatment are helpful to improve the crystallinity
and to release the surface-absorbed water molecules of the electrodeposited SnO₂ film. With the addition of HNO₃ in the water vapour treatment process, the particle size was decreased and new scattering peak was found in the Raman spectra. The SnO₂ film after the combination treatment of the water vapour treatment with HNO₃ solution and UV-treatment gives a photoelectric conversion efficiency of about 0.35 with open circuit voltage 340 mV, short circuit current 1.65 mA cm⁻², and fill factor 0.63 which are all comparable with the films sintered at 550°C.

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References


