Research Article

Dye-Sensitized Solar Cells Based on Bi$_4$Ti$_3$O$_{12}$

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Abstract

Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) particles were synthesized by hydrothermal treatment and nanoporous thin films were prepared on conducting glass substrates. The structures and morphologies of the samples were examined with X-ray diffraction and scanning electron microscope (SEM). Significant absorbance spectra emerged in visible region which indicated the efficient sensitization of Bi$_4$Ti$_3$O$_{12}$ with N3 dye. Surface photovoltaic properties of the samples were investigated by surface photovoltage. The results further indicate that N3 can extend the photovoltaic response range of Bi$_4$Ti$_3$O$_{12}$ nanoparticles to the visible region, which shows potential application in dye-sensitized solar cell. As a working electrode in dye-sensitized solar cells (DSSCs), the overall efficiency reached 0.48% after TiO$_2$ modification.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted the attention of scientists all over the world because of their relatively high efficiency and low-cost production [1, 2]. In dye-sensitized solar cells, the most important part is the nanoporous electrode made of wideband gap semiconductor for supporting dye molecules and transporting photo-injected electrons. Previous research has been limited to simple binary oxides, including TiO$_2$, ZnO [3], SnO$_2$ [4], Nb$_2$O$_5$ [5], WO$_3$ [6], and In$_2$O$_3$ [7], and so forth. Little attention has been carried out on the ternary oxides, except for SrTiO$_3$ [8] and Zn$_2$SnO$_4$ [9]. However, the multication oxides show more advantages for the tuning of materials’ chemical and physical properties by altering the compositions [10, 11]. It is interesting to investigate the potential applications of new ternary oxides in DSSCs for higher photoelectric conversion efficiency.

Bismuth titanate, Bi$_4$Ti$_3$O$_{12}$, behaves as an n-type semiconductor with an indirect band gap of 3.2 eV [12, 13]. It is an important ceramic material widely studied on its nonvolatile memory, optical memory, piezoelectric, and photocatalytic properties [14–17]. Its photovoltaic properties, however, have scarcely been reported. In the previous work, we have investigated the surface photovoltage response of thin compact Bi$_4$Ti$_3$O$_{12}$ film on fluorine-doped tin oxide conductive glass substrate [13]. In this work, nanoporous Bi$_4$Ti$_3$O$_{12}$ electrode was prepared and sensitized with N3 dye and the photoelectric properties was investigated.

2. Experimental

2.1. Preparation and Characterization of Nanocrystal Bi$_4$Ti$_3$O$_{12}$ Electrode. Bi(NO$_3$)$_3$·5H$_2$O and Ti(OC$_4$H$_9$)$_4$ were used as the bismuth and titanium sources, respectively, for the hydrothermal synthesis of Bi$_4$Ti$_3$O$_{12}$. The two sources were dissolved in glacial acetic acid to form two transparent solutions. A little acetylacetone were added as stabilizer. Then, bismuth nitrate solution was slowly added to the tetrabutyl titanate solution. Eight percent excess Bi(NO$_3$)$_3$·5H$_2$O was added to compensate for the Bi loss during the thermal annealing. After magnetic stirring for 24 hours, sodium carbonate (Na$_2$CO$_3$) aqueous solution was added dropwise to the mixture under vigorous stirring to form a yellow colloid. The mixture was autoclaved at 190°C for 12 h. The resulting precipitates were ultrasonically dispersed and washed thoroughly with deionized water and ethanol successively, then dried at 60°C in an oven. The sample was sintered at 690°C for two hours to form Bi$_4$Ti$_3$O$_{12}$.

Bi$_4$Ti$_3$O$_{12}$ particles were suspended, mixing 0.6 g with 0.1 g of ethylcellulose in 5 mL of 1-butanol. Thin porous
Bi$_4$Ti$_3$O$_{12}$ films were prepared by spreading the suspension onto conducting glass substrates (30 Ω□), followed by heating at 450°C for 30 min in air to eliminate the ethylcellulose. TiO$_2$ coated Bi$_4$Ti$_3$O$_{12}$ was also prepared by adding tetrabutyl titanate to the colloid of Bi$_4$Ti$_3$O$_{12}$ in 1-butanol before the doctor blading process.

The crystalline phases of the samples were characterized by DX-2500 X-ray diffractometer (XRD) with a monochromatized Cu Ka irradiation (λ = 0.154145 nm). The morphologies of the samples were determined using a HitachiS-4300 field emission scanning electron microscope (SEM). The absorption spectrum was measured by a UV-vis-NIR photospectrometer (Varian Cary 5000). To investigate the charge separation behavior at the surface of the samples, the surface photovoltage spectroscopy (SPS) was carried out with a home-built apparatus including a 500 W xenon lamp (CHF XQ500 W), a double-grating monochromator (Zolix SP500), a lock-in amplifier (SR830-DSP), a light chopper (SR540), and so on [18].

2.2. Fabrication and Characterization of Dye-Sensitized Solar Cells. Nanoporous Bi$_4$Ti$_3$O$_{12}$ films were dipped into the 5 × 10$^{-4}$ mol ethanol solution of cis-bis(thiocyanato)-N,N’-bis(2,2’-bipyridyl-4,4’-dicarboxylate) ruthenium (II) (N3 dye) for more than 48 h to absorb enough sensitizer. The counter electrode was Pt foil. 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 DSSCs. The counter electrode and the dye-sensitized Bi$_4$Ti$_3$O$_{12}$ electrode were clamped firmly together. The redox electrolyte solution was introduced into the porous nanocrystalline Bi$_4$Ti$_3$O$_{12}$ film by capillary action.

The photoelectrochemical characteristics of DSSCs were measured by the photocurrent-voltage curve (I-V curves) measurement with an Electrochemical Workstation (Shanghai Chen-hua Instrument Co, China) 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 cm$^2$. The flat band potential was measured by the Mott-Schottky analysis method with the potential range from 0 to 1.0 V [19, 20].

3. Results and Discussion

3.1. Structures and Morphologies. The XRD pattern of the as-prepared Bi$_4$Ti$_3$O$_{12}$ and TiO$_2$ coated Bi$_4$Ti$_3$O$_{12}$ nanoparticles is shown in Figure 1. The samples exhibit well-crystallized perovskite phase of Bi$_4$Ti$_3$O$_{12}$ according to the JCPDS database card number 47-0398. The average particle size calculated is around 56 nm by Scherrer formula. There was no diffraction peak for TiO$_2$ after the coating process.

Figure 2 shows the surface morphology image of the Bi$_4$Ti$_3$O$_{12}$ film (a) and TiO$_2$ coated Bi$_4$Ti$_3$O$_{12}$ (b) in top views. It can be seen that the Bi$_4$Ti$_3$O$_{12}$ film grown on FTO substrates possesses a high degree of porosity which was the key factor to obtain efficient dye-sensitized solar cells. The size of the nanoparticles is in the range of 100–200 nm which is much larger than the XRD result. The thickness of the Bi$_4$Ti$_3$O$_{12}$ film is about 15 μm. After the modification, most of the Bi$_4$Ti$_3$O$_{12}$ nanoparticles were coated with TiO$_2$.

3.2. UV-vis Absorption Spectra. The UV-vis absorption spectra of N3 dye in ethanol solution (curve a), Bi$_4$Ti$_3$O$_{12}$ nanoparticles (curve b), and N3-sensitized Bi$_4$Ti$_3$O$_{12}$ nanoparticles (curve c) are illustrated in Figure 3. The spectrum (curve b) of Bi$_4$Ti$_3$O$_{12}$ nanoparticles exhibits a typical optical absorption behavior of a wide-band gap semiconducting oxide, having an intense absorption band with a steep edge. When N3 dye molecules are adsorbed onto the surface of the Bi$_4$Ti$_3$O$_{12}$ nanoparticles, a new absorption band around 524 nm emerges in the visible region (curve c) compared with that of bare Bi$_4$Ti$_3$O$_{12}$ nanoparticles (curve b) which evidently originates from the absorption of dye molecules. However, the maximum absorption at 500 nm of pure N3 dye is shifted to 524 nm. The red shift might be attributed to the interaction between the dye molecules and semiconductor surface which shows the potential application in dye-sensitized solar cells [21–23].

3.3. Surface Photovoltage Spectroscopy Analysis. In our previous work, it has been found that the Bi$_4$Ti$_3$O$_{12}$ thin compact film exhibited obvious surface photovoltaic response, which is attributed to the electronic transition from the O 2p valence band to the Ti 3d conduction band. Figure 4 shows the SPS spectra of bare and N3 sensitized Bi$_4$Ti$_3$O$_{12}$ nanoparticles. The surface photovoltaic response of the bare Bi$_4$Ti$_3$O$_{12}$ nanoparticles appeared in the wavelength range of 310–420 nm with a maximum at 361 nm. After the absorption of N3, a new SPS response band emerges in the visible region of 420–600 nm, which extends the onset of the surface photovoltaic response of Bi$_4$Ti$_3$O$_{12}$ from 420 to 600 nm. The clear SPV peak indicates that photo-induced electron-hole pairs are easily and effectively separated on the basis of the SPS principle in the visible light.
3.4. Performance of DSSCs. Based on the previous study, application of Bi$_4$Ti$_3$O$_{12}$ film in dye-sensitized solar cells seems to be possible. However, the adsorption of dye on Bi$_4$Ti$_3$O$_{12}$ film is slow. In this study, all the photoelectrode was soaked in the dye ethanol solution at least for 48 h to achieve better dye adsorption. Figure 5 shows the $J$-$V$ characteristics of the DSC based on pure Bi$_4$Ti$_3$O$_{12}$, pure TiO$_2$, and TiO$_2$-modified Bi$_4$Ti$_3$O$_{12}$ nanoporous electrodes. It can be seen that the photoelectrical performance of Bi$_4$Ti$_3$O$_{12}$ is similar with the simple binary oxides, such as TiO$_2$ and ZnO. But the overall light to electricity conversion efficiency is as low as 0.02%. The factors which contribute to the conversion efficiency are short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), and the fill factor ($FF$). The three main parameters are 0.13 mA cm$^{-2}$, 0.38 V, and 0.40, respectively (shown in Table 1.).

To improve the photoelectrical performance of Bi$_4$Ti$_3$O$_{12}$ electrode, the efficient way is coating the photoelectrode with other semiconducting oxide, such as Al$_2$O$_3$, ZnO, and so on [4, 24]. Here, we modified the Bi$_4$Ti$_3$O$_{12}$ film with TiO$_2$ by addition of 5% (a.t.) tetrabutyl titanate to the colloid of Bi$_4$Ti$_3$O$_{12}$ in 1-butanol before the doctor blading process. Remarkable improvements were found in every aspect of short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), and the fill factor ($FF$) (shown in Table 1.). The $J_{SC}$ was improved by nearly seven times. The $V_{OC}$ and fill factor also showed an improvement of 340 mV and 0.29. The overall efficiency reached 0.48%. The Property of the pure TiO$_2$ electrode prepared by the doctor blading of the 1-butanol solution of tetrabutyl titanate was also given in Figure 5. It can be seen that the TiO$_2$ modified Bi$_4$Ti$_3$O$_{12}$ also shows higher
Table 1: Photoelectrochemical parameters of DSSCs using bare and 5 at % TiO₂-modified Bi₄Ti₃O₁₂ nanoporous electrodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( J_{SC} ) /mA cm(^{-2} )</th>
<th>( V_{OC} ) /mV</th>
<th>( \eta ) /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Bi₄Ti₃O₁₂/N₃</td>
<td>0.13</td>
<td>0.38</td>
<td>0.02</td>
</tr>
<tr>
<td>TiO₂/N₃</td>
<td>1.64</td>
<td>0.65</td>
<td>0.53</td>
</tr>
<tr>
<td>Bi₄Ti₃O₁₂/TiO₂/N₃</td>
<td>0.97</td>
<td>0.72</td>
<td>0.48</td>
</tr>
</tbody>
</table>

open circuit voltage than the pure TiO₂ electrode. To explore the causes for the enhancement of the photoelectrochemical properties of DSCs, the dye absorption, flat band potential, and dark current were investigated.

The restriction of charge recombination at the semiconductor/dye/electrolyte interface is an efficient method for the improvement of \( V_{OC} \) and FF of DSSCs [25, 26]. The dark current arises from the reduction of triiodide and oxidized dye molecule by conduction band electrons of semiconductor films [25, 26]. The dark current measurement is an apparent analysis on the interface charge recombination. Figure 6 addresses the dark current for the dye-sensitized solar cells using pure Bi₄Ti₃O₁₂, pure TiO₂, and TiO₂-coated Bi₄Ti₃O₁₂ nanoporous electrodes. The TiO₂-modified Bi₄Ti₃O₁₂ shows lower recombination than pure Bi₄Ti₃O₁₂, and pure TiO₂ which contributes to the elevation of \( V_{OC} \) and fill factor.

The flat band potential (\( V_{fb} \)) of pure Bi₄Ti₃O₁₂, pure TiO₂, and TiO₂-coated Bi₄Ti₃O₁₂ electrode were evaluated through the Mott-Schottky analysis method. This analysis method is based on the capacitance versus applied potential measurement. The relationship between the capacitance and the applied potential can be expressed by the following equation:

\[
\frac{1}{C_{SC}^2} = \frac{2(|V - V_{fb}| - kT/\varepsilon)}{\varepsilon \varepsilon_0 e N_D},
\]

[27] where \( C_{SC} \) is the space-charge capacitance, \( \varepsilon \) is the dielectric constant of the semiconductor, \( \varepsilon_0 \) is the permittivity of free space, \( N_D \) is the dopant density, \( V_{fb} \) is the flat band potential, and \( V \) is the applied potential. Figure 7 shows the Mott-Schottky curves of pure Bi₄Ti₃O₁₂, pure TiO₂, and TiO₂-coated Bi₄Ti₃O₁₂ films. The plot of \( C_{SC}^2 \) versus polarization potential shows an X-intercept corresponding to \( V_{fb} \). The flat band potential of pure Bi₄Ti₃O₁₂ and pure TiO₂ was determined to be about \(-0.58 \) V and \(-0.47 \) V (versus Ag/AgCl). But the \( V_{fb} \) of TiO₂-coated Bi₄Ti₃O₁₂ shifts significantly toward the cathodic potential which should cause the improvement of open-circuit voltage (\( V_{OC} \)) [27, 28].

The amount of dye absorption is one of the important factors on the short-circuit current of DSSCs. The dye absorbed on Bi₄Ti₃O₁₂ electrode is about 1.4E-8 mol cm⁻² which contributes to the low photocurrent. However, no significant change was found in our study before and after TiO₂ coating on the Bi₄Ti₃O₁₂ films. So other controlling process should exist, such as the electron transfer process from excited dye molecular to the conduction band of Bi₄Ti₃O₁₂ and the electron transport process in the Bi₄Ti₃O₁₂ film. Though the overall efficiency of Bi₄Ti₃O₁₂ is severely lower than that of TiO₂, there are many ways to ameliorate the performance for this multication oxide, the variation of the relative Bi/Ti ratio, the partial replacement of Bi or Ti...
by other metal ion. From this work we can conclude that Bi$_4$Ti$_3$O$_12$ film is a potential photoanode material for DSSCs.

4. Conclusions

In conclusion, Bi$_4$Ti$_3$O$_12$ film could be efficiently sensitized with N3 dye. The sensitized Bi$_4$Ti$_3$O$_12$ film shows significant absorbance and surface photovoltaic response in visible light which indicates the emergence of chemical interaction between the dye molecules and semiconductor surface. This ternary oxide exhibited similar photocurrent performance with TiO$_2$. But poor performance was obtained because of the severe charge recombination and lower conduction band edge. After TiO$_2$ modification, the three main parameters short-circuit current ($I_{SC}$), open-circuit voltage ($V_{OC}$), and the fill factor ($FF$) are 0.97 mA cm$^{-2}$, 0.72 V, and 0.69, respectively. The overall efficiency reached 0.48%. Potential improvement can be anticipated by the decrease of the particle size and optimization of the compositions.

Acknowledgments

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