Preparation of Dye Sensitized Solar Cells with high photocurrent and photovoltage by using mesoporous TiO$_2$ particles as photoanode material

Yi Zhang$^{1,2}$, Bao Zhang$^{1,†}$, Xiao Peng$^1$, Lin Liu$^1$, Shuo Dong$^1$, Liping Lin$^1$, Si Chen$^1$, Shuxian Meng$^1$, and Yaqing Feng$^{1,2,†}$ ($\dagger$)

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$^1$School of Chemical Engineering and Technology, China
$^2$Collaborative Innovation Center of Chemical Science and Engineering, China

The DSSCs with mesoporous TiO$_2$ particles as photoanode could show high photocurrent and photovoltage by the unique structure of these materials.

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Author 2, webside 2
Preparation of Dye Sensitized Solar Cells with high photocurrent and photovoltage by using mesoporous TiO$_2$ particles as photoanode material

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1 School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China
2 Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, PR China
*Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China.
Tel./fax: +86 22 27892323.
E-mail addresses: baozhang@tju.edu.cn (B. Zhang), yqfeng@tju.edu.cn (Y. Feng).

ABSTRACT

Several mesoporous TiO$_2$ (MT) materials were synthesized under different conditions following a hydrothermal procedure using Poly(ethylene-glycol)-block-poly(propylene-glycol)-block-poly(ethylene-glycol) (P123) as template and titanium isopropoxide as titanium source. The molar ratios of Ti/P123 and the pH values of reaction solution in autoclave were investigated. Various techniques such as Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), laser Raman spectrometry (LRS), scanning electron microscope (SEM) and high resolution transmission electron microscopy (HRTEM) were used to characterize the products. Then, these materials were assembled into dye sensitized solar cells (DSSCs). The analysis of J-V curves and electrochemical impedance spectroscopy (EIS) were applied to characterize the cells. The result indicated the specific surface area and crystalline structure of materials provided the possibility of high photocurrent for cells, and the structural characteristics of specimen led to the increased electron transfer resistance of cells which was beneficial for the improvement of the photovoltage of DSSCs. The highest photoelectric conversion efficiency of the cells involving MT materials reached 8.33% which, compared to that of P25-based solar cell (5.88%), increased by 41.7%.

1 Introduction

Sunlight is arguably the most abundant clean source of energy that is capable of enabling “indefinite” and sustainable economic growth, with minimum detrimental impact on the environment. Crystalline silicon solar cells have been continuously advancing in efficiency and reducing in cost of fabrication over the last 40 years [1-2], but in most places of the world, they are still expensive compared to the price of electricity generated from fossil fuels [3]. In order to cut the cost of photovoltaic energy, there are many other new solar cell technologies that have attracted considerable attentions, such as dye-sensitized solar cells (DSSCs). DSSC represents an attractive alternative with the advantages of low material costs, simple
manufacture process, desired durability and compatibility with flexible substrates [4-5].

The photoanode material of DSSCs is one of the key factors affecting the photoelectric conversion efficiency. Nanoparticles were conventional and most widely studied for use in DSSCs to form photoanode film [6-7]. However, due to the restriction of characteristics itself, the small size of individual nanoparticles has been regarded as an unfavorable factor that may increase interfacial charge recombination occurring between the photogenerated electrons and the redox species in electrolyte [8-9]. In order to improve the efficiency of solar cells, several semiconductor materials with special morphology were prepared for use in photoanodes. For example, Chen et al. [9] and Diamant et al. [10-11] prepared a series of core-shell nanostructures to decrease the charge recombination based on hypothesis that a coating layer could build up an energy barrier at the semiconductor/electrolyte interface. However, this nanostructure has been proved to be less effective and lack of consistency and reproducibility. One-dimensional nanostructures, such as nanowires [12-13], nanorods [14] and nanotubes [15-16], were synthesized to solve this problem based on a consideration that these materials can provide direct pathways for electron transport from the site occurring electron injection to the conducting film of collector electrode. However, these materials face drawback of insufficient internal surface area, leading to relatively low conversion efficiency. The oxide aggregates, so called three-dimensional nanostructures, are addressed to be a potentially promising structure since it is believed that the aggregates may simultaneously generate light scattering and provide a “highway” for electrolyte diffusion in view of the existence of pores [17-18]. But the surface area of usual aggregates was not obviously higher than that of nanoparticles.

Since 1991, mesoporous materials with high surface area, large pore size and narrow pore size distribution have caused the extensive interest of researchers [19-20]. From the view-points of adsorption, the mesoporous materials can increase greatly the adsorption capacity of dye. Hence, DSSCs assembled using mesoporous TiO₂ materials (denoted as “MT” hereinafter) as photoanode films should show immense potential to improve photocurrent and photoelectric conversion efficiency. And the mesoporous TiO₂ could provide extra channels to transmit light ray besides the stacking mesoporous of traditional scaffold particle. In our studies, a series of MT materials were prepared by a hydrothermal soft-templating method employing different Ti:P123 molar ratios and pH values. The properties of these materials were characterized using XRD, XPS, LRS, BET and HRTEM techniques. For a comparison, DSSCs with newly prepared MT materials and with the commercial P25 as photoanode materials were fabricated via a doctor coating method. The cells were analysed by J-V curves and EIS. The photoelectric conversion efficiencies of these cells were examined and it was shown that the cell performance could be influenced by the characteristics of MT materials. The highest photoelectric conversion efficiency of the cells involving MT materials reached 8.33%. And the photovoltaic results were well explained based on the properties of MT materials.

2 Experimental

2.1. Synthesis of MT materials

The MT materials were synthesized under various conditions (Table 1), since the synthesis conditions of materials were closely related with their morphology [21]. Firstly, to decrease the hydrolysis rate of titanates, 0.05 mol of titanium isopropoxide and an equivalent amount of acetylacetone were transferred into a beaker and stirred at room temperature (RT). Then, an appropriate amount of P123 was dissolved with 100 mL of distilled water (DW) and the concentration of P123 was represented as x wt% in Table 1. After stirring at 40 °C for 12 h, the treated mixed solution was added dropwise to the aforementioned water solution. In the meantime, 1 mol/L of H₂SO₄ solution was used to adjust pH with stirring continually for another 2 h. Finally, the obtained sol was transferred into a Teflon-lined autoclave and hydrothermal synthesis was conducted at 90 °C for 12 h. The products were filtered, washed to neutral and calcined at 550 °C for 3 h. The obtained samples were then denoted as “MT-x-pH” hereinafter.

2.2. Fabrication of DSSC
According to the reported procedure [22-24], the pastes used for fabricating porous films were prepared by mixing 1 g TiO₂, 0.5 g ethyl cellulose (EC), 3.5 g terpineol and 25 g ethanol together. After ball milling for 3 h, the mixture was concentrated using a rotary evaporator to obtain viscous pastes.

FTO was ultrasonically cleaned with soapsuds, distilled water and ethanol, respectively, and then treated with 50 mmol TiCl₄ at 70 °C for 0.5 h. A thin coating was assembled by the pastes on an FTO glass using a doctor blade method, and the film thickness of all samples was 12±2 μm. After dried at 80 °C for 30 min, these samples were annealed at 500 °C for 1 h and then treated with 50 mmol TiCl₄ at 70 °C for 30 min. Another heat treatment proceeded at 500 °C for 30 min. After they were cooled to 110 °C, the films were immersed in an ethanol solution of N719 (3 × 10⁻⁴ M) for 20 h. The final TiO₂ film electrodes were obtained by rinsing these films with anhydrous ethanol and drying them at 100 °C in oven. The photoelectrode was assembled with Pt counter electrode and electrolyte to form a sandwich-type cell. And the injected electrolyte consisted of 0.6 M DMPII, 0.03 M I₂, 0.5 M 4-TBP and 0.1 M GuSCN in acetonitrile and valeronitrile (the volume ratio of 85/15).

2.3. Characterization of synthesized materials

The nitrogen adsorption isotherms of MT materials were measured on a home-made N₂ adsorption apparatus at 77 K [25-26]. Prior to analysis, the samples were treated in vacuum at 200 °C for 2 h. The BET surface area, pore volume and pore size of the samples were calculated by Barrett-Joyner-Halenda (BJH) method via correlative isotherms. Wide-angle powder X-ray diffraction (XRD) investigation was conducted over a PANalytical X'Pert PRO Diffractometer with Cu Kα radiation (λ = 0.15406 nm) and Ni filter at settings of “40 kV, 50 mA”. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (h =1253.6 eV). The X-ray anode was run at 250 W and high voltage was kept at 14.0 kV with a detection angle at 54°. The whole spectra (0~1100 (or 1200) eV) and the narrow spectra of all the elements with high resolution were recorded using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. The effect of surface charging was calibrated via the C 1s binding energy (BE) (284.6 eV) of contaminant carbon.

The laser Raman spectroscopy (LRS) study was performed by single spectrum using a Thermo Fisher DXR Raman Microscope. We select the 50×objective of the confocal microscope together with a laser source of 532 nm at 10 mW in mode laser power at 100%. Ten spectrum signals of 10 s exposure were averaged to improve the signal to noise ratio. Spectra were analyzed using the OMNIC for Dispersive Raman Software. The scanning electron microscope (SEM) images were performed on a Hitachi S4800 electron microscopy operated at 15 kV. The high resolution transmission electron micrograph (HRTEM) images and selected area electron diffraction (SAED) analysis were performed on a Tecnai G2 F20 electron microscopy operated at 200 kV.

<table>
<thead>
<tr>
<th>Synthesis conditions</th>
<th>Physical properties of materials</th>
<th>Calcined sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh sample</td>
<td></td>
</tr>
<tr>
<td>S_BET (m²/g)</td>
<td>V_T (m³/g)</td>
<td>D_a (nm)</td>
</tr>
<tr>
<td>MT-12-0.8</td>
<td>218</td>
<td>242</td>
</tr>
<tr>
<td>MT-12-1.2</td>
<td>247</td>
<td>203</td>
</tr>
<tr>
<td>MT-12-1.6</td>
<td>209</td>
<td>207</td>
</tr>
<tr>
<td>MT-12-2.0</td>
<td>196</td>
<td>131</td>
</tr>
<tr>
<td>MT-8-1.2</td>
<td>232</td>
<td>247</td>
</tr>
<tr>
<td>MT-10-1.2</td>
<td>217</td>
<td>248</td>
</tr>
<tr>
<td>MT-14-1.2</td>
<td>252</td>
<td>211</td>
</tr>
</tbody>
</table>
which were about 4 times larger than fresh P25 nanoparticle [27]. All the average pore sizes (Da) were higher than 2 nm that was the minimum size for mesoporous materials. As reported by Kresge et al. [28], when mesoporous materials were calcined, the $S_{BET}$ of materials decreased as well as the Da increased evidently. Based on comprehensive consideration of $S_{BET}$ and Da, it was indicated that the physical properties of MT-10-1.2, MT-12-1.2 and MT-12-1.6 were more suitable for support of dye molecules.

3.2 XRD and LRS analysis of materials

The $N_2$ adsorption isotherms and the corresponding pore size distributions of fresh MT materials were shown in Fig. 1A. The isotherms of samples synthesized at different conditions could be classified as type-IV isotherm (Fig. 1A), which indicated that these samples were typical mesoporous materials. The maximum of the pore size distribution for MT materials (Fig. 1A(b)) slightly declined with increasing pH and parabolically changed with the rise of concentration of P123, the peak at x = 10. When samples were calcined at 550 °C for 2 h, the isotherms of samples still maintained as type-IV (Fig. 2A). And the property difference among different calcined MT materials was in consonance with fresh materials, which denoted that these samples were high-temperature stable. Table 1 summarized physical properties for both fresh and calcined MT materials prepared at different conditions. For fresh samples, the values of specific surface area ($S_{BET}$) remained more or less at 200 m²/g.
interaction between the TiO$_2$ and ruthenium-based dye molecules, which shows low surface energies, enables the dye molecules to form high density monolayer chemisorption on the particle surface and the electrons in dye molecules to inject into semiconductor highly efficiently. Moreover, according to the analysis of BET, the $S_{BET}$ property of MT-10-1.2 was also excellent relatively. After the samples were calcined in air for 3 h at 550 °C, and then calcined under the same conditions of assembling photoanode, there were still the diffraction peaks of anatase crystal phase and the MT-10-1.2 peak area of (1 0 1) planes was still the largest (Fig. 2B). And the grain sizes of calcined samples increased by about 10 nm. For comparison, the XRD pattern of commercial P25, calcined under the same conditions of assembling photoanode, was also shown in Fig. 2C. Obviously, the FWHM of MT samples were much wider than that of P25, and the grain sizes of MT samples were smaller compared to those of P25.

3.3 SEM and TEM characterization of materials

The calcined samples of P25 and MT-10-1.2 were characterized via RT laser Raman spectroscopy (LRS) as a complementary structural characterization of XRD, and the corresponding structural results were exhibited in Fig. 3. As shown in Fig. 3a, several Raman bands of MT material were observed at about 144, 196, 396, 516, and 638 cm$^{-1}$, which could be assigned to the $E_{g}(1)$, $E_{g}(2)$, $B_{1g}(1)$, $A_{1g} + B_{1g}(2)$, and $E_{g}(3)$ vibration modes of anatase TiO$_2$, respectively [31-32]. For comparison, the Raman spectrum of P25 was also shown in Fig. 3b. It was found that compared with MT material, the LRS band of P25 occurred a slight shift toward red, and the peak height of it was significantly low. According to the report of Zuo et al. [33-34], this phenomenon represented that the P25 particle was smaller and more highly dispersed. Interestingly, the previous analysis of XRD denoted that the grain size of P25 was much larger than MT samples. This difference might originate from the different analysis mechanism for two characterization technique. XRD studied particles with common crystal planes (grains) and LRS analyzed particles by linking of the chemical bond. Therefore, we could reasonably infer that the MT samples were larger particles which formed via smaller grains by bond-linking.

![Figure 3](image_url) Laser Raman spectroscopies (LRS) of calcined (a) MT-10-1.2 and (b) P25.

In order to understand the type of morphology clearly and directly, SEM and HRTEM images of calcined MT-10-1.2 were obtained in Fig. 4. The low power SEM image of MT-10-1.2 (Fig. 4a) showed this sample was monodispersed spherical TiO$_2$ particles. The high power SEM image of MT-10-1.2 indicated that the specimen surface was not smooth, as shown...
in Fig. 4b, and constructed by massive nano-particles, which was in consistent with the analysis of XRD and LRS. In order to assess the internal structure of MT-10-1.2, HRTEM images of sample were measured and revealed in Fig. 4c. It was shown that there were circular holes in this sample and the diameter is approximately 7 nm, which pointed out that the mesoporous structure is present in this sample and the pore size accorded with the analysis of BET. The high power HRTEM images (Fig. 4d) showed the size of the crystal lattices of the sample was found to be approximately 0.353 nm which was similar to the calculated value of SAED fringes (the inset of Fig. 4d) via reciprocity reciprocal. The above results suggested that these crystal lattices belonged to (1 0 1) crystal plane of anatase [4].

3.4 XPS analysis of materials

The elemental states of calcined MT-10-1.2 and P25 could be obtained accurately from the XPS analysis (Fig. 5). As shown in Fig. 5A, the XPS spectra at 458 and 464 eV should be assigned to Ti 2p\(^{3/2}\) and Ti 2p\(^{1/2}\) and the splitting width of 5.8 eV between Ti 2p\(^{3/2}\) and Ti 2p\(^{1/2}\) suggested that the normal state of Ti\(^{4+}\) (TiO\(_2\)) is dominant in all these samples [35]. However, the Ti 2p binding energy in P25 was slightly lower than those of the reported Ti\(^{4+}\) values (458.8–459.3 eV/464.4–464.8 eV), which denoted that a small amount of titanium suboxide species such as Ti\(^{3+}\) (~457 eV/463.1 eV) and Ti\(^{2+}\) (~455.3 eV/461.7 eV) might also exist in these samples [36-37]. It is clear from Fig. 5B that the O 1s peak of MT-10-1.2 can showed the peak appeared at 530.09 eV [38], and that of P25 showed a small shift of 0.18 eV to lower binding energy. As the analysis above, the Ti:O ratio of P25 was greater than that of MT-10-1.2. That is to say, in P25, the oxygen element was encompassed by greater number of titanium element than that in MT-10-1.2 samples, which could decrease the binding energy of O 1s in P25 and result in slightly decreased O 1s peak of it.

3.5 J-V curves of DSSC

![Figure 6](image)

Figure 6 Photocurrent–voltage curves of DSSCs based on different photoelectrode films.

The N-719 sensitized solar cells involving newly prepared mesoporous TiO\(_2\) materials such a MT-12-0.8, MT-12-1.2, MT-12-1.6, MT-12-2.0, MT-8-1.2, MT-10-1.2, MT-14-1.2 and commercial p25 (all in the similar thickness of 12 ± 2 μm and active area of 0.16 cm\(^2\)) as the photoanode films were fabricated. And then, as shown in Fig. 6, the photovoltaic properties of these cells were characterized using sunlight simulator under one-sun illumination, and the step of scanning was 10 mV. The related photoelectric performance parameters and the amount of dye loading for each photoelectrode film are collected in Table 2. It was shown that the dye adsorption of MT films was obviously greater than that of P25 film.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Parameters of photovoltaic performance of cells based on different photoelectrode films.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT-12-0.8</td>
<td>MT-12-1.2</td>
</tr>
<tr>
<td>MT-12-1.6</td>
<td>MT-12-2.0</td>
</tr>
<tr>
<td>MT-8-1.2</td>
<td>MT-10-1.2</td>
</tr>
<tr>
<td>MT-14-1.2</td>
<td>P25</td>
</tr>
</tbody>
</table>

![Table 2](image)
According to the BET results, the $S_{\text{BET}}$ values of MT materials, compared with P25, were much larger, which could provide more sites for the adsorption of dye molecules. And the larger area for the dye adsorption could lead to more “active sites” for photocurrent property of MT films was the common effect of specific surface structure and crystal structure. Furthermore, generally, the DSSC which showed higher photocurrent would exhibit lower photovoltage for similar photoanodes [6]. However, interestingly, the solar cells with MT materials as photoanode, compared with P25 material, revealed higher photocurrent and photovoltage, simultaneously. So some special structural characteristics of MT materials must be suitable for DSSC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$J_{\text{sc}}$ (mA/cm$^2$)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$\Gamma$ (mol/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT-12-0.8</td>
<td>14.45</td>
<td>0.762</td>
<td>66.39</td>
<td>7.31</td>
<td>1.685x10^-7</td>
</tr>
<tr>
<td>MT-12-1.2</td>
<td>15.85</td>
<td>0.747</td>
<td>69.01</td>
<td>8.17</td>
<td>2.082x10^-7</td>
</tr>
<tr>
<td>MT-12-1.6</td>
<td>14.38</td>
<td>0.746</td>
<td>69.82</td>
<td>7.49</td>
<td>1.784x10^-7</td>
</tr>
<tr>
<td>MT-12-2.0</td>
<td>14.15</td>
<td>0.760</td>
<td>68.63</td>
<td>7.38</td>
<td>2.553x10^-7</td>
</tr>
<tr>
<td>MT-8-1.2</td>
<td>16.06</td>
<td>0.740</td>
<td>67.15</td>
<td>7.98</td>
<td>2.181x10^-7</td>
</tr>
<tr>
<td>MT-10-1.2</td>
<td>15.72</td>
<td>0.767</td>
<td>69.09</td>
<td>8.33</td>
<td>2.305x10^-7</td>
</tr>
<tr>
<td>MT-14-1.2</td>
<td>13.99</td>
<td>0.745</td>
<td>67.64</td>
<td>7.05</td>
<td>1.691x10^-7</td>
</tr>
<tr>
<td>P25</td>
<td>11.16</td>
<td>0.739</td>
<td>71.22</td>
<td>5.88</td>
<td>1.412x10^-7</td>
</tr>
</tbody>
</table>

3.6 EIS analysis of DSSC

To further understand the electrochemical and photoelectron transfer processes in our DSSCs, especially to reveal the charge transfer resistance at the interface of conducting layer/TiO$_2$, Pt/electrolyte, dye-coated TiO$_2$/electrolyte and diffusion of the I$_3}$/I$^-$ redox electrolyte, the EIS was performed [39-41]. Fig. 7a shows the typical Nyquist plots of DSSCs and the equivalent circuit model of them was shown in the inset. Two semicircles were observed for the MT-based cells while three semicircles were observed for the cell involving P25 under the measured frequency range of 0.05 Hz-1 MHz. The three semicircles of P25 cell showed the kinetics of electrochemical processes at the FTO/TiO$_2$ interface and the redox reaction occurring at the platinum counter electrode ($Z_\Gamma$), the electron transfer at the dye-coated TiO$_2$/electrolyte interface and the electron transport at the inner of TiO$_2$ photoanode ($Z_\infty$), and the Nernst diffusion impedance ($Z_\infty$), respectively [42].
Table 3 The values of resistances of $R_s$, $R_1$, $R_2$ and frequency at the first peak in Bode plots of each DSSC sample.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_1$ ($\Omega$)</th>
<th>$Y_{OC}$ (S·sec$^2$/cm$^2$)</th>
<th>$\tau$</th>
<th>$R_2$ ($\Omega$)</th>
<th>$\tau_s$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT-12-0.8</td>
<td>8.671</td>
<td>7.86</td>
<td>0.004595</td>
<td>0.8777</td>
<td>27.76</td>
<td>61.2</td>
</tr>
<tr>
<td>MT-12-1.2</td>
<td>9.591</td>
<td>7.906</td>
<td>0.005482</td>
<td>0.8465</td>
<td>25.61</td>
<td>67.7</td>
</tr>
<tr>
<td>MT-12-1.6</td>
<td>9.195</td>
<td>10.08</td>
<td>0.005795</td>
<td>0.8381</td>
<td>25.05</td>
<td>70.6</td>
</tr>
<tr>
<td>MT-12-2.0</td>
<td>9.079</td>
<td>6.582</td>
<td>0.005404</td>
<td>0.8443</td>
<td>31.41</td>
<td>73.1</td>
</tr>
<tr>
<td>MT-8-1.2</td>
<td>9.873</td>
<td>7.893</td>
<td>0.005439</td>
<td>0.832</td>
<td>32.48</td>
<td>74.1</td>
</tr>
<tr>
<td>MT-10-1.2</td>
<td>8.496</td>
<td>6.739</td>
<td>0.005011</td>
<td>0.8534</td>
<td>35.34</td>
<td>67.8</td>
</tr>
<tr>
<td>MT-14-1.2</td>
<td>9.031</td>
<td>8.12</td>
<td>0.005627</td>
<td>0.853</td>
<td>28.41</td>
<td>73.9</td>
</tr>
<tr>
<td>P25</td>
<td>8.113</td>
<td>8.359</td>
<td>0.002636</td>
<td>0.9115</td>
<td>21.55</td>
<td>28.2</td>
</tr>
</tbody>
</table>

Table 3 presented the fitting results of the parameters for the MT or P25-based cells in the light at a bias of DSSCs’ open current voltage (Voc). The resistance elements, $R_s$, $R_1$, $Y_{OC}$, $\tau_s$ and $R_2$ are summarized in Table 3. $R_s$, $R_1$, and $R_2$ represent the resistance of FTO, $Z_1$ and $Z_2$, respectively. The Bode phase plots were shown in Fig. 7b, and the electron lifetimes ($\tau_s$) can be obtained via the conversion of the first peak value in these plots [43]. As shown in Nyquist plots, the diameter of the middle frequency semicircle of the DSSCs based on MT electrodes was much bigger than that of P25-based solar cell. And for MT-based cells, only two arcs in the EIS plot were observed, which is because the middle frequency impedances were great enough to cover low frequency impedances.

According to the report of Liu et al., the middle frequency impedance reflected the electron transport resistance at the inner of TiO$_2$ photoanode which is inversely correlated to the photocurrent of DSSC, and the electron transfer resistance at the dye-covered TiO$_2$/electrolyte interface which is inversely related to electron recombination at this interface [42]. Obviously, as the analysis of $I$-$V$ curves (Fig. 6), the photocurrent of MT-based cells were much greater than that of the P25-cell cells, which indicated that in our systems the electron transport resistance cannot remarkable affect the photoelectric properties of DSSCs. According to the analysis of XRD and LRS, the MT samples were larger particles which formed via smaller grains by bond-linking, which could effectively decrease the grain boundary of TiO$_2$ particles and, thus, increase the electron transfer resistance of cells. And, for DSSCs, the higher electron transfer resistance implied that the degree of electron recombination at the dye-covered TiO$_2$/electrolyte interface was lesser, which maintained the lower concentration of I$^\ast$ nearby photoanode. It is well known that Voc depends logarithmically on the inverse concentration of I$^\ast$ and increases with an incident photon flux $I$.

$$V_{OC} = \frac{RT}{F} \ln(\frac{AI}{n_k[I/F^2] + n_k[D^+]^2})$$

Therefore, as showed in Fig. 6., the MT-based could cells show higher photovoltage. $Y_{OC}$ and $\tau_s$ are the parameter of constant phase element (CPE) of $Z_2$ and $Y_{OC}$ could represent the differential capacity of DSSCs in the case where $\tau_s$ is more than 0.7 [45]. Moreover, as shown in Table 3, the electrical capacitance of MT materials was smaller than the P25 one. Consistent with previous XPS analysis, there is more oxygen vacancies present in P25, which could accept more electrons leading to higher capacity. However, these oxygen vacancies could also work as a “recombination centre” of dark current for DSSCs, which increased the electron recombination and decreased the photovoltage of DSSCs. That is to say, the MT-based cells showed higher photovoltage were the result by common-effect of lesser grain boundary and surface vacancies of MT materials. The Bode phase plots in Fig. 7b showed that the middle frequency peaks of the MT-based DSSCs shift to a lower frequency relative to the P25 cell, which indicated a longer electron lifetime for the MT-based DSSCs. The electron lifetime of the DSSCs based on MT materials was calculated to be in the range 61.2-74.1 ms, which are significantly greater than that the P25 cell (28.2 ms). The structure of MT materials could effectively reduce the grain boundaries of TiO$_2$ particles, and the surface of them exposed less oxygen vacancies, which all could result in the decreased electron recombination and, therefore, increased electron lifetime of cells. In conclusion, compared with the traditional photoanode P25...
material, the structural characteristics of MT materials could afford the DSSCs with greater photocurrent and photovoltage, simultaneously.

4 Conclusions

The MT materials were synthesized by hydrothermal procedure using P123 as template and titanium isopropoxide as titanium source. A series of DSSCs were assembled by using doctor coating methods with these materials. The BET, XRD, LRS, XPS, SEM and HRTEM techniques were employed to characterize the fresh and calcined materials and the $J-V$ curves and EIS were used to analyze the DSSCs. The results showed that the MT materials presented excellent structural properties and the $S_{\text{BET}}$ values of them were even four times higher than that of P25, which could contribute to enhanced photocurrent of cells. XRD analysis showed that the MT materials were pure anatase phase and MT-10-1.2 exposed the most (1 0 1) crystal planes, which was also propitious to enhanced photocurrent of cells. Combined results from XRD and LRS indicated that the MT materials were a series of large particles composed of numerous small nanocrystal grains via connection of chemical bondings. SEM and HRTEM images of samples further verified these studies. This decreased the grain boundary among TiO$_2$ particles and, consistent with the analysis of EIS, indicated that MT-based cells could show higher middle frequency impedances than P25 cells, which leads to increase the photovoltage of cells. XPS results revealed that, for MT materials, the amount of titanium suboxide species was less than that for P25. These titanium suboxide species could increase the amount of “recombination centre” of dark current for DSSCs, which also decreased photovoltage of cells. Overall, compared to P25, The MT-based DSSCs presented higher photoelectric conversion efficiency by increasing photocurrent and photovoltaic, simultaneously. The highest photoelectric conversion efficiency of the cells involving MT materials reached 8.33% which, compared to that of P25-based solar cell (5.88%), increased by 41.7%.

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References


