Increasing the Oxygen Vacancy Density on the TiO₂ Surface by La-Doping for Dye-Sensitized Solar Cells

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Facilitated by TiO₂ particles absorbing La³⁺ in hydrosol, La-doped TiO₂ was prepared by a sol-hydrothermal method. Electron paramagnetic resonance and Brunauer—Emmett—Teller (BET) surface area analysis showed that the obtained La-doped anatase TiO₂ surface provided a higher density of oxygen vacancies without a change in the BET surface area. A theoretical calculation was carried out to explain the generation mechanism of the increased oxygen vacancies. The results showed that the La-doped anatase TiO₂ (101) surface tends to engender oxygen vacancies. The photoelectric conversion efficiency of dye-sensitized solar cells fabricated from 1 mol % La-doped TiO₂ reached 6.72%, which gave an efficiency improved by 13.5% compared with that of the cells fabricated from pure TiO₂. The improvement in the efficiency was ascribed to more dye absorbed on the surface of TiO₂.

1. Introduction

As a promising material for photocatalysis and dye-sensitized solar cells (DSSCs), TiO₂ is excellent for its high efficiency, stability, nontoxicity, and low cost.¹,² Recently, researchers have found that oxygen vacancies are the active sites for water dissociation,³—⁵ as well as an origin of photoactivity under visible light.⁶ In DSSCs, dye molecules anchor themselves on Ti atoms by the carboxyl group.⁷,⁸ Meng and Kaxiras indicated that more oxygen vacancies on the surface of TiO₂ could induce more dye absorption,⁹ thus enhancing the light absorption and then improving the photoelectric conversion efficiency of DSSCs.

There are several methods to increase the oxygen vacancies of TiO₂, such as annealing TiO₂ under a vacuum or reductive ambient,¹⁰,¹¹ electron irradiation,¹⁰ Ar⁺/plasma sputtering,¹² N-doping,¹³,¹⁴ and F-doping.¹⁵ However, these methods are not adaptable for DSSCs. The reasons can be explained as follows. To increase oxygen vacancies, the temperature of annealing is usually higher than 600 °C.¹⁰,¹¹ Such a high temperature induces anatase TiO₂ to transform into rutile TiO₂, which is deleterious for DSSCs.¹⁶ With electron irradiation or Ar⁺/plasma sputtering, it is difficult to penetrate the TiO₂ film, which is usually as thick as 10 µm. Even if the irradiation or sputtering is carried out on TiO₂ powder, the oxygen vacancies will vanish during the annealing process when the TiO₂ powder is fabricated into film. The N/F-doping is also confronted with annealing under high temperature.¹³—¹⁵ Therefore, the traditional ways to increase oxygen vacancies are not applicable to DSSCs.

Doping in TiO₂ at relatively low temperature may be a choice to increase oxygen vacancies on the TiO₂ surface. The sol-hydrothermal method could be an effective way. A chemical bond is an attraction between atoms or molecules. Atoms with stronger chemical bonds to O atoms can be easier to connect to the O atom than those with weaker chemical bonds. The chemical bond energy for Ti—O is 662 kJ/mol. The strength of chemical bonds beginning with the largest are (C—O) 1076 kJ/mol, (B—O) 806 kJ/mol, (Ta—O) 805 kJ/mol, and (La—O) 799 kJ/mol. On the basis of the sol-hydrothermal method, carbon and boron are excluded for their insoluble ion in water and Ta³⁺ is excluded for its instability in water. La³⁺ is not bothered by the above problem. Thus, it may be the most suitable ion for doping by the sol-hydrothermal method. When La³⁺ is doped onto the surface of TiO₂, it will “plunder” oxygen in TiO₂ and oxygen vacancies will be easier to form because the chemical bond strength of La—O is stronger than that of Ti—O. There are many reports that La-doping improved the thermal stability of anatase¹⁷—¹⁹ and decreased the particle size of TiO₂.¹⁷,²⁰ Jing et al. reported that La-doping could increase the amount of oxygen vacancies on the TiO₂ surface.²¹ However, it has not been pointed out whether the increased total amount of oxygen vacancies stemmed from the increased Brunauer—Emmett—Teller (BET) surface area or the increased density of oxygen vacancies. The reason why oxygen vacancies increased has not been explained either. A similar situation appeared in another previous paper.²² On the basis of the above analysis, it is technically desirable to have a strategy to prepare La-doped TiO₂ with a higher density of oxygen vacancies to enhance the dye absorption. Furthermore, the generation mechanism for oxygen vacancies is also highly in demand considering that the mechanism should be of great importance for the design of materials applied in DSSCs, photocatalysis, and other research areas.

In this study, La-doped TiO₂ was synthesized by the sol-hydrothermal method. TiO₂ particles absorb cation in the TiO₂ hydrosol,²³ so La³⁺ could be absorbed on the TiO₂ particle surface and La-doped TiO₂ could be obtained after a sol-hydrothermal process. La-doped TiO₂ provided a higher density of oxygen vacancies without changing the BET surface area. A theoretical calculation was given to explain the generation mechanism for the increased oxygen vacancies.
2. Experimental Section

2.1. Preparation of La-Doped TiO₂. To obtain La-doped TiO₂ nanoparticles, TiO₂ colloid was first synthesized as reported.⁸ Acetic acid (2.11 g) was added to 10 g of titanium isopropoxide. The mixture was stirred at room temperature for 15 min and then poured into 50 mL of deionized water under vigorous stirring. After hydrolysis for 1 h, 1.33 mL of HNO₃ (65 wt %) was added to the mixture and the resulting mixture heated from room temperature to 80 °C evenly in 50 min. Various amounts of La(NO₃)₃ were added to the colloid. The sol was stirred at room temperature for 30 min. Then the resulting mixture was transferred into a 100 mL Teflon-lined autoclave for hydrothermal treatment at 240 °C for 12 h. Following this step, 0.42 mL of 65 wt % HNO₃ was added, and the mixture was treated with an ultrasonic horn for dispersion. Finally, the resulting colloid was triply centrifuged and washed with ethanol to remove HNO₃ and organics, producing about 2.8 g of white precipitate.

2.2. Preparation of Paste. The obtained precipitate was dispersed in 20 mL of ethanol by an ultrasonic horn. Terpinol (13.72 g) and ethyl cellulose (0.8 g) were added to the colloid. The mixture was treated with an ultrasonic horn until it became a stabilized colloid. Finally, the colloid was concentrated with a rotary evaporator for 2 h at 40 °C. Thus, a paste was obtained.

2.3. Preparation of the Electrode. Fluorine-doped tin oxide (FTO) conductive glass (15 Ω/sq) was cleaned by being scoured with a surfactant, treated with ultrasonic washing, and swilled with deionized water. The clean conductive glass substrate was then coated with a thin layer of TiO₂ by immersion in 40 mM aqueous TiCl₄ at 70 °C for 20 min to prevent the short circuit caused by the direct contact between the electrolyte and the FTO. An 80 μm layer of paste was coated onto the substrate using a doctor-blade technique. After being dried at 125 °C in the air, the film was annealed at 450 °C in the air. Another layer of TiO₂ and another layer of paste were coated onto the film again. After being annealed at 450 °C, the film was immersed in 40 mM aqueous TiCl₄ at 70 °C for 20 min again to get better mechanical contact among the TiO₂ nanoparticles. Then the double layer of film was sintered at 500 °C for 20 min in an air flow. When being cooled to 80 °C, the film was immersed into N719 ethanol solution. The counter electrode was a magnetron sputter platinum mirror. The substrate, film, and counter electrode constituted a sandwich-like open cell. The electrolyte was composed of 1.0 M BMII, 50 mM LiI, 30 mM I₂, and 0.5 M tert-butylpyridine in a mixed solvent of acetonitrile and water. When being dried at 125 °C, the film was immersed into 40 mM aqueous TiCl₄ at 70 °C for 20 min again to get better mechanical contact among the TiO₂ nanoparticles. Then the double layer of film was sintered at 500 °C for 20 min again to get better mechanical contact among the TiO₂ nanoparticles. Then the double layer of film was sintered at 500 °C for 20 min again to get better mechanical contact among the TiO₂ nanoparticles.

3. Results and Discussion

3.1. X-ray Diffraction Analysis. The XRD patterns of pure and La-doped TiO₂ are shown in Figure 1 (Figure 1a for wide-angle XRD and Figure 1b for an enlarged view of Figure 1a between 24.0° and 26.5°). Hereafter, TL0, TL0002, TL0005, TL001, and TL002 denote the samples in which the additions of La(NO₃)₃ are 0, 0.2, 0.5, 1, and 2 mol % with respect to the molar concentration of TiO₂. It can be seen from Figure 1a that all the samples exhibit the anatase pure phase (JCPDS 84-1286), which is suitable for DSSCs.⁹ This means that La-doping does not change the phase of TiO₂. No crystalline La₂O₃ phase could be observed from XRD patterns because the amount of dopant is small. The peak at about 25.3° is assigned to the (101) diffraction (Figure 1b). There is no obvious shift for the peak, which indicates that there is no distortion in the TiO₂ lattice. The unchanged lattice parameter of TiO₂ (see Figure S1 in the Supporting Information) illustrates that La does not enter into the bulk lattice of TiO₂. It is induced by the disparity of the radius between La³⁺ (1.03 Å) and Ti⁴⁺ (0.61 Å). The particle size is calculated as 13.3 ± 0.4 nm in [101] and 14.2 ± 0.3 nm in [100] from the (101) peak and (200) peak by Scherrer formulation (see Table S1, Supporting Information). Thus, La-doping does not change the particle size of TiO₂. In summary, La-doping does not change the anatase phase and particle size of TiO₂. Also, La does not enter into the bulk lattice.

3.2. X-ray Photoelectric Spectrum. The La 3d XPS spectrum of TL002 is shown in Figure 2. It can be seen that the spectrum is mainly composed of two doublet peaks distributed near 837 and 853 eV. The peaks at 834.3 and 851.0 eV are ascribed to the main peaks of La 3d⁵/₂ and La 3d³/₂, respectively, and the peaks at 838.4 and 855.1 eV are the shake-up satellite peaks of La 3d⁵/₂ and La 3d³/₂. Compared with the binding energy of La₂O₃ (835.2 eV),⁹ the shift of La 3d⁵/₂ (834.3 eV) to lower binding energy indicates La exists in the form of Ti−O−La.³⁰ In summary, the XPS spectrum illustrates that La exists in the samples in the form of Ti−O−La.
3.3. HRTEM Image. To further clarify the existing form of the doped La, HRTEM was carried out on TL002, as shown in Figure 3. It can be calculated from the image that the spacing between lattices is 0.35 nm, corresponding to the lattice spacing of (101) of TiO$_2$. It can be seen from the image that TiO$_2$ is well crystallized with a clear outline. There is no loaded lanthanum oxide on the surface of TiO$_2$. Neither crystalloid nor amorphous lanthanum oxide can be seen on the surface of TiO$_2$. Thus, La was dispersed uniformly onto the surface of TiO$_2$.

The XRD patterns, XPS spectrum, and HRTEM image illustrate that the La atom does not enter into the bulk lattice of TiO$_2$ but exists in the form of Ti-O-La dispersed uniformly onto the surface of TiO$_2$. All these characterizations together illustrate that the La atom is substituted for the Ti atom in the surface lattice of TiO$_2$.

3.4. Electron Paramagnetic Resonance Analysis. To investigate the effect of La-doping on oxygen vacancies, EPR was carried out at room temperature under UV light illumination, as shown in Figure 4. The signals between 1.998 and 2.012 are ascribed to the electrons trapped by oxygen vacancies on the TiO$_2$ surface.31 The intensity of the signals represents the total amount of oxygen vacancies on the TiO$_2$ surface. It can be seen from the patterns that the signals become stronger as the dopant increases when the dopant is less than 1 mol % but attenuates when the dopant increases to 2 mol %.

For the disparity between the Ti$^{4+}$ radius and La$^{3+}$ radius and the relatively mild sol-hydrothermal synthesis process compared with that of Huo,24 La can only be doped into the exterior or surface lattices. Excessive doping induces the accretion of La on the TiO$_2$ surface, which results in a decrease of oxygen vacancies. To summarize, EPR illustrates that the total amount of oxygen vacancies increases as the dopant increases when the dopant is less than 1 mol %, but it slight decreases when the dopant is elevated to 2 mol %.

3.5. BET Surface Area and Amount of Absorbed Dye Analysis. The increased quantitative oxygen vacancies stem from the increased surface area or increased density of oxygen vacancies on the TiO$_2$ surface. To further clarify the origin of the increased oxygen vacancies, the BET surface area was measured (Table 1). It was found that the BET surface areas of TiO$_2$ without doping and with various amounts of dopant are almost the same (87.5 ± 1.7 m$^2$/g), which is further validated by the nearly unchanged particle size. Thus, the increased oxygen vacancies should stem from the increased density of oxygen vacancies on the surface of La-doped TiO$_2$. The amount of absorbed dye per unit surface area (desorbed from the electrode by NaOH aqueous solution) is also listed in Table 1. It can be seen that the amount of absorbed dye per unit surface area increases, from $2.99 \times 10^{-7}$ to $3.70 \times 10^{-7}$ mol/m$^2$, as the dopant concentration increases when the dopant concentration is less than 1 mol %. However, it slightly decreases when the dopant concentration increases to 2 mol %, which accords well with EPR.

<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>amt of absorbed dye per unit surface area (10$^{-7}$ mol/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL0</td>
<td>85.8</td>
<td>2.99</td>
</tr>
<tr>
<td>TL0002</td>
<td>87.8</td>
<td>3.32</td>
</tr>
<tr>
<td>TL0005</td>
<td>89.1</td>
<td>3.49</td>
</tr>
<tr>
<td>TL001</td>
<td>88.2</td>
<td>3.70</td>
</tr>
<tr>
<td>TL002</td>
<td>88.8</td>
<td>3.40</td>
</tr>
</tbody>
</table>

*a* All the samples show almost the same BET surface area, but TL001 possesses the largest amount of absorbed dye per unit surface area. *b* Desorbed from the electrode by NaOH aqueous solution.
3.6. Theoretical Calculation. To investigate the generation mechanism of the increased oxygen vacancies, for the most ordinary (101) surface of anatase TiO₂, the formation energy of an oxygen vacancy on the surface of pure TiO₂ (Figure 5b) and La-doped TiO₂ (Figure 5d) from the (101) surface of anatase TiO₂ (Figure 5a) and La-doped (101) surface of anatase TiO₂ (Figure 5c) was calculated using the formula:

\[ E_{f[O]} = E_{tot}[O] - E_{tot}[TiO₂,\text{bulk}] - \Delta \mu_0 \]  

(1)

where \( E_{f[O]} \) is the formation energy of an oxygen vacancy, \( E_{tot}[O] \) is the total energy derived from a supercell calculation with one oxygen vacancy in the cell, \( E_{tot}[TiO₂,\text{bulk}] \) is the total energy for the equivalent supercell containing only bulk TiO₂, and \( \Delta \mu_0 \) is the difference in the oxygen chemical potentials. The calculated result is shown in Figure 6. It can be seen that the formation energy of an oxygen vacancy formed from the La-doped TiO₂ surface is lower than that formed from the pure TiO₂ surface in reducing or oxidizing conditions, respectively.

3.7. Photoelectric Performance. Current density–voltage (J–V) curves of five DSSCs under AM1.5 (100 mW/cm²) illumination with an active area of 0.400 cm² are presented in Figure 7. The upper group of curves is measured under AM1.5, and the lower group of curves is measured in the dark. TL001 shows the largest current density.

<table>
<thead>
<tr>
<th>sample</th>
<th>film thickness (µm)</th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA/cm²)</th>
<th>FF (%)</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL0</td>
<td>11.7</td>
<td>0.660</td>
<td>12.7</td>
<td>70.7</td>
<td>5.92</td>
</tr>
<tr>
<td>TL0002</td>
<td>11.4</td>
<td>0.661</td>
<td>13.2</td>
<td>70.3</td>
<td>6.13</td>
</tr>
<tr>
<td>TL0005</td>
<td>11.5</td>
<td>0.650</td>
<td>13.5</td>
<td>71.8</td>
<td>6.30</td>
</tr>
<tr>
<td>TL001</td>
<td>11.6</td>
<td>0.661</td>
<td>14.2</td>
<td>71.3</td>
<td>6.72</td>
</tr>
<tr>
<td>TL002</td>
<td>11.9</td>
<td>0.655</td>
<td>13.4</td>
<td>71.1</td>
<td>6.25</td>
</tr>
</tbody>
</table>

For almost the same film thickness, five cells give almost the same \( V_{OC} \) and FF, but TL001 has the highest \( \eta \) for its largest \( J_{SC} \).
4. Conclusion

In conclusion, La-doped TiO₂ was synthesized facilitated by TiO₂ particles absorbing La³⁺ in the TiO₂ hydrosol. The density of oxygen vacancies on the anatase TiO₂ (101) surface was elevated by La-doping, which increased the amount of absorbed dye per unit surface area. When the dopant concentration was 1 mol %, the photoelectric conversion efficiency of the DSSC reached 6.72%. This efficiency was elevated by 13.5% compared with that of cells without doping. The generation mechanism of the increased oxygen vacancies was also given. The strategy to increase the oxygen vacancy density may be applied in photocatalysis, luminescence, and other research areas.

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Supporting Information Available: UV–vis diffusion reflectance spectra, Ti 2p XPS analysis, lattice parameters, and particle sizes. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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