Preparation and photocatalytic activity of nano-TiO$_2$ codoped with fluorine and ferric

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Abstract: Nano-F$^-$/Fe$^{3+}$/TiO$_2$ particles were prepared by hydrolysis of tetrabutyl titanate in a mixed CF$_3$COOH-Fe(NO$_3$)$_3$-H$_2$O solution. The photocatalytic decomposition of methylene blue in aqueous solution was used as a probe to evaluate their photocatalytic activities. The powders were characterized by X-ray diffraction (XRD), energy dispersion X-ray spectrum (EDS) and Brunauer-Emmett-Teller (BET) surface area analysis. The results show that F$^-$ and Fe$^{3+}$ are doped into TiO$_2$. The F$^-$ and Fe$^{3+}$ doping can help to enhance the nano-TiO$_2$ photocatalytic activity greatly. The appropriate codoping conditions for F-Fe are $n$(F)/$n$(TiO$_2$)=2%, $n$(Fe)/$n$(TiO$_2$)=0.05%, and the degradation rate of methylene blue at 1 h is improved from 73.2% to 87.5%. The codoped nano-F$^-$/Fe$^{3+}$/TiO$_2$ particles have higher BET specific surface area, smaller crystallite size and higher photocatalytic activity than those of undoped TiO$_2$ particles.

Key words: nano-TiO$_2$; F$^-$/Fe$^{3+}$/TiO$_2$; codoping; photocatalytic activity

1 Introduction

Titanium dioxide is widely used as a photocatalyst because of its photochemical stability, non-toxicity and low-cost[1]. However, the low efficiency for the utilization of visible light and recombination between the photogenerated electrons and holes are often two major limiting factors that impede the enhancement of photocatalytic activity. Many studies have been devoted to the improvement of photocatalytic efficiency of TiO$_2$, such as doping metal or non-metal ions[2–4], depositing noble metals[5–6], surface sensitization[7] and composite semiconductor[8–9].

Doping transition metals or non-metal ions are effective method to improve photocatalytic activity of nano-TiO$_2$. XIN et al[10] revealed the mechanisms of photoinduced carriers separation and recombination of Fe$^{3+}$-TiO$_2$ photocatalysts, that is, Fe$^{3+}$ captured the photoinduced electrons, inhibiting the recombination of photoinduced electron-hole pairs. YU et al[11] prepared F$^-$-doped TiO$_2$ powders by hydrolysis of titanium tetraisopropoxide in a mixed NH$_4$F-H$_2$O solution and found that photocatalytic activity of F$^-$-doped TiO$_2$ powders exceeded that of Degussa P25 when the molar ratio of NH$_4$F to H$_2$O was kept in the range of 0.5–3.0.

In this work, F$^-$ and Fe$^{3+}$-codoped TiO$_2$ nanoparticles were prepared from tetrabutyl titanate through sol-gel method, characterized by means of X-ray diffraction (XRD), energy dispersion X-ray spectrum (EDS) and Brunauer-Emmett-Teller (BET) surface area analysis. The photocatalytic activities of the prepared powders were studied following the degradation of methylene blue.

2 Experimental

2.1 Preparation of F$^-$/Fe$^{3+}$/TiO$_2$ nanoparticles

Specimens of F$^-$/Fe$^{3+}$/TiO$_2$ containing different amounts of F$^-$ and Fe$^{3+}$ were prepared by sol–gel method.
10 mL of Ti(OC4H9)4 was added slowly into mixed solution containing 15 mL C2H5OH and 4.5 mL CH3COOH to form solution A. Meanwhile CF3COOH and Fe(NO3)3·9H2O were added into mixed solution containing 4 mL water, 7.5 mL C2H5OH and 4.5 mL CH3COOH to form solution B. Then the solution B was added dropwise into the solution A under vigorous stirring at room temperature. The resulting transparent colloidal liquid was continuously stirred till the gel was formed. The gel was dried at 110 °C for 6 h, calcined at 450 °C for 2 h in air and ground to obtain the F−-Fe3+-TiO2 nanoparticles. The molar ratios of F to Ti are 0 and 2%, and the molar ratios of Fe3+ to Ti are 0, 0.01%, 0.03%, 0.05%, 0.1% and 0.15%.

2.2 Characterization of samples
The XRD patterns obtained on a BRUKER D8-ADVANCE X-ray diffractometer using Cu Kα radiation (λ=0.154 2 nm) at a scan rate of 0.05/s were used to determine the crystal structure and crystallite size. The accelerating voltage and the applied current were 15 kV and 20 mA, respectively. The crystallite size of the anatase was determined by applying Scherrer equation to XRD data. Energy dispersive X-ray spectroscopy (EDS) was recorded on a PHILIP XL-30 ESEM. The BET surface area was determined using a specific surface area analysis meter (Quantachrome NOVA2000).

2.3 Photocatalytic activity measurement
The photocatalytic degradation of methylene blue over photocatalysts was carried out in XPA-Ⅱ photochemical reactor (Nanjing Xujiang Electromechanical Factory). A 500 W high-pressure mercury lamp was used as light source, whose photo intensity was 0.22 kW·m−2 at 365 nm. In each run, 0.05 g photocatalysts were added into 100 mL methylene blue solution of 13 mg·L−1. After premixing for 5 min, the light was turned on to initiate the reaction for 1 h. A 723 spectrometer was used to determine the concentration of methylene blue solution before and after photocatalytic degradation.

3 Results and discussion
3.1 EDS spectrum
The EDS spectrum of the F−-Fe3+/TiO2 sample with molar ratios of F and Fe to Ti of 2% and 0.05% is shown in Fig.1. The EDS spectrum indicates that there are F and Fe elements in the sample, that is, F− and Fe3+ can be doped into TiO2 through hydrolysis of tetrabutyl titanate by using CF3COOH and Fe(NO3)3 as dopant.

3.2 XRD and BET analysis
Fig.2 shows the XRD patterns of TiO2 and F−-Fe3+-TiO2 powders calcined at 450 °C for 2 h: (a) 2%F-0.15%Fe-TiO2; (b) 2%F-0.10%Fe-TiO2; (c) 2%F-0.05%Fe-TiO2; (d) 2%F-0.03%Fe-TiO2; (e) 2%F-0.01%Fe-TiO2; (f) TiO2.

With the increase of Fe-doping concentration, the peak intensities of anatase slightly decrease and the width of plane diffraction peak becomes broader. Therefore, it is reasonable to deduce that the larger the amount of Fe-doping, the poorer the crystallization of TiO2 powders and the smaller the crystallite size of TiO2. The results are the same as those of the BET surface area analysis shown in Table 1. It can be seen that the codoping of F− and Fe3+ can inhibit the growth of TiO2 crystal.

3.3 Evaluation of photocatalytic activity
Table 2 lists the photocatalytic degradation rate of methylene blue over F−-Fe3+-TiO2 photocatalysts with n(F)/n(Ti) of 2% and different Fe3+ dopant contents. F−-doping can convert some Ti4+ to Ti3+ by charge
Table 1 Effects of Fe-doping concentration on physical properties of TiO2 powders with n(F)/n(TiO2) of 2%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystalline size/nm</th>
<th>Surface area/(m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>15.8</td>
<td>92.3</td>
</tr>
<tr>
<td>2%Fe-0.01%Fe₃⁺TiO₂</td>
<td>15.0</td>
<td>98.5</td>
</tr>
<tr>
<td>2%Fe-0.03%Fe₃⁺TiO₂</td>
<td>13.8</td>
<td>110.3</td>
</tr>
<tr>
<td>2%Fe-0.05%Fe₃⁺TiO₂</td>
<td>11.9</td>
<td>123.5</td>
</tr>
<tr>
<td>2%Fe-0.10%Fe₃⁺TiO₂</td>
<td>10.7</td>
<td>130.6</td>
</tr>
<tr>
<td>2%Fe-0.15%Fe₃⁺TiO₂</td>
<td>10.1</td>
<td>138.5</td>
</tr>
</tbody>
</table>

Table 2 Degradation ratio of methylene blue by codoped TiO₂ with different concentrations of F⁻ and Fe³⁺

<table>
<thead>
<tr>
<th>n(F)/n(Ti)%</th>
<th>n(Fe)/n(Ti)%</th>
<th>Degradation ratio of methylene blue%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>73.2</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>76.1</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>84.7</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>87.5</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>82.2</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>75.3</td>
</tr>
</tbody>
</table>

compensation[11–12]:

\[(1-x)\text{TiO}_2 + x\text{F} \rightarrow \text{Ti}_x^3\text{+O}_{2-x}^\text{2—} + x/2\text{O}^{2—}\text{.}\]

Since TiO₂ is an n-type semiconductor, Ti³⁺ in TiO₂ forms a donor level between the band gaps of TiO₂. Ti³⁺ may trap the photogenerated electrons and then reduce the recombination rate of electrons and holes and enhances photocatalytic activity. In the work, the molar ratio of F to Ti is fixed at 2%.

It can also be found that the photodegradation ratio of methylene blue increases with the increase of content of Fe³⁺ dopant. When the content of Fe³⁺-TiO₂ is over 0.05%(molar fraction), the degradation ratio of methylene blue is the highest, which can be attributed to the following reasons. Appropriate amount of the doped Fe³⁺ (≤ 0.05%) in TiO₂ can effectively capture the photoinduced electrons, which inhibits the holes-electrons recombination and induces more photo-generated electrons and holes to participate in the photocatalytic reactions. When the content of Fe³⁺ dopant exceeds 0.05%(atom fraction), it can be seen that the degradation ratio decreases. The reason is that the photocatalytic activity of Fe-doped TiO₂ is strongly dependent on the dopant concentration since Fe³⁺ can serve as not only a mediator of interfacial charge transfer but also a recombination center[10, 13]. In this case, an optimal dopant concentration is 0.05%(molar fraction). Above that concentration, Fe³⁺ steadily becomes recombination center of the photoinduced electrons and holes, which is unfavorable to photocatalytic reactions.

4 Conclusions

1) Nano-F⁻/Fe³⁺/TiO₂ particles are prepared by hydrolysis of tetraethyl titanate in a mixed CF₃COOH-Fe(NO₃)₃-H₂O solution. The EDS spectrum indicates that there are F and Fe elements in the sample.

2) At an optimal concentration of n(Fe)/n(Ti)= 0.05% and n(F)/n(Ti)=2%, the photocatalytic activity of F⁻–Fe³⁺-TiO₂ powders prepared by this method and calcined at 450 °C shows the highest activity. The degradation rate of methylene blue at 1 h is improved from 73.2% to 87.5%.

3) The codoping of F⁻ and Fe³⁺ can inhibit the growth of TiO₂ crystal. Nano-F⁻/Fe³⁺/TiO₂ particles have higher BET specific surface area and smaller crystallite size than those of undoped TiO₂ particles.

References


[10] LIN H, KUMON S, KOZUKA H, YOKO T. Electrical properties of Fe-doped TiO₂ particles prepared by hydrolysis of tetrabutyl titanate in a mixed CF₃COOH-Fe(NO₃)₃-H₂O solution. The EDS spectrum indicates that there are F and Fe elements in the sample.