Photocatalytic degradation glyphosate with cerium and nitrogen co-doped TiO₂ under visible irradiation

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Cerium and nitrogen co-doped TiO₂ nanocrystals were synthesized by a simple sol-gel process, using tetrabutyl titanate as the raw materials with (NH₄)₂Ce(SO₄)₃ and urea as ion donors. The co-doped TiO₂ nanoparticles were characterized by X-ray diffraction and transmission electron microscopy. The photodegradation of glyphosate has been investigated in aqueous suspensions of doped TiO₂ under visible irradiation. The results exhibit a higher thermal stability of anatase than pure TiO₂. The uniform test results show the optimal conditions: n_Ce/n_Ti, n_N/n_Ti and calcining temperature was 0.08, 0.01 and 800°C. The highest degradation rate for co-doped TiO₂ show five times photocatalytic activity of Degussa P₂₅.

Keywords: Cerium; Photocatalytic; TiO₂; Visible light

1. INTRODUCTION

Nowadays, semiconductor oxide photocatalyst such as TiO₂ is gaining attention in the conversion of photon energy into chemical energy [1]. Much more attention has been focused on the treatment of wastewater containing organic pollutants use TiO₂ as photocatalyst with solar as energy [2, 3]. The anatase form of TiO₂ exhibits extensive applications in the degradation of various organic pollutants. However, as the TiO₂ band-gap is 3.2eV, only 4% of the solar radiation reaching the earth surface can be utilized. Developing the new photocatalytic materials working with sunlight as energy sources become an appealing challenge. For reducing the bandgap of available materials, various attempts have been reported, Such as doping with cations or anions or coupling with others materials. Recently, rare earth elements like Ln, Eu and Ce mixed with TiO₂ has been reported excellent activity in the visible region [4-11]. At the same time, nitrogen-doped TiO₂ with electron-deficient structure can extended the useful wavelength to the visible light range [12]. The aim of this work is to investigate the visible light photocatalyst of N, Ce co-doped TiO₂ with glyphosate as groundwater pollutants. The results were compared to the activities obtained with Degussa P25 titanium dioxide as the photocatalyst.

2. EXPERIMENTAL

2.1. Catalyst synthesis

N, Ce co-doped TiO₂ was synthesized by a sol-gel method using (NH₄)₂Ce(SO₄)₃, tetrabutyl titanate and urea as the raw materials. A desired amount of (NH₄)₂Ce(SO₄)₃ and urea was mixed with absolute alcohol. The mixture was slowly dropped into the solution which obtained by dissolving tetrabutyl titanate into absolute alcohol with thoroughly stirring for 2h. The formed gel precipitation was aged at 70°C for 24-48 h until it formed uniform gel. Subsequently, the obtained
gel was heated under different temperature for 2 h. The product of the N, Ce co-doped TiO₂ photocatalysts were obtained. To investigate the effect of preparing conditions, uniform experimental design has been used for the preparation experiments. The Ce-doped initial concentration (x) was chosen as 0.001, 0.002, 0.004, 0.008, 0.01, 0.02, 0.04 and 0.08, which was the mole percentage of Ce⁴⁺ in the oretical titania powder (in Table 1). The obtained corresponding concentration photocatalysts were denoted as sample 1-8.

2.2. Catalyst characterization

The crystal phase of as-prepared photocatalysts were analyzed by powder X-ray diffraction (XRD) pattern using a Shimadzu XRD6000 X-ray diffractometer with Cu-Ka radiation (λ=0.15418 nm) at 50kV and 35mA in room temperature. The structural properties of the as-prepared photocatalysts were analyzed with Transmission electron microscopy (TEM) images which taken on a JEOL JEM-2010 TEM instrument.

2.3. Photocatalytic activity

With extensive use of herbicide in agricultural products, herbicide pollution becomes serious day by day. Glyphosate was selected as a model pollutant to evaluate the photocatalytic activities of N, Ce co-doped TiO₂ and P25 samples. The photocatalytic experiments were carried out under visible light irradiation with glyphosate initial concentration of 50mg/L. A 120W halogen lamp was used as the visible light source of the homemade photoreactor, the short wavelength components (λ< 420 nm) of the light were cut off using a glass optical filter. For a typical photocatalytic experiment, a total of 0.5 g L⁻¹ catalyst powders were added into 250 mL glyphosate solution in beaker with continuously stirring. Prior to irradiation, the suspensions were magnetically stirred in dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium. At given time intervals, about 5mL aliquots were sampled, centrifuged and filtered through a 0.22μm membrane filter to remove the particles. The filtrates were analyzed by National standards (GB 12686—90) using a U-3010 Ultraviolet-visible spectrometer. In order to diminishing the experimental error, we repeated experiment at least three times for the same sample and chose the mean value in our experiment. Moreover, the photocatalytic tests of the same sample concentration are parallel determined at the same time and conditions.

3. RESULTS AND DISCUSSION

The TEM image is shown in Fig. 1. It can be seen that the as-prepared sample has agglomerated, which have mean particle size above 100 nm.

![Fig. 1. TEM image of N, Ce co-doped TiO₂.](image)

However, the image reveals that the sample is consisted of primary particles with an average diameter of 20 nm. Fig. 2, shows the XRD patterns of N, Ce co-doped TiO₂ calcined at 1073 K.
From the figure, we can see that the pattern can be indexed to TiO$_2$ in the anatase phase only. The strongest peak at 25.3 °C, is representative for (101) anatase phase reflections (JCPDS 21-1272). Generally, the phase transformation temperature of anatase to rutile is about 873 K [11]. These results reveal partial N, Ce co-dopants incorporated into the TiO$_2$ network might enhance the thermal stability of the anatase phase and also hinder the growth of crystallite size. In addition, no significant XRD peaks indicative of Ce-species were observed, indicating a high dispersion of the Ce-dopants in TiO$_2$.

![Fig. 2. XRD of N,Ce co-doped TiO$_2$ calcined at 1073 K.](image)

Since the metal ion dopant can act as a mediator of interfacial charge transfer or as a recombination center, the activities of the doped TiO$_2$ are changed. Many factors can affect the efficiency of photodecomposition, such as preparation method, doping concentration, energy level of the dopant within the TiO$_2$ lattice and the distribution of the dopant in the particle. Therefore, the doping concentration has an optimal value. In this work, uniform experimental design in Table 1 was used to investigate the preparation method. The photocatalytic activity was investigated by determining the glyphosate photodecomposition efficiency in 100 min. The preparation conditions (such as $n_{\text{Ce}}/n_{\text{Ti}}, n_{\text{N}}/n_{\text{Ti}}$ and calcining temperature) were denoted as $x_1$, $x_2$, and $x_3$. According to the data in Table 1, regression equations are obtained as Eq.1. Optimal preparation conditions have been accessed by this equation.

**Table 1** Uniform test plan.

<table>
<thead>
<tr>
<th>No.</th>
<th>$n_{\text{Ce}}/n_{\text{Ti}}$</th>
<th>$n_{\text{N}}/n_{\text{Ti}}$</th>
<th>Temperature (°C)</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001</td>
<td>0.08</td>
<td>700</td>
<td>50.00</td>
</tr>
<tr>
<td>2</td>
<td>0.002</td>
<td>0.80</td>
<td>500</td>
<td>41.20</td>
</tr>
<tr>
<td>3</td>
<td>0.004</td>
<td>0.04</td>
<td>300</td>
<td>12.50</td>
</tr>
<tr>
<td>4</td>
<td>0.008</td>
<td>0.40</td>
<td>100</td>
<td>30.00</td>
</tr>
<tr>
<td>5</td>
<td>0.010</td>
<td>0.02</td>
<td>800</td>
<td>66.70</td>
</tr>
<tr>
<td>6</td>
<td>0.020</td>
<td>0.20</td>
<td>600</td>
<td>44.80</td>
</tr>
<tr>
<td>7</td>
<td>0.040</td>
<td>0.01</td>
<td>400</td>
<td>48.90</td>
</tr>
<tr>
<td>8</td>
<td>0.080</td>
<td>0.10</td>
<td>200</td>
<td>27.90</td>
</tr>
</tbody>
</table>

$$y = -82.5107 + 381.87x_1 + 206.99x_2 + 0.377x_3 + 0.237x_1x_3 - 0.567x_2x_3 + 86.499x_2^2 - 0.00024x_3^2$$  \hspace{1cm} (1)

According to the equation and investigation range, the highest degradation rate have reached 99.98% in 100 min when $x_1$, $x_2$, and $x_3$ was 0.08, 0.01 and 800°C, but the degradation rate of Degussa P25 was only 21% at the same reaction conditions. That is to say, the co-doped TiO$_2$ shows five times photocatalytic activity of Degussa P25 (in Fig. 3). The uniform test regression equations analysis reveals that the appropriate increase of the amount Ce dopant and calcination temperature can be beneficial to improve the photocatalytic activity in visible light.
It is generally accepted new impurity level can be formed between the valence band and the conduction band for the pure TiO$_2$ by nitrogen doping and Ce ion doping. New states lie above the valence band or higher in the gap for the substitution nitrogen can be formed by nitrogen doping. At the same time, metal Ce ion doping form new impurity level under the conduction band, so that the electron can be excited from the valence band and the conduction band through the help of impurity level in the visible light region. Forever, the co-doped of nitrogen and Ce ion can inhibit the recombination of the photogenerated electron and hole. So the co-doped can significant improve the photocatatic activity than pure TiO$_2$. But in this work, it was found the increase of nitrogen ion concentration decrease the photocatalytic activity, the probably mechanism lies in recombination efficiency faster or the unsuitable doping concentration. So further experiments are needed.

![Graph](image)

**Fig. 3.** Effect of catalyst on glyphosate degradation.

4- CONCLUSION

Cerium and nitrogen co-doped TiO$_2$ photocatalysts were successfully synthesized by sol-gel process. Ce doping could stabilize the anatase phase of TiO$_2$ and was favorable for the separation of photogenerated electron-hole pairs in this study. Though uniform experimental design and regression analysis, the optimal preparation conditions have been obtained. The optimal synthesis conditions was: n$_{Ce}$/n$_{Ti}$, n$_{N}$/n$_{Ti}$ and calcining temperature was 0.08, 0.01 and 800 °C respectively. Base on this, the co-doped TiO$_2$ shows five times activity of Degussa P25 in glyphosate photocatalytic degradation reactions.

REFERENCES