Preparation and photocatalytic activity of La and Y co-doped nano TiO₂

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Abstract: La and Y co-doped TiO₂ nano photocatalyst (La-Y/TiO₂) was prepared by sol-gel method, and characterized by X-ray diffraction (XRD), specific surface area (BET), scanning electron microscope (SEM) and high resolution transmission electron microscopy (HRTEM). The photocatalytic activity of the La-Y/TiO₂ was evaluated by the degradation of methylene blue (MB) under UV light. Parameters effecting photocatalytic process such as La and Y doping concentration, calcination temperature, the dosage of catalyst and the pH of MB solution were investigated. The co-doped TiO₂ catalyst showed obviously higher photocatalytic activity for the degradation of methylene blue (MB). The presence of La and Y ions in the TiO₂ particles would prevent the recombination of the electron-hole on the surface of TiO₂ effectively.

Keywords: rare earth; photocatalyst; nanometer; TiO₂; methylene blue

1. Introduction

Photocatalytic degradation and complete mineralization of toxic organic compounds in wastewater and air by nanometer semiconductor catalysis has received much attention in the recent years. TiO₂ is considered the most promising photocatalyst due to its high efficiency, excellent physical, chemical stability, nontoxicity, and relative cost. However, the use of TiO₂ is impaired by its wide band gap, which requires ultraviolet irradiation for photocatalysis. Modification of TiO₂ is necessary to enhance the efficiency to enhance the efficiency of TiO₂ photocatalysis and to improve the photocatalytic activity. Using dopants in TiO₂ lattice is one of the methods to reach this goal [1-7]. Some studies indicated that the photocatalytic activity of TiO₂ can be significantly enhanced by doping with lanthanide ions/oxides with 4f electron configurations and the interaction of the functional groups with their f-orbital. Numerous studies of rare earth ions in recently years have been focused on the photocatalytic activities of rare earth elements hosted in crystalline matrices [8-11]. However, two kinds of rare earth metal co-doped TiO₂ and their catalytic properties have seldom been presented so far. In this paper, La and Y co-doped TiO₂ nano photocatalyst (La-Y/TiO₂) was prepared by sol-gel process. The photocatalytic activity of the prepared catalyst was evaluated via the degradation of methylene blue (MB) in the aqueous solution under UV irradiation. Parameters effecting photodegradation process such as variant doping amount, catalyst dosage, calcination temperature, and pH were studied.

2. Experimental

2.1 Materials

Tetra-n-butyloxy titanium [Ti(OBu)₄], La(NO₃)₃, Y(NO₃)₃, acetic acid, absolute ethanol, nitric acid, MB are all analytically pure.

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2.2 Preparations of catalysts

Catalysts were prepared by sol-gel method with following procedure: 34mL Ti(Obu)₄ was dissolved in 44mL absolute ethanol with stirring for several minutes, then 3mL acetic acid was added as suppressant to given solution A. Solution B containing 44mL absolute ethanol, 7.2mL H₂O, and rare earth metal salt in the required stoichiometry was slowly added to solution A. The mixture was hydrolyzed at room temperature for 30min under agitation and a transparent sol was obtained. The gelation was prepared by aging the sol for 24h at room temperature. The gelation was dried at 60℃, then ground to power and calcined at different temperture.

2.3 Characterization of the catalyst

The XRD (X-ray diffraction) patterns were recorded on a PANalytical X’pert Por X-ray diffractometer using Cu Kα radiation as the X-ray source. The diffractograms were recorded in the 2θ range 20~100° in steps of 0.017°.

The specific surface area (BET method), specific pore volume and average pore diameter (BJH method) of the sample were determined by nitrogen adsorption-desorption isotherms using Quantachrome NOVA-2000 sorption analyzer. The samples were analyzed at 77K by nitrogen adsorption-desorption.

The particle size and morphology of La-Y/TiO₂ was observed using high resolution scanning electron microscope (HRSEM) using VEGA TS-5130SB produced by TESCAN Company in Czech. Light source of electron-beam was tungsten lamp, the voltage was 10~30 kV.

2.4 Photocatalytic degradation

The photocatalytic activity of La-Y/TiO₂ was evaluated by degradation of MB. The initial concentration of MB was 20mg·L⁻¹, put a fixed weight of the catalyst. Prior to the irradiation, the reaction mixture was kept in the dark for 20min to ensure sufficient adsorption of the MB. The mixture was then irradiated with UV light of 125W Hg lamp in a pyrex cylindrical photo reactor. The samples were collected at regular intervals of time and concentration changes of MB solution were measured using a UV-vis spectrometer at 665nm (λmax). The activity of catalyst was evaluated by the decolor rate (D) of the samples. The equation of the decolor rate followed

\[
D = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%
\]

Where D is the decolor rate, A₀ is the initial absorbance of MB and Aₜ is the absorbance of MB after ‘t’ minutes.

3. Results and discussion

3.1 Characterization of the photocatalysts

XRD patterns of nano TiO₂ (prepared by sol-gel method), La-TiO₂ (dopant of La is 0.005mol), La-Y/TiO₂ (the dopant of La is 0.005mol and the dopant of Y is 0.008mol) calcined at 600℃ are shown figure 1. The pattern of TiO₂ corresponds to both anatase and rutile phase but the former is the predominant one. The XRD patterns of La-TiO₂ and La-Y/TiO₂ indicate the anatase phase. It can be seen from figure 2 that the peak intensity of anatase increases with the increase of calcination
temperature from 400°C to 900°C, and the width of (101) plane becomes narrow. The rutile phase appears at 900°C for La-Y/TiO₂, the phase transformation to rutile but the anatase phase was dominant up to 900°C. Thus the dopant is expected to play a significant control in the selective crystallization of anatase phase during sol-gel process [12]. Further, among the two main kinds crystalline of TiO₂, anatase is proved to exhibit higher photocatalytic activity. The anatase phase also exhibits low rate of recombination in comparison to rutile due to its ten-fold greater rate of hole trapping [13].

![Figure 1 XRD patterns of TiO₂, La-TiO₂, La-Y/TiO₂ calcined at 600°C](image1)

![Figure 2 XRD patterns of La-Y/TiO₂ calcined at different temperature](image2)

![Figure 3 Nitrogen adsorption-desorption isotherm La-Y/TiO₂](image3)

![Figure 4 Pore size distribution plot of La-Y/TiO₂](image4)

The nitrogen adsorption-desorption isotherm and the pore size distribution plot of the La-Y/TiO₂ can be seen in the figure 3, figure 4 respectively. The nitrogen adsorption-desorption isotherm was characteristic of a type Langmuir IV isotherm with a H2 hysteresis loop. The pore size distribution calculated from the desorption branch of nitrogen isotherm by BJH method, which indicated that the pore diameter of the sample was about...
3-7nm, the pore volume was 0.127 cm$^3$ g$^{-1}$ and the BET specific surface area of the sample was 102 m$^2$ g$^{-1}$. These pores may allow rapid diffusion of MB molecules during photocatalytic reaction, and also enhance the adsorption of MB and its intermediates on nano La-Y/TiO$_2$ surface.

**Figure 5** SEM of La-Y/TiO$_2$  
**Figure 6** HRTEM of La-Y/TiO$_2$ calcined at 500 ℃ (a) and 900 ℃ (b)

Morphology of the La-Y/TiO$_2$ catalyst was determined by SEM (figure 5) and HRTEM (figure 6) pictures. SEM and HRTEM pictures confirmed that the La and Y co-doped nano TiO$_2$ particles are spherical with an average grain size of 50-70nm. Further, the HRTEM micrographs in figure 6 characterized the surface morphology of the sample. It is observed that the sample is consist of good crystallized area of nanosized La-Y/TiO$_2$. The HRTEM picture of La-Y/TiO$_2$ calcined at 900 ℃ showed that many small particles deposit over nano TiO$_2$ surface, and these tiny particles may be La$^{3+}$ and Y$^{3+}$. This is quite reasonable as the ionic radius of La$^{3+}$ and Y$^{3+}$ is larger than Ti$^{4+}$. So it can prevent the recombination of the electron-hole on the surface of TiO$_2$ effectively.

### 3.2 Photocatalytic degradation

**Figure 7** Effect of calcination temperature  
**Figure 8** Effect of La and Y dopant amount
The efficiency of MB photodegradation as a function of operating parameters is shown in figure 7-10. To study the effect of catalyst structure on photodegradation, the sample should be calcined at different temperature that shows different crystal structures. It can be shown from figure 7 that the highest degradation is achieved with the sample calcined at 600°C, and the peak intensity of anatase increases and the width of (101) plane becomes narrow. The anatase structure has a better photocatalytic activity[14]. The catalytic activity of La-Y/TiO\textsubscript{2} declined when calcining temperature rise 900°C where the rutile structure formed, but the decolor rate of MB still can reach 78% after irradiation 120 min with 125W Hg lamp. So the doping La and Y can enhance the stability of the catalyst.

Figure 8 shows the effect of La\textsuperscript{3+} and Y\textsuperscript{3+} dopant concentration on MB photodegradation. For a solution containing initially 20mg/L MB after 120 min UV irradiation, the photocatalytic degradation efficiency of La-Y/TiO\textsubscript{2} is higher than P-25 and La-TiO\textsubscript{2}. The degradation efficiency increase with increasing Y concentration and a maximum of 100% is obtained with sample containing 0.005mol La\textsuperscript{3+} and 0.008mol Y\textsuperscript{3+}, a further increase in Y\textsuperscript{3+} concentration to 0.01mol leads to a slight decrease in degradation efficiency to 99%. As the content of doping ions increases, the surface barrier becomes higher, and the space charge region becomes narrower. The electron-hole pairs within the region are efficiently separated by the large electric field before recombination which led to the higher photocatalytic activity. However, when the content of doping ions is excessively high, the space region becomes very narrow and the penetration depth of the light into TiO\textsubscript{2} greatly exceeds the space charge layer[15], therefore the recombination of the photo-generated electron-holes pairs becomes easier, which leads to lower photocatalytic activity for MB degradation. Otherwise, the La\textsuperscript{3+} an Y\textsuperscript{3+} co-existence leads to a synergistic effect.

The effect of the dosage of La-Y/TiO\textsubscript{2} on MB degradation is illustrated in figure 9. It is expected that MB degradation increases with increasing the dosage of La-Y/TiO\textsubscript{2} (the dopant of La is 0.005mol; the dopant of Y is 0.008mol), and reaches a maximum of 100% at a dosage of 0.2g/50mL. However, a further increase in catalyst dosage slightly reduces the photodegradation efficiency. It is known that the photodegradation rate of the solution is
affected by not only the active sites but also the photo-absorption of the catalyst. Adequate dosage of the photocatalyst increases the generation rate of electron-hole pairs for enhancing photodegradation, but a high dosage of the photocatalysts will decrease the light penetration by the suspension and reduce the degradation rate[16].

Solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic degradation reactions. It influences adsorption and dissociation of the substrate, catalyst surface charge, oxidation potential of the valence band and other physico-chemical properties[17]. The effect of solution pH on MB degradation is illustrated in figure 10. It can be seen that the highest photocatalytic activity can be reach when the pH of MB solution is 11, the high degradation rate in the alkaline pH range due to the MB is cationic dye, the catalyst surface has negative charge in the alkaline condition, which benefit to absorption of MB.

4. Conclusions
La-Y/TiO₂ nano photocatalyst was prepared via an acid-peptized sol-gel method. Particles that were annealed at 600°C revealed the highest MB photodegradation efficiency, primarily because of the anatase structure. When La³⁺ and Y³⁺ doped 0.005 mol and 0.008 mol respectively in 1 mol TiO₂, the photocatalyst has the highest activity, the decoloration rate of MB can reach 100% in irradiation time 120 min with 20 mg catalyst and 125W Hg lamp. The photodegradation efficiency is higher than La-YiO₂ and P-25 in the same conditions.

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