Preparation of Eu-doped TiO_2 Photocatalyst by Microwave Hydrothermal Method and its Photocatalytic Activity

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Abstract: In order to improve the photocatalytic activity of TiO_2, many methods have been explored to cope with the problem of wide band gap of TiO_2. The doping of rare earth elements is a hot topic in recent research. The rare earth europium has great potential in improving the photocatalytic activity of TiO_2. It can not only extend the absorption region of TiO_2 to the visible range, but also increase the transformation temperature of crystal form in TiO_2 (i e, anatase to rutile). In addition, the europium has a special electronic layer structure which can form a complex with a large amount of Lewis base, which obviously increases the electron transfer between the surface of TiO_2 and the contaminant [1-3].

1. Introduction

The Eu-doped TiO_2 nanomaterials were prepared by microwave assisted sol-gel method by Khade [4]. The degradation of methyl orange by TiO_2-Eu under ultraviolet light and visible light was studied. The degradation of methyl orange by Eu-TiO_2 and pure TiO_2 under ultraviolet light was 98% and 81%, respectively. Due to the high absorption of rare earth ion Eu and the transition of 4f electrons, the degradation efficiency of Eu-doped TiO_2 was improved by 17% (relative to 17%. Pure TiO_2). Song [5] synthesized rare earth doped TiO_2 nanorods (TiO_2-RE NRs) as photocatalysts and degraded lignin under sunlight. It was also proved that TiO_2-Eu NRs is one of the best materials for degrading methyl orange by using methyl orange as a probe molecule, and the rate constant is 4.2×10^{-3} $s^{-1.}$ In this paper, the rare earth metal element Eu-doped TiO_2 photocatalyst TiO_2-Eu was prepared by microwave hydrothermal method. The simulated water was simulated by methyl orange solution. The photocatalytic activity of Eu-doped TiO_2 photocatalyst prepared under microwave hydrothermal conditions was investigated.

2. Experiment

2.1. Main Reagent.

Tetra-n-butyl titanate (AR, Sinopharm Chemical Reagent Co. Ltd.); Bismuth nitrate hexahydrate $Eu(NO_3)_3\cdot6H_2O$ (AR, Aladdin reagent); Anhydrous ethanol (AR, Tianjin Sailboat Chemical Reagent Technology Co. Ltd. Company); Concentrated nitric acid (CP, Shanghai Chemical Reagent General Plant); Methyl orange (AR, Sinopharm Chemical Reagent Co. Ltd.); Ultrapure water (homemade).

2.2. Preparation of Catalyst and Photocatalytic Activity Test.

Take a quantitative amount of 4.40 mL of tetra-n-butyl titanate and 17.50 mL of absolute ethanol, and stir for 10 min to obtain solution A. The quantitative europium nitrate is dissolved in 18.00 mL of dilute nitric acid (pH=2~3) and added dropwise to A. The B solution formed in the liquid is magnetically stirred for 10 minutes, and then placed in a microwave water-heat parallel synthesizer for a certain period of time to obtain a TiO_2 sol, which is filtered, dried, milled, and calcined in a

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muffle furnace to obtain a TiO_2-Eu photocatalyst. The bottling is placed in a desiccator for use. The photocatalytic activity test method of the catalyst is detailed in the literature [6, 7].

2.3. Catalyst Structure Testing and Characterization.

The X-ray diffraction (XRD) pattern of the photocatalyst, the B diffractometer, and the Cu-Kα radiation were collected in a region of 2θ = 15-80° using Rigaku Giegerflex D / Max. The instrument used for X-ray photoelectron spectroscopy (XPS) is a 250 XI ESCA system, a MgKα X-ray source (1253.6 eV), and a vacuum pressure <10-6 Pa. A C1s with a combined energy of 284.6 eV is used for the charge correction reference. Fourier transform infrared (FTIR) spectroscopy was recorded with a Magna-IR 750 spectrometer at a resolution of 1 cm^{-1} using KBr particles in the range of 4000-400 cm^{-1}.

3. Results and Discussion

3.1. Effect of Eu Doping Amount on Photocatalytic Activity of TiO2-Eu.

Change the Eu doping amount [n(Eu^{3+}): n(Ti^{4+})=0.02%, 0.04%, 0.06%, 0.08%, 0.1%, 0.12%] to prepare a TiO_2-Eu photocatalyst in order to investigate the Eu doping amount. The effect of TiO_2-Eu photocatalytic activity is shown in Figure 1. It can be seen from Fig. 1 that when the Eu doping amount n(Eu^{3+}):n(Ti^{4+})=0.08%, the degradation rate of the prepared TiO_2-Eu to methyl orange reaches a maximum value of 96.7%, and a small amount or an excess of Eu will be Reducing the photocatalytic activity of TiO_2-Eu, it is clear that there is an optimal doping amount in the experiment of Eu-doped modified TiO_2 to improve its photocatalytic activity.

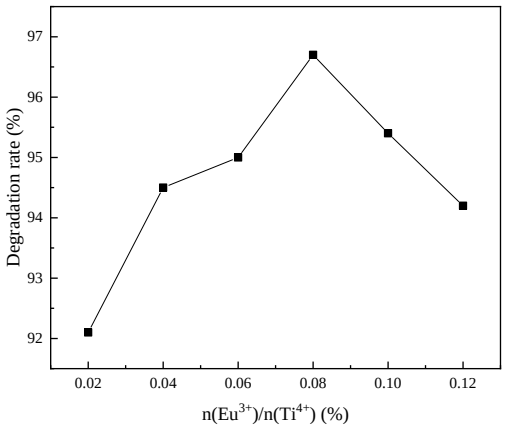

Figure 1. Effect of Eu doping amount on photocatalytic activity

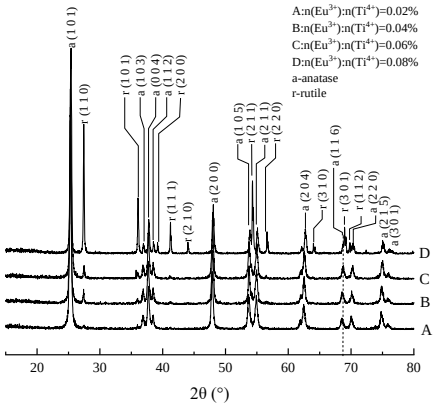

Figure 2. XRD spectrum of TiO_2-Eu prepared by different Eu doping amounts

Fig. 2 is an XRD spectrum of TiO_2-Eu prepared by different Eu doping amounts. It can be clearly observed from Fig.2 that the {110} crystal plane diffraction peak of rutile (PDF-#21-1276) appears at 27.384° in the B, C, and D lines. Obviously, low concentration of Eu does not inhibit TiO_2. The growth of rutile; therefore, the low doping amount of Eu is not conducive to the photocatalytic activity of TiO_2. The high doping amount of Eu reduces the photocatalytic activity of TiO_2, which may be caused by the oxide of Eu covering the surface of TiO_2, resulting in the reduction of the effective specific surface area of TiO_2 photocatalyst[8], which in turn affects the photocatalytic activity of TiO_2.

3.2. Effect of Calcination Temperature on Photocatalytic Activity of TiO2-Eu.

The calcination temperature mainly affects the growth of TiO_2 crystals and the transformation between crystal forms. For TiO_2, there are mainly changes of amorphous TiO_2 to anatase TiO_2 to rutile TiO_2. Different calcination temperatures can lead to the presence of TiO_2. Different crystal forms [9], and the effect of different crystal forms on the photocatalytic activity of TiO_2 is significant.

The TiO_2-Eu photocatalyst was prepared by changing the calcination temperature (500, 550, 600, 650, 700 °C, respectively) to investigate the effect of calcination temperature on the photocatalytic activity of TiO_2-Eu. The results are shown in Figure 3, at 500~700 °C. In the range of 500~700 °C, the photocatalytic activity of TiO_2-Eu increases first and then decreases with the increase of temperature. The degradation of methyl orange by TiO_2-Eu prepared at 600 °C can reach 96.7%. It also shows that high temperature calcination requires a suitable temperature to optimize the photocatalytic activity of TiO_2-Eu.

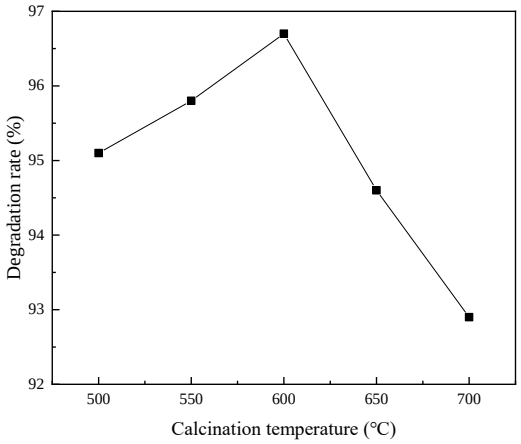

Figure 3. Effect of calcination temperature on photocatalytic activity of TiO_2-Eu

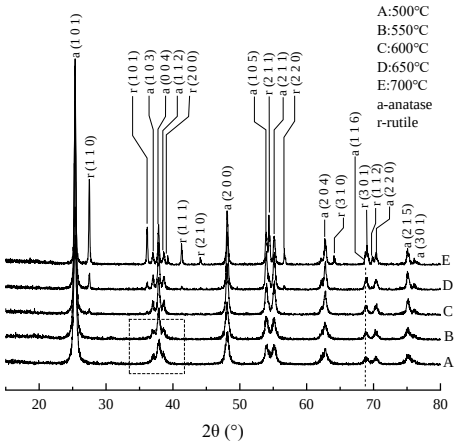

Figure 4. XRD pattern of TiO2-Eu prepared at different calcination temperatures

RD scanning was performed on the TiO_2-Eu photocatalyst prepared at different calcination temperatures, and the results are shown in Figure 4, and the crystal faces corresponding to the respective diffraction peaks are indicated in Fig. 4. It can be seen from Fig. 4 that some characteristic diffraction peaks are not obvious when the calcination temperature is low (500 °C and 550 °C), for example, as indicated by the dotted line in Fig. 4: {103} and {112} crystal faces of anatase As the calcination temperature increases, the individual diffraction peaks become more pronounced, the main peaks are sharper, and the crystallinity is significantly increased [10]. In addition, the grain size of TiO_2-Eu prepared by different calcination temperatures was obtained by processing the data by Jade software, and the phase retrieval was also carried out. The results are shown in Table 1. It can be seen from Table 1 that the grain size of TiO_2-Eu increases simultaneously with the increase of calcination temperature, and the larger the crystallite, the lower the photocatalytic activity. The calcination temperature is 650 °C and 700 °C, accompanied by rutile phase. It appears that this will reduce the photocatalytic activity of TiO_2-Eu.

Table 1 Grain size of TiO_2-Eu prepared at different calcination temperatures

Calcinationtemperature [°C]	500	550	600	650	700
TiO_2-Eu grain size [nm]	19.0	19.3	30.3	40.2	47.6

It can be seen from Fig. 3 that when the calcination temperature is low, the influence of crystallinity on photocatalytic activity is dominant in TiO_2-Eu, and when the calcination temperature is increased to a certain extent, its crystallinity and crystal phase composition are photocatalytic activity. The influence is dominant, therefore, the appropriate crystallinity, grain size and crystal phase together determine the photocatalytic activity of TiO_2-Eu, obviously, the TiO_2-Eu obtained by calcination at 600 °C has the best photocatalytic activity.

3.3. XPS Analysis.

The prepared TiO_2-Eu was subjected to XPS scanning to obtain the results as shown in Figure 5. Fig. 5-A shows that Ti, O and C are the main elements in the sample. Fig. 5-B shows that Ti2p exhibits a typical bimodal Ti2p1/2-Ti2p3/2 with binding energies of 464.20 eV and 458.46 eV, respectively. Fig. 5-C is an O_{1s} scan spectrum showing that the binding energy is 529.61 eV, which is

O in TiO_2. In addition, the binding energy may be from the surface of TiO_2, such as H_2O or TiO_2 surface active hydroxyl groups, in the vicinity of 531.18 eV. 11, 12]. Fig. 5-D is the scanning spectrum of Eu. The main peak of the Eu3d scan appears at 1134.85eV, which is characteristic of the typical Eu^{3+} [13]. The TiO_2-Eu is calcined during the preparation process, and Eu is mainly on the TiO_2 surface. It exists in Eu_2O_3.

Figure 5. XPS scan of TiO_2-Eu (A: XPS full spectrum of TiO_2-Eu, B: Ti2p photoelectron spectrum, C: O1s photoelectron spectrum, D: Eu3d photoelectron spectroscopy)

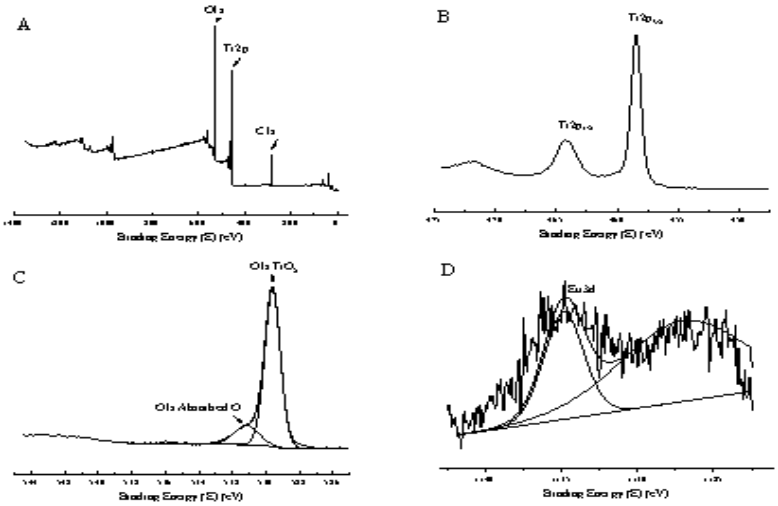

Figure 5. XPS scan of TiO_2-Eu (A: XPS full spectrum of TiO_2-Eu, B: Ti2p photoelectron spectrum, C: O1s photoelectron spectrum, D: Eu3d photoelectron spectroscopy)

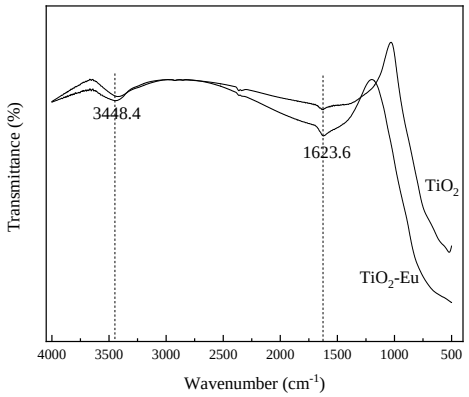

Figure 6. FTIR diagram of pure TiO2 and TiO2-Eu

3.4. FTIR Analysis

Figure 6 is an FTIR diagram of pure TiO_2 and TiO_2-Eu. FTIR is mainly used to obtain the active hydroxyl group on the surface of TiO_2 on TiO_2 photocatalyst. The wave number is 1623.6 cm^{-1}, which is the typical hydroxyl peak on TiO_2 surface, and TiO_2-Eu is stronger than pure TiO_2, which indicates that TiO_2 under UV light. Eu is more likely to form hydroxyl radicals with higher oxidation activity than TiO_2, so the doping of Eu increases the photocatalytic activity of TiO_2.

4. Conclusion

The TiO_2-Eu photocatalyst was prepared by TiO_2 doping with rare earth Eu under microwave hydrothermal synthesis. It was found that Eu can effectively improve the photocatalytic activity of TiO_2. The amount of Eu doping and calcination temperature have a great influence on the

photocatalytic activity of TiO_2-Eu. When the doping amount is n(Eu^{3+}):n(Ti^{4+})=0.08% and the calcination temperature is 600°C, TiO_2-Eu has a higher Excellent photocatalytic activity, which can degrade methyl orange by 96.7%. TiO_2-Eu was analyzed by XPS and FTIR. It was found that Eu was present on the surface of TiO_2 at +3, and Eu doping could effectively change the amount of active hydroxyl groups on the surface of TiO_2, thereby increasing the photocatalytic activity of TiO_2.

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