Preparation of Zn-Eu Co-doped TiO_2 Photocatalyst by Microwave Hydrothermal Method and Its Photocatalytic Activity

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Abstract: The Zn and rare earth Eu co-doped TiO_2 photocatalyst TiO_2-Zn-Eu were prepared by microwave hydrothermal synthesis. The optimal preparation conditions for TiO_2-Zn-Eu were as follows: $n(Zn^{2+}):n(Ti^{4+})=0.06\%$, $n(Eu^{3+}):n(Ti^{4+})=0.12\%$, microwave hydrothermal synthesis power 600 W, the microwave heating time 2.5 h, the microwave heating temperature 150 ℃, the calcination temperature 575 ℃ and the calcination time 3h. The TiO_2-Zn-Eu prepared under the optimal conditions was used for photocatalytic degradation. The degradation rate of methyl orange could reach 98.6% by self-made UV lamp for 30 min. The methyl orange was almost completely degraded with visible light irradiation for 3.5 h, which indicated that the TiO_2-Zn-Eu prepared by microwave method had higher photocatalytic activity.

1. Introduction

Nano-TiO_2 can be widely used as a photocatalyst and adsorbent due to its good adsorption and chemical properties. The photocatalytic performance makes the TiO_2 have many unique properties, such as high photocatalytic oxidation, etc., in water treatment, etc. However, due to the wide band gap of TiO_2, it is necessary to irradiate with ultraviolet light to form electrons. Hole pairs, and electrons and holes are easily recombined, which reduces the photocatalytic properties and limits its practical application. The metal ion doping, surface sensitization and composite semiconductor are often used to improve its photocatalytic activity. Zinc ion doping can reduce the grain size of photocatalyst and enhance its UV absorption ability. At the same time, zinc ion can inhibit the recombination of electrons and holes [1]. Rare earth metals have great potential in improving the photocatalytic activity of TiO_2. They not only extend the absorption region of TiO_2 to visible light, but also have a special electronic layer structure, which can form complexes with a large number of Lewis bases. Obviously this increases electron transfer between TiO_2 surface and contaminants[2-4]. In order to explore the effect of the metal element and the rare earth co-doping on the photocatalytic property, the Zn and Eu were used for co-doping to improve the photocatalytic activity of TiO_2.

2. Experiment

The reagent selection of nitric acid, zinc nitrate and europium nitrate, preparation methods and photocatalytic activity detection methods are described in the paper [5-7]

3. Results and Discussion

3.1. Effect of Zn and Eu Doped Amounts on Photocatalytic Activity of TiO_2-Zn-Eu.

By Changing the Zn and Eu doping amount to prepare TiO_2-Zn-Eu in order to investigate the Zn and Eu doping amount. It can be seen from Figure 1 that the TiO_2-Zn-Eu prepared by microwave hydrothermal method has higher photocatalytic activity, and more the degradation rate of the methyl orange can reach a maximum value of 98.6% when $n(Zn^{2+}):n(Ti^{4+})$ is 0.06% and $n(Eu^{3+}):n(Ti^{4+})$ is

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0.12%. The reason for the increase of photocatalytic activity may be that the structure of dopant TiO_2 photocatalyst changed due to the addition of metal ions, which can be further illustrated by the structure test and characterization of dopant TiO_2 photocatalyst.

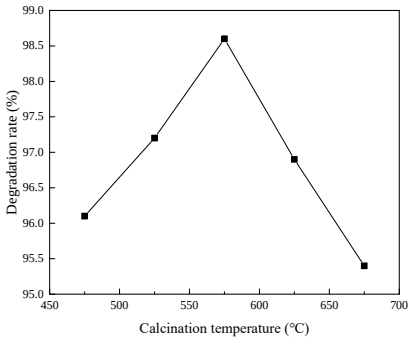

Figure 1. Effect of calcination temperatures on photocatalytic activity of TiO_2-Zn-Eu

Figure 2 is an XRD pattern of TiO_2-Zn-Eu prepared at different calcination temperatures. It can be seen from Fig. 2 that the peak width is large and the crystallinity is low when the calcination temperature is low. The crystallinity is increased as the calcination temperature increasing and the peak width is narrowed, the peak shape is sharp and accompanied by the appearance of rutile. It is found by software Jade that the grain size also increases with the increase of the calcination temperature.

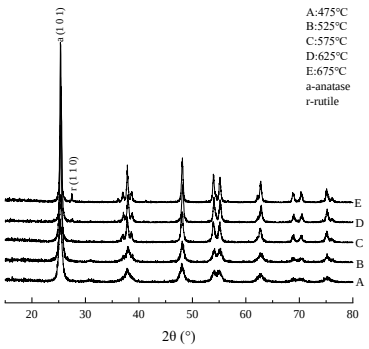

Figure 2. XRD spectrum of TiO2-Zn-Eu prepared at different calcination temperatures

3.2. EDS Analysis.

The EDS scan is performed on a specific area. The results are shown in Figure 3 and Table 1. It can be seen from Fig.3 and Table 1 that Ti and O is mainly composed of TiO_2-Zn-Eu, and a certain amount of C is also detected. There is a very small amount of Zn and Eu, which indicates that TiO_2-Zn-Eu is indeed loaded with both Zn and Eu elements.

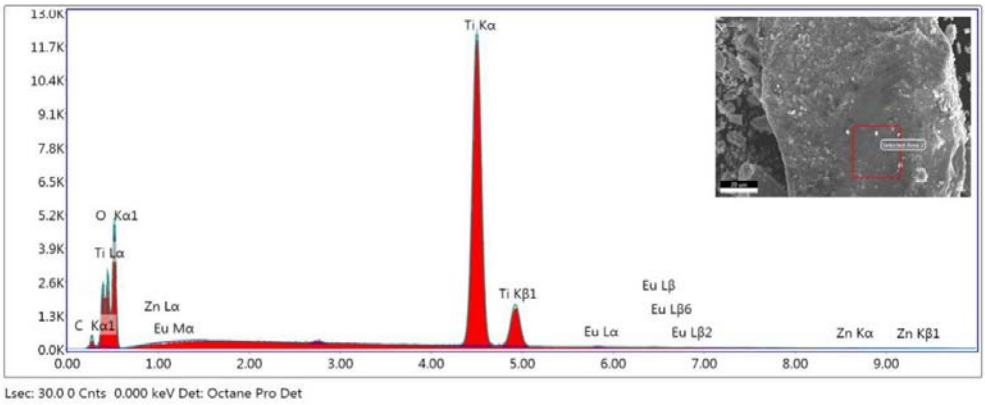

Figure 3. EDS diagram of TiO2-Zn-Eu

Table 1 Analysis results of EDS elements of TiO2-Zn-Eu

Element	Weight %	Atomic %
C K	1.10	2.65
O K	30.69	55.77
Ti K	66.32	40.25
Zn L	0.60	0.27
Eu L	0.86	0.17

3.3. BET Analysis.

Figure 4 is an isotherm and pore size distribution of the TiO_2-Zn-Eu photocatalyst. The isotherm in Fig. 4 is a typical type IV isotherm adsorption curve. At the same time, the typical H_1 hysteresis loop appears in P/P_0 between 0.75 and 0.9. The pore size is mainly concentrated at about 10 nm. Obviously, TiO_2-Zn-Eu is a typical mesoporous material with uniform pore size and regular shape, which will benefit the improvement of the photocatalytic activity of TiO_2-Zn-Eu.

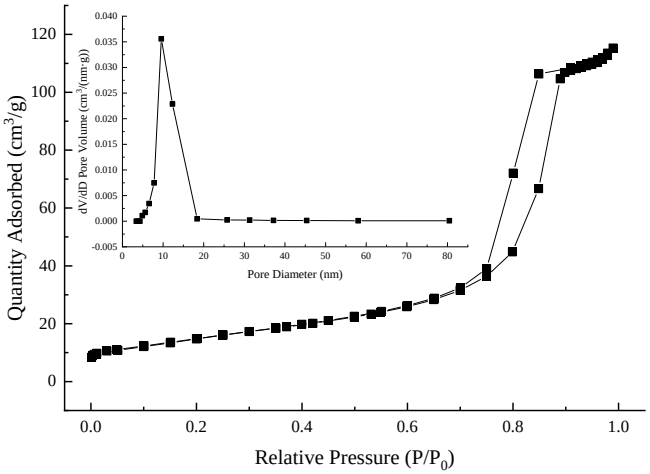

Figure 4. N2 adsorption-desorption isotherms and pore size distribution of TiO2-Zn-Eu

3.4. XPS Analysis.

The chemical state of the elements in TiO_2-Zn-Eu was analyzed by XPS, and the results are shown in Figure 5. It can be seen from Fig.5-A that TiO_2-Zn-Eu is composed of Ti, O, Zn and Eu, which is consistent with the Zn-Eu co-doped TiO_2 result. Fig.5-B is a Ti2p spectrum with peaks at 458.56 eV and 464.35 eV which are characteristic peaks of $Ti2p_{3/2}$ and $Ti2p_{1/2}$, respectively, indicating that Ti present at +4. In addition, it can be observed that there is a peak with a small intensity around 427.03 eV, which is due to the presence of Ti^{3+} in TiO_2-Zn-Eu. Fig.5-C is the O1s spectrum, where the two main peaks are at 529.66 eV and 531.08 eV, respectively, which can be attributed to the lattice O^{2-} in TiO_2 and the metal hydroxyl group or free reactive hydroxyl group [8] on the surface which play a vital role in the photocatalytic oxidation process. Fig.5-D is the Eu3d spectrum, the main peak positions are 1134.79 eV and 1163.94 eV. It can be shown that Eu is in the form of +3 valence in TiO_2 [9]. Fig.5-E is the Zn2p spectrum. The binding energies of Zn2p3/2 and Zn2p1/2 are spin-orbital splitting at 1021.56 eV and 1044.65 eV, respectively. Only this indicates that Zn exists at +2 in TiO_2-Zn-Eu, there is no other evidence that any other Zn sub-oxide exists [10].

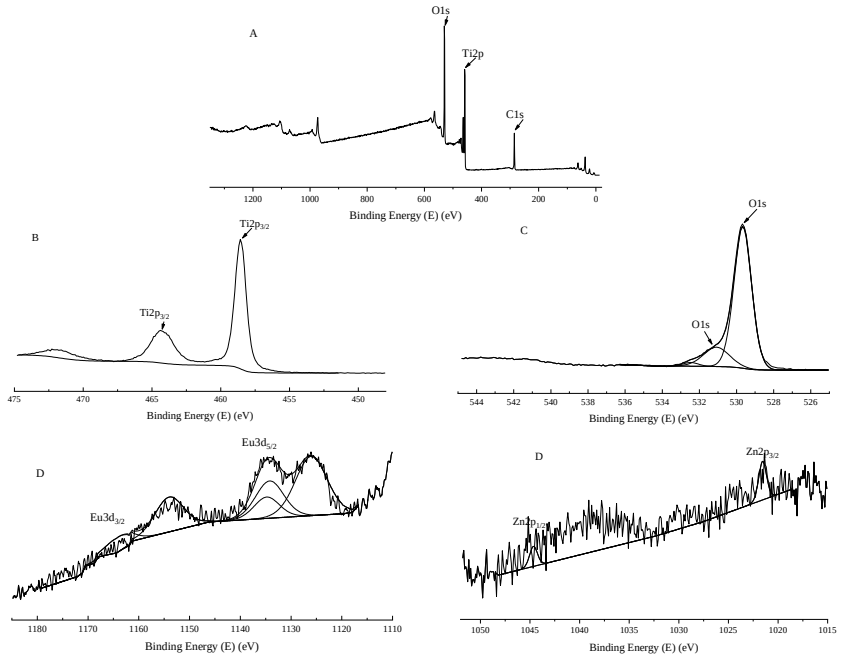

Figure 5. XPS scan of TiO2-Zn-Eu (5-A XPS full spectrum of TiO2-Zn-Eu, 5-B Ti2p photoelectron spectrum, 5-C O1s photoelectron spectrum, 5-D Eu3d photoelectron spectroscopy, 5-E Zn2p photoelectron spectroscopy)

4. Conclusion

(1) TiO_2-Zn-Eu photocatalyst was prepared by microwave hydrothermal method. The optimal conditions for preparing TiO_2-Zn-Eu were that $n(Zn^{2+}):n(Ti^{4+})=0.06\%$ and $n(Eu^{3+}):n(Ti^{4+})=0.12\%$, microwave hydrothermal synthesis power 600 W, the microwave heating time 2.5 h, the microwave heating temperature 150 ℃, the calcination temperature 575 ℃, the calcination time 3h.

(2) XRD, N_2 adsorption-desorption and other testing methods have found that the TiO_2-Zn-Eu has the advantages of single crystal form, high crystallinity, small crystal grain size, uniform distribution, large specific surface area and regular pore structure.

(3) The EDS and XPS analysis shows that TiO_2-Zn-Eu is indeed loaded with both Zn and Eu elements, and more Eu and Zn exist respectively in the form of +3 and +2 valent oxide in TiO_2 photocatalyst, which are also key substances for enhancing the photocatalytic activity of photocatalyst.

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