Preparation of Yb-Er Doped with TiO2 Photo-catalyst in Microwave Ionic Liquids and Microwave Enhanced Photo-catalvtic Activitv

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Abstract—Yb and Er co-doped TiO2 photo-catalysts were synthesized by microwave drying method and sol-gel method with room temperature ionic liquid as a reaction medium. The purpose of the experiment was order to improve the photo-catalytic activity and accelerate the degradation of pollutants, for example methyl orange. The structure and morphology of TiO2-Yb-Er were characterized with XRD, IR and SEM. The photo-catalytic activity was respectively investigated by microwave irradiation (MW) and ultraviolet irradiation (UV) and microwave irradiation with ultraviolet irradiation (MW-UV) with the photo-catalytic degradation of methyl orange solution as simulated pollutants. The results showed that the TiO2-Yb-Er catalysts prepared at the optimum condition had higher photo-catalytic activity.

Keywords—Yb-doped; Er-doped; TiO2 photo-catlysts; Microwave enhancing effect; Photo-catalytic activity

I. INTRODUCTION

Nano-crystalline titania is a photo-catalyst which has attracted considerable attention for its potential use in environmental cleaning[1]. In particular, lanthanide-ion doped titania samples have been shown to increase photo-catalytic efficacy of selected reactions[2,3]. Because of the rare earth elements unique to the electronic structure of the 5d space, it can provide a good electron transfer orbit for the formation of the TiO2 light. Therefore, TiO2 can effectively inhibit the electron hole recombination and broaden the absorption spectrum, so as to improve the photo-catalytic activity of the catalyst [4].

The research group in ionic liquid medium by microwave auxiliary heating method of synthesis of rare earth element ytterbium and erbium Co-doped TiO2 photo catalyst and with methyl orange solution as model pollutant. The effects of the photo-catalytic degradation activity, in order to explore the effect of two kinds of rare earth elements Co-doped on TiO2 photo-catalytic degradation, further improve the rare earth elements doped on the modification of TiO2 photo-catalyst catalytic activity.

II. EXPERIMENTAL SECTION

A. *Experimental Reagents and Instruments*

The main reagents: Ytterbium nitrate, Erbium nitrate and other reagents, the preparation of ionic liquid and the structure test and characterization of the catalyst [4.5].

B. *Preparation of TiO2-Yb-Er Catalyst*

The preparation of TiO2-Yb-Er photo-catalyst for reference [4,5].

C. *Photocatalytic Activity Test of TiO2-Yb-Er Catalyst*

In the reaction of TiO_2-Yb-Er photo-catalytic activity of photo-catalytic degradation of methyl orange solution absorbance determination of reaction and catalyst of the visible light catalytic tests are detailed in reference [4,5].

III. RESULTS AND DISCUSSION

A. *Effect of ytterbium and erbium Doped on the Photo-catalytic Activity of TiO2-Yb-Er*

TiO_2-Yb-Er catalyst in the preparation process, in a fixed volume of ionic liquid is 2.0 ml, microwave drying power 210W, microwave drying time is 20min, calcination temperature of 650℃, calcining time 3h conditions, to keep the percentage of n (Er^{3+}) / n (Ti^{4+}) always is 0.2%, by changing the ytterbium nitrate addition of different amount of ytterbium dopant TiO_2-Yb-Er catalyst, and methyl orange solution to simulate the degradation products, in a fixed UV irradiation time 1.0h conditions, study the influence of the amount of ytterbium doping on the photo-catalytic degradation of reactive and income results as shown in Figure 1; While the percentage of n (Yb^{3+}) /n (Ti^{4+}) was 0.08%, and the other was the same as that of the above, the effect of erbium doping on the photo-catalytic activity of the catalyst was investigated by changing the amount of ammonium nitrate.

From Fig 1. we can see that in the same amount of erbium doped, when ytterbium addition amount of n (Yb^{3+}) /n (Ti^{4+})< 0.08%, the catalyst TiO_2-Yb-Er on degradation of methyl orange solution rate with ytterbium nitrate addition increased; When n (Yb^{3+}) /n (Ti^{4+}) > 0.08%, the

catalytic activity decreased with the increase of the amount of ytterbium addition; And when the n (Yb^{3+}) /n (Ti^{4+}) is 0.08%, TiO_2-Yb-Er catalyst on degradation of methyl orange rate reached 97.5% (Homemade device reaction in 60 min) of maximum has higher photo-catalytic activity. The reason may be due to the coordination between the f orbitals and the degradation of the rare earth element Ytterbium, which can improve the catalytic activity of TiO_2 doped with rare earth element ytterbium. If the amount of ytterbium nitrate is too high, too many ytterbium can be deposited on the surface of TiO_2, which is blocked by the electron hole transfer to the catalyst surface [6-8].

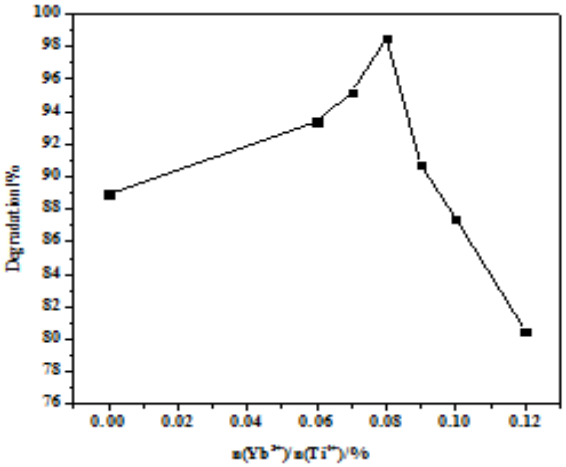


Figure 1. The influence of Yb-doped amount n(Yb3+) /n(Ti4+) for TiO2-Yb-Er on the degradation rate of methyl orange

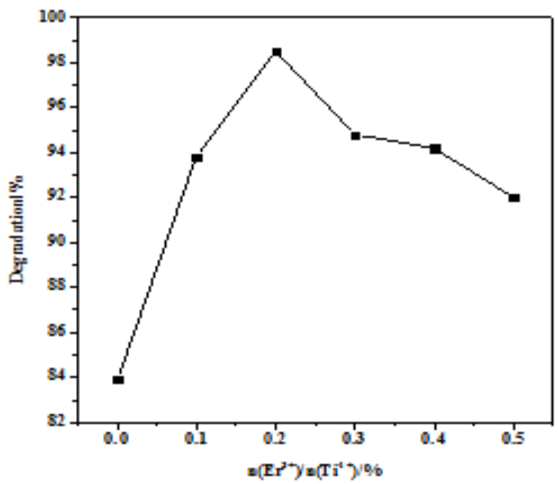


Figure 2. The influence of Er-doped amount n(Er3+) / n(Ti4 +) for TiO2Yb- Er on the degradation rate of methyl orange

From Fig 2. we can see that ytterbium doping amount is the same, when Erbium is added, the amount of n (Er^{3+}) / n (Ti^{4+}) < 0.2%, the catalyst TiO_2-Yb-Er on degradation of methyl orange solution rate with erbium addition increased. When n (Er^{3+}) /n (Ti^{4+}) > 0.2%, the catalytic activity but with erbium nitrate addition amount decreases with increasing; and when the n (Er^{3+}) / n (Ti^{4+}) was 0.2%, TiO_2-Yb-Er catalyst on degradation of methyl orange rate reached 97.5% (Homemade device reaction in 60 min) of maximum, which has higher photo-catalytic activity.

E. Comparison of TiO_2-Yb, TiO_2-Er and TiO_2-Yb-Er Three Catalysts

TABLE I DEGRADATION RATE OF METHYL ORANGE FOR TIO2-YB, TIO2-ER AND TIO2-YB- ER CATALYSTS BY UV,MW AND UV-MW FOR 50 MIN

The degradation rate	TiO_2-Yb	TiO_2-Er	TiO_2-Yb-Er
	η	η	η
MW	3.9%	3.9%	3.9%
UV	97.0%	97.6%	98.7%
UV-MW	98.1%	98.5%	99.3%

Under the optimum conditions, three kinds of catalysts were studied, and the degradation of the pollutants in MW-UV, UV and MW were investigated. The results were shown in Table 1. The catalytic activity of TiO_2-Yb-Er/ TiO_2-Yb /TiO_2-Er catalyst with single rare earth element or double doped with rare earth element is significantly higher than that in the same degradation conditions. The reason may be due to the Er^{3+} and Yb^{3+} Co-doped, TiO_2-Yb-Er is the electron acceptor, which can capture the electron and hole the pairs, and the Yb^{3+} valence state is lower than that of Ti^{4+}, and the electron hole pair can reduce the catalyst surface. In addition, from table 1, the degradation rate of TiO_2-Yb-Er catalyst in UV-MW was also significantly higher than that of MW or UV. This shows that microwave irradiation has the effect of enhancing the TiO_2-Yb-Er degradation of pollutants. Under the constant temperature condition (298K), the degradation rate was very low, and only a few of the simulated pollutants were degraded by microwave irradiation; Under the condition of UV irradiation, using microwave irradiation can improve the degradation rate of pollutants, which shows that the degradation rate of microwave and ultraviolet irradiation is higher than that of the ultraviolet irradiation or under microwave irradiation. Microwave radiation can increase the catalytic activity of TiO_2-Yb-Er catalyst, which may cause more $\cdot OH$ free radicals, which is beneficial to the degradation and mineralization of pollutants, and can also inhibit the electron hole recombination, so as to improve the photo-catalytic activity of the catalyst. This indicates that the microwave radiation heating is beneficial to the synthesis of Co-doped TiO_2-Yb-Er catalyst, and also has the function of enhancing the photo-catalytic degradation of the Co-doped TiO_2-Yb-Er catalyst for simulating the pollutant.

TABLE II DEGRADATION RATE OF METHYL ORANGE FOR TIO2-YB, TIO2-ER AND TIO2-YB-ER CATALYSTS BY THE SUN LIGHT FOR 4H

Degradation rate	TiO_2-Yb	TiO_2-Er	TiO_2-Yb-Er
η	96.8%	97.5%	98.7%

According to Table 2, the degradation activity of the three catalysts in the solar irradiation is still the highest, which indicates that the TiO_2-Yb-Er catalyst has good

photo-catalytic activity under the sun light. The possible reason is that the absorption range of TiO_2 is increased when is doped Yb^{3+} and Er^{3+}, which is favorable for the generation of charge carriers, which can improve the photo-catalytic activity of TiO_2-Yb-Er catalyst.

F. Analysis of XRD, IR and TiO_2-Yb-Er of SEM catalys

XRD, IR and SEM of TiO_2-Yb, TiO_2-Er and TiO_2-Yb-Er three catalysts are shown in Figure 3, figure 4 and figure 5. According to observed in Figure 3, diffraction angle 2θ =25.33 °, 37.88° , 48.06° near, three kinds of doped TiO_2 catalyst have obvious main diffraction peaks appear, they with the standard card anatase TiO_2 peak than consistent. The three kinds of catalysts, TiO_2-Yb, TiO_2-Er and TiO_2-Yb-Er , were prepared by the method. The particle sizes of, and TiO_2-Yb were calculated according to Scherrer formula, and the particle sizes of TiO_2-Er, and TiO_2-Yb-Er were 12.45, 10.65 and 10.80 nm respectively.

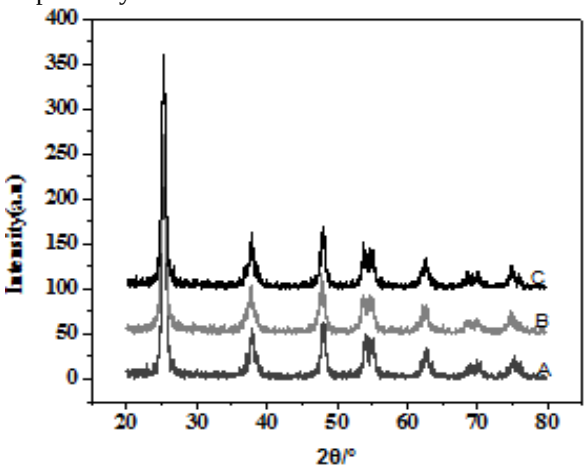


Figure 3. XRD patterns of TiO2-Yb，TiO2-Er and TiO2-Yb-Er

(A: TiO2-Yb； B: TiO2-Er； C: TiO2-Yb-Er)

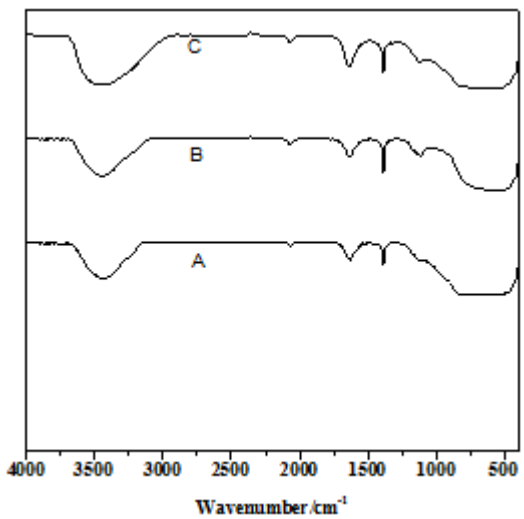
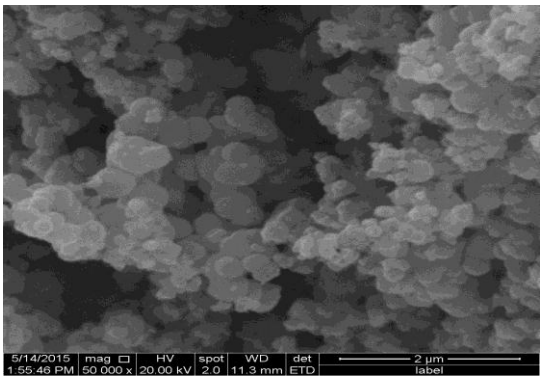


Figure 4. IR spectra of TiO2-Y，TiO2-Ce and TiO2-Y-Ce

According to the IR spectra of three catalysts (Figure 4), TiO_2-Yb,TiO_2-Er and TiO_2-Yb-Er in the 3446cm^{-1}, respectively, near the 1631cm^{-1}, Ti-OH, and wide absorption band at 501 cm^{-1} type corresponding to the anatase TiO_2 in Ti-O stretching vibration，Among them, 1631cm^{-1} and 3446cm^{-1} appear to absorb larger peaks, which represent the characteristics of O-H bond stretching vibration and bending vibration caused by the surface of TiO_2 catalyst. Compared with the peak of the three catalysts, TiO_2-Yb-Er catalyst has a strong absorption peak at 1631cm^{-1} and 3446cm^{-1}, which indicates that the surface hydroxyl adsorption of Co-doped catalyst is more than that of single element doped TiO_2.



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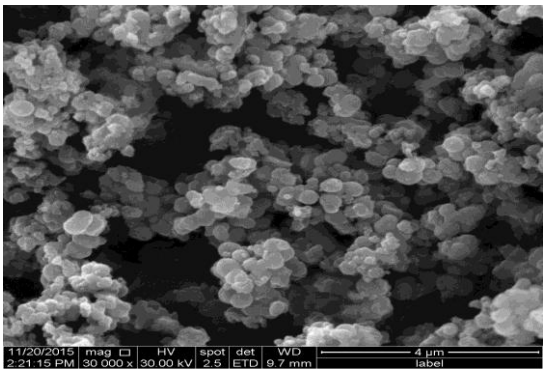

C

Figure 5. SEM images of TiO2-Yb，TiO2-Er and TiO2-Yb-Er
(A: TiO2-Yb; B: TiO2-Er； C: TiO2-Yb-Er)

Under the interaction of microwave and ultraviolet light, the surface of the catalyst was changed to form OH, and the content of. OH, and the content of the catalyst had an effect on the activity of the catalyst. In addition, hydroxyl radical or oxidant can promote the adsorption of O_2 into O^{2-}, HO^{2-} and other active groups, so as to promote the photo-catalytic degradation of organic pollutants. Therefore, Co-doped TiO_2-Yb-Er catalyst has more surface hydroxyl groups, which shows that it has high photo-catalytic activity. At 1500~1300 cm-1 within the scope of the absorption peak was caused by -CH_3 symmetric deformation caused by vibration. Although most of the organic solvent in the process of heat treatment can eliminate, but IR analysis showed that the surface is still a small amount of residual organic matter. From the SEM diagrams of three kinds of catalysts (Figure 5), the Nano particles of TiO_2-Yb, TiO_2-Er and TiO_2-Yb-Er three kinds of catalysts were obviously refined. The morphology of the nanoparticles was nearly spherical and the particle size was nanometer. The specific surface area was larger, which could make full contact with the simulated pollutants, so that the photo-catalytic activity of the catalysts could be improved [9-11].

IV. CONCLUSION

Optimum conditions for preparation of rare earth element ytterbium and erbium Co-doped TiO_2-Yb-Er catalyst by microwave assisted ionic liquid medium: $n(Yb^{3+})/n(Ti^{4+})=0.08\%$,$n(Er^{3+})/n(Ti^{4+})=0.2\%$, Ionic liquid dosage 210W, microwave drying power 2.0mL, microwave drying time 20min, calcination temperature 650℃, calcination time 3h. Under the condition of TiO_2-Yb-Er photo-catalyst, in MW, UV and UV-MW conditions after degradation of methyl orange and phenol solution 50 min, methyl orange drop and phenol degradation rate in the UV-MW under the condition of is the best. The structural analysis of the catalyst showed that the activity of TiO_2-Yb-Er catalyst was greater than that of TiO_2-Yb or TiO_2-Er catalyst, and the size of the photo-catalytic activity of the three was: TiO_2-Yb-Er > TiO_2-Er> TiO_2-Yb.

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