Preparation of Yb-Er Doped with TiO$_2$ Photocatalyst in Microwave Ionic Liquids and Microwave Enhanced Photo-catalytic Activity

Zhang Mei1
Institute of Chemistry and Chemical Engineering
Yunnan Normal University
Yunnan Kunming, China
e-mail: 1085515542@qq.com

Bi Xian-jun*
Institute of Chemistry and Chemical Engineering
Yunnan Normal University
Yunnan Kunming, China
e-mail: bixj159@aliyun.com

Lu Yue-jie2
Institute of Chemistry and Chemical Engineering
Yunnan Normal University
Yunnan Kunming, China
e-mail: 1079260276@qq.com

Abstract—Yb and Er co-doped TiO$_2$ photocatalysts 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 in order to improve the photo-catalytic activity and accelerate the degradation of pollutants, for example methyl orange. The structure and morphology of TiO$_2$-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 TiO$_2$-Yb-Er catalysts prepared at the optimum condition had higher photo-catalytic activity.

Keywords—Yb-doped; Er-doped; TiO$_2$ photo-catalysts; Microwave enhancing effect; Photo-catalytic activity

I. INTRODUCTION

Nano-crystalline titania is a photocatalyst 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 TiO$_2$ light. Therefore, TiO$_2$ 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 TiO$_2$ photocatalyst 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 TiO$_2$ photo-catalytic degradation, further improve the rare earth elements doped on the modification of TiO$_2$ 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 TiO$_2$-Yb-Er Catalyst

The preparation of TiO$_2$-Yb-Er catalytic activity for reference [3,5].

C. Photocatalytic Activity Test of TiO$_2$-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 [3,5].

III. RESULTS AND DISCUSSION

A. Effect of ytterbium and erbium Doped on the Photo-catalytic Activity of TiO$_2$-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$^{4+}$) / $n$ (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 photocatalytic 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 \( (\text{Yb}^{3+}) / n (\text{Ti}^{4+}) \) 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](image1.png)

**Figure 1.** The influence of Yb-doped amount \( n(\text{Yb}^{3+}) / n(\text{Ti}^{4+}) \) for TiO\(_2\)-Yb-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 \( n (\text{Er}^{3+}) / n (\text{Ti}^{4+}) < 0.2\% \), the catalyst TiO\(_2\)-Yb-Er on degradation of methyl orange solution rate with erbium addition increased. When \( n (\text{Er}^{3+}) / n (\text{Ti}^{4+}) > 0.2\% \), the catalytic activity but with erbium nitrate addition amount decreases with increasing; and when the \( n (\text{Er}^{3+}) / n (\text{Ti}^{4+}) \) 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.

![Figure 2](image2.png)

**Figure 2.** The influence of Er-doped amount \( n(\text{Er}^{3+}) / n(\text{Ti}^{4+}) \) for TiO\(_2\)-Yb-Er on the degradation rate of methyl orange

**E. Comparison of TiO\(_2\)-Yb, TiO\(_2\)-Er and TiO\(_2\)-Yb-Er Three Catalysts**

<table>
<thead>
<tr>
<th>The degradation rate</th>
<th>TiO(_2)-Yb</th>
<th>TiO(_2)-Er</th>
<th>TiO(_2)-Yb-Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>( \eta )</td>
<td>( \eta )</td>
<td>( \eta )</td>
</tr>
<tr>
<td>UV</td>
<td>97.0%</td>
<td>97.6%</td>
<td>98.7%</td>
</tr>
<tr>
<td>UV-MW</td>
<td>98.1%</td>
<td>98.5%</td>
<td>99.3%</td>
</tr>
</tbody>
</table>

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\(_2\)-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 2** Degradation rate of methyl orange for TiO\(_2\)-Yb, TiO\(_2\)-Er and TiO\(_2\)-Yb-Er catalysts by the sun light for 4h

<table>
<thead>
<tr>
<th>Degradation rate</th>
<th>TiO(_2)-Yb</th>
<th>TiO(_2)-Er</th>
<th>TiO(_2)-Yb-Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta )</td>
<td>96.8%</td>
<td>97.5%</td>
<td>98.7%</td>
</tr>
</tbody>
</table>

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 catalysts

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 =25.3°, 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](image)

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$_2$.

![Figure 4. IR spectra of TiO2-Y, TiO2-Ce and TiO2-Y-Ce](image)

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].

![Figure 5. SEM images of TiO2-Yb, TiO2-Er and TiO2-Yb-Er](image)
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°C, 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.

REFERENCE