# Preparation of Rare Earth Yb Doped $TiO_2$ Photo-catalyst by Microwave Hydrothermal Method and Its Photo-catalytic Activity

Xin Wang[a], Cheng Chen[b] and Xianjun Bi[c,*]

Institute of Chemistry and Chemical Engineering Yunnan Normal University, Yunnan Kunming, China

[a] 965184394@qq.com, [b] 470013181@qq.com, [c,*] bixj159@qq.com

**Keywords:** Microwave hydrothermal method; Yb doping; $TiO_2$ photo-catalyst; UV irradiation; Solar illumination; Photo-catalytic activity

**Abstract.** The rare earth Yb doped $TiO_2$ photo-catalysts $TiO_2$-Yb were prepared by microwave hydrothermal method and its photo-catalytic activity under UV irradiation and solar irradiation were investigated. The optimal conditions for the preparation of $TiO_2$-Yb photo-catalyst were obtained by optimizing the reaction condition. They were that Yb and Ti molar ratio n ($Yb^{3+}$) /n ($Ti^{4+}$) =0.14%, microwave power 600 W, reaction temperature 160℃, reaction time 3.5 h in parallel synthesis reaction and calcination temperature 650℃, calcination time 2.5 h in the high temperature box resistance furnace. The degradation rate of methyl orange was 98.71% when the $TiO_2$-Yb was used for degradation of methyl orange in the UV irradiation for 50 min. But the degradation rate of methyl orange could almost reach 100% in the sunlight degradation of methyl orange for 4 h, which indicated that the $TiO_2$-Yb prepared by microwave hydrothermal method had higher photo-catalytic activity.

## Introduction

Semiconductor $TiO_2$ photo-catalyst has the characteristics of good chemical stability, high catalytic efficiency, non-toxic and so on. It has become an ideal environmental friendly photo-catalyst [1-2]. However, The band gap of $TiO_2$ is only 3.2eV, the utilization rate of solar light is low, and the recombination rate of photo-generated electron hole pairs is high. The phenomenon of agglomeration is easy to occur and the surface area is reduced, resulting in lower photo-catalytic activity under visible light [3]. The research results show that the light response range of $TiO_2$ catalyst can be improved by doping with elements, and the absorption range will be red shifted to visible region, thus enhancing the catalytic activity of $TiO_2$ catalyst in visible light range [4-7]. Rare earth elements have 4f electron, not full of electronic track, electron screening effect of $5S_2$ and $5P_6$, the rare earth elements can form several electronic configuration, which is similar to the ground state energy of the excited state, 4f electron transition probability increases, thus improving the photo-catalytic activity of rare earth doped $TiO_2$. The preparation of rare earth Yb doped $TiO_2$ photo-catalyst and its photo-catalytic activity by sol-gel method have been reported. It is found that Yb doping could really increase the photo-catalytic activity of $TiO_2$-Yb[8]. This paper attempts to prepare Yb doped $TiO_2$ photo-catalyst by microwave hydrothermal method, through the optimization of reaction conditions to obtain the best preparation conditions of $TiO_2$-Yb, so as to further improve the photo-catalytic activity of doped $TiO_2$ photo-catalyst.

## Experimental Section

**Experimental Instruments and Drugs.** XH-800S Microwave hydrothermal parallel synthesizer, SX-4-10 High temperature box resistance furnace, 722N Visible spectrophotometer, XH-300UL Computer microwave ultrasonic combined catalytic synthesis instrument, Ytterbium nitrate, Absolute ethanol, Titanic acid four butyl ester.

**Preparation of $TiO_2$-Yb Catalyst.** The Ytterbium nitrate with butyl titanate four according to n ($Yb^{3+}$) /n ($Ti^{4+}$) =0.14% dissolved in 18 mL PH=2-3 dilute nitric acid solution formation A; amount of 17.5 mL ethanol mixing 10 min with 3.4 mL butyl titanate four form B solution and A solution drop B solution stirring 10 min a period of time, reaction in the microwave parallel synthesis in hot water after washing and filtering, after vacuum drying at high temperature box resistance furnace in the calcining and drying, to obtain the $TiO_2$-Yb catalyst.

**Catalytic Activity Test of $TiO_2$-Yb Catalyst**. The catalytic activity test methods for $TiO_2$-Cu catalysts refer to the references [8].

## Results and Discussion

**Effect of Yb Doped Content.** The effect of Yb doped content on photo-catalytic activity of $TiO_2$-Yb was investigated by fixing the power of microwave reaction parallel synthesizer 600 W, the reaction temperature 160 ℃, the reaction time 3.5 h and high temperature box type resistance furnace temperature 650 ℃and time 2.5 h. The result was shown in Fig. 1. From Fig. 1, the photo-catalytic degradation rate of methyl orange showed a sharp downward trend after rising with the Yb increase and the degradation rate of methyl orange in the UV irradiation for 50 min reached a maximum value of 98.71% when the doped amount of n ($Yb^{3+}$)/n ($Ti^{4+}$) was 0.14%. This showed that there was an optimum proportion of Yb doped (0.14%), which could increase the separation rate of photo-generated electron hole, thus the photo-catalytic activity of $TiO_2$-Yb was enhanced.

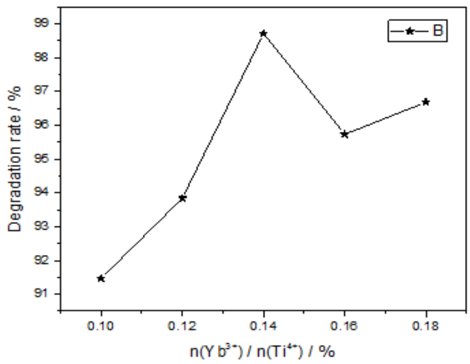


Fig. 1 Effect of Yb doped content on the photo-catalytic activity of $TiO_2$-Yb

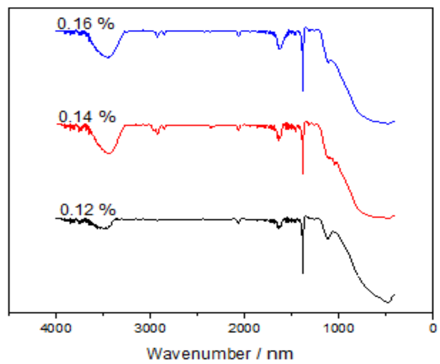


Fig. 2 IR of $TiO_2$-Yb prepared by the different Yb doped content

Fig. 2 showed the Infrared Spectra of $TiO_2$-Yb prepared by the different Yb doped content. From Fig. 2, the peak at about 3447 nm was the stretching vibration absorption peak of hydroxyl (O-H), caused by the stretching vibration of the Ti-O-H group on the $TiO_2$ surface[9]. The absorption peak near 1635 nm was caused by the deformation vibration of water molecules [10]. The stretching vibration absorption peak near 1114 nm was the stretching vibration of the C-O-C bond, and the peak at 472 nm was generally considered as the Ti-O stretching vibration peak [11]. The size of the order to the hydroxyl peak at 3447 nm was that the hydroxy peak was larger for Yb doped 0.14%, the second was for Yb doped 0.16%, the smaller was for Yb doped 0.12%. This indicates that the level of the order to the hydroxyl content was the highest for Yb doped 0.14%, the lowest was for Yb doped 0.12%. Due to the surface hydroxyl content was an important factor in determining the photo-catalytic activity, as a result the $TiO_2$-Yb had the highest photo-catalytic activity when the Yb doped content was 0.14%.

**Influence of Reaction Time**. The effect of microwave reaction time on photo-catalytic activity of $TiO_2$-Yb was investigated by fixing the power of microwave reaction parallel synthesizer 600 W, the reaction temperature 160 ℃and high temperature box type resistance furnace temperature 650 ℃ and time 2.5 h. The result was shown in Fig. 3. From Fig. 3, the degradation of methyl orange firstly increased sharply and then decreased rapidly with the increase of microwave reaction time and the degradation rate of methyl orange in the ultraviolet irradiation for 50 min reached a maximum value of 98.71% when the reaction time was 3.5 h. The best reaction time for preparing $TiO_2$-Yb photo-catalyst was 3.5 h.

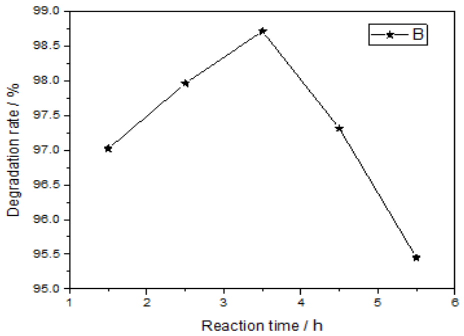


Fig. 3 Effect of microwave reaction time on the photo-catalytic activity of $TiO_2$-Yb

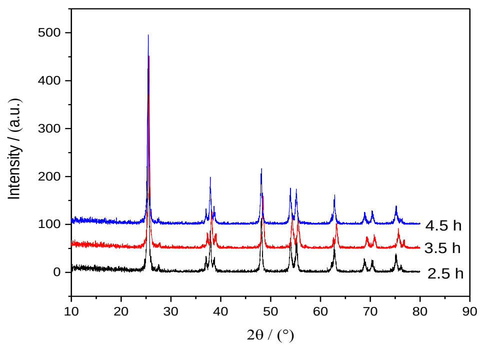


Fig. 4 XRD of $TiO_2$-Yb prepared by different reaction time

The XRD for $TiO_2$-Yb prepared at the different reaction times was shown in Fig. 4. Through the jade 6.5 analysis, the $TiO_2$-Yb was anatase (PDF#: 78-2486) and rutile (PDF# 34-0180), the diameter of 26.85 nm and 25.29 (degrees) at the peak as the non-crystalline phase and the crystallinity of 57.02 (1.51)% for reaction time 2.5 h. The $TiO_2$-Yb was anatase (PDF#: 71-1168) and rutile (PDF# 34-0180), the diameter of 27.34 nm and 25.26 (degrees) at the peak as the non-crystalline phase and the crystallinity of 50.73 (1.69)% for reaction time 4.5 h. The $TiO_2$-Yb was anatase (PDF #: 83-2243) and rutile (PDF# 34-0180), the diameter of 26.44 nm and 25.26 (degrees) at the peak as the non-crystalline phase and the crystallinity of 57.47 (1.33)% for reaction time 3.5 h. The particle sizes of $TiO_2$-Yb were respectively 26.85, 26.44 and 27.34 nm. The crystallinity was respectively 57.02 (1.51)%, 57.47 (1.33)% and 50.73 (1.69)%. The crystallinity was an important factor affecting the activity and the regular crystalline structure was the prerequisite for the high photo-catalytic activity. This showed that the best reaction time was 3.5 h.

**Effect of Reaction Temperature**. The effect of microwave reaction temperature on photo-catalytic activity of $TiO_2$-Yb was investigated by fixing the other preparing conditions. The result was shown in Fig. 5. From Fig. 5, the degradation of methyl orange firstly increased sharply and then decreased rapidly with the increase of microwave reaction temperature and the degradation rate of methyl orange in the ultraviolet irradiation for 50 min reached a maximum value of 98.71% when the reaction temperature was 160 ℃. The best reaction temperature for preparing $TiO_2$-Yb photo-catalyst was 160 ℃.

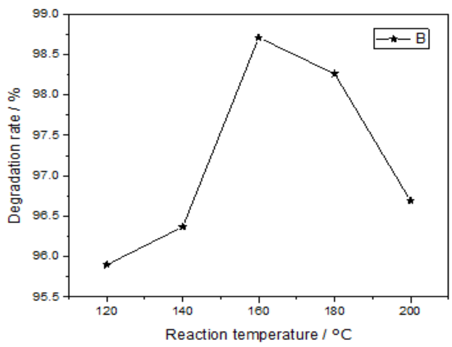


Fig. 5 Effect of reaction temperature on Photo-catalytic activity of $TiO_2$-Yb

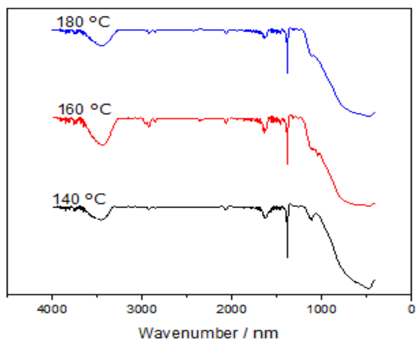


Fig. 6 IR of $TiO_2$-Yb prepared by different reaction temperature

Fig. 6 showed the Infrared Spectra for $TiO_2$-Yb prepared by the different reaction temperature. From Fig. 6, the crystal growth was not complete and the crystallization degree was relatively low when the reaction temperature was lower than 160 ℃, but the nucleation of aggregation phenomenon was resulted in the increase in particle size when the reaction temperature was higher than 160 ℃. The magnitude of the hydroxyl stretching vibration absorption peak at 3447 nm was 160 ℃ >180℃>140 ℃. Therefore, the $TiO_2$-Yb had the higher photo-catalytic activity when the reaction temperature was 160 ℃.

**Effect of Calcination Temperature**. The effect of calcination temperature in the high temperature box resistance furnace on photo-catalytic activity of $TiO_2$-Yb was investigated by fixing the other preparing conditions. The result was shown in Fig. 7. From Fig. 7, the degradation of methyl orange first increased and then decreased rapidly with the increase of calcination temperature and the degradation rate of methyl orange in the ultraviolet irradiation for 50 min reached a maximum value of 98.71% when the calcination temperature was 650 ℃. The best calcination temperature for preparing $TiO_2$-Yb photo-catalyst was 650 ℃.

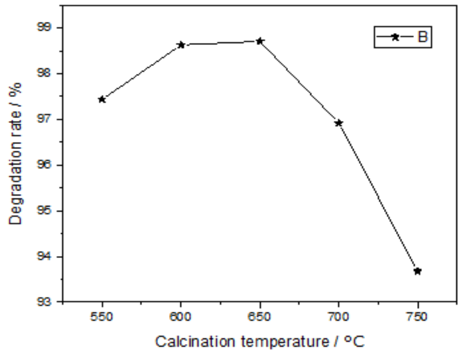


Fig. 7 Effect of calcination temperature on the photo-catalytic activity of $TiO_2$-Yb

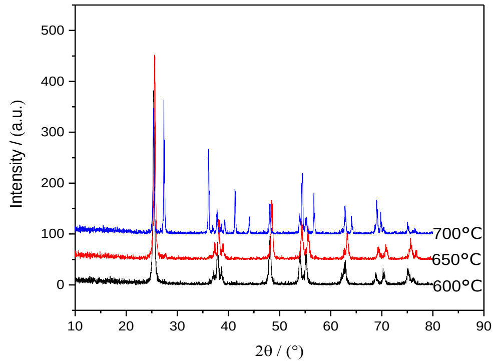


Fig. 8 XRD of $TiO_2$-Yb prepared by the different calcination temperature

The XRD for $TiO_2$-Yb prepared at the different calcination temperatures was shown in Fig. 8. From Fig. 8, the crystal nucleus was in the developmental stage when the calcination temperature was below 650 ℃. The specific surface area gradually increased with the increase of temperature. When the calcination temperature was higher than 650 ℃, the high temperature led to the transformation from anatase to rutile, and nucleation of aggregation phenomenon was resulted in the catalytic activity decreasing. Through the jade 6.5 analysis of Fig. 8, the $TiO_2$-Yb was anatase and the particle size was 31.52 nm when the calcination temperature was 600 ℃. It was anatase (PDF#: 71-1168) and rutile (PDF#: 77-0443), and more the particle size was 72.62nm(the lattice parameters a=4.6192, c=5.2520) when the calcination temperature was 700 ℃. Due to the lattice parameters was in the different from standard parameters(a=4.611, c=2.973), therefore the $TiO_2$-Yb may contain two crystal structure. When the calcination temperature was 650 ℃, the $TiO_2$-Yb was mainly anatase and contained a small amount of rutile phase. The mixed crystal structure led to the $TiO_2$-Yb with higher photo-catalytic activity [13].

**Influence of Calcination Time.** The effect of calcination time in the high temperature box resistance furnace on photo-catalytic activity of $TiO_2$-Yb was investigated by fixing the other preparing conditions. The result was shown in Fig. 9. From Fig. 9, the degradation of methyl orange firstly increased sharply and then decreased rapidly with the increase of calcination time and the degradation rate of methyl orange in the ultraviolet irradiation for 50 min reached a maximum value of 98.71% when the calcination time was 2.5 h. The best calcination time for preparing $TiO_2$-Yb photo-catalyst was 2.5 h.

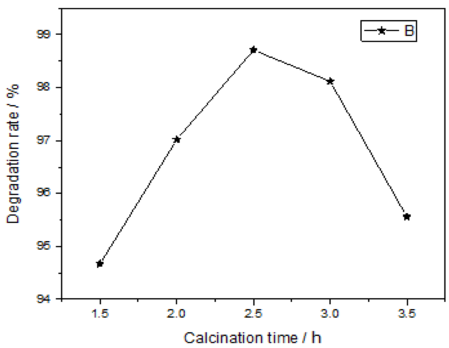


Fig. 9 Effect of calcination time on the photo -catalytic activity of $TiO_2$-Yb

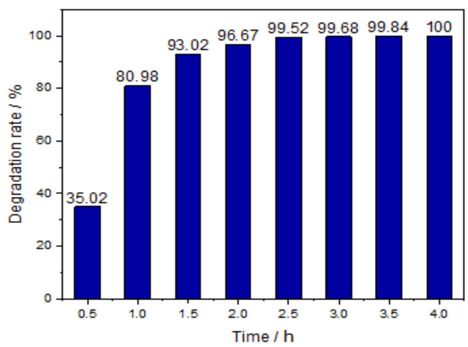


Fig. 10 The degradation rate of $TiO_2$-Yb under the sunlight

**Degradation Rate under the Irradiation of Sunlight.** Taking 0.5 g $TiO_2$-Yb placed in 50 mL 10 mg/L methyl orange solution, the mixture irradiated under the sun light, every 30 min from the supernatant measuring its absorbance and calculate the degradation rate. The results were shown in Fig. 10. From Fig. 10, the degradation rate of methyl orange increased with the duration of solar irradiation and the methyl orange was almost completely degraded when the irradiation time was 4 h. This indicated that Yb doping could make the absorption wavelength of the catalyst shift red shift, thus the photo-catalytic activity of the catalyst under the irradiation of the sun was enhanced. Obviously, the degradation rate of $TiO_2$-Yb prepared by microwave hydrothermal method was higher than that of $TiO_2$-Yb prepared by sol-gel process( the degradation rate was 96.8% )[8].

## Conclusion

(1) The best conditions for preparing $TiO_2$-Yb catalyst by microwave hydrothermal method were as follows: the ratio of ytterbium to titanium n ($Yb^{3+}$) /n ($Ti^{4+}$) =0.14%, the power of microwave reaction parallel synthesizer 600 W, reaction temperature 160 ℃, reaction time 3.5 h and the high temperature box resistance furnace calcination temperature 650 ℃, calcination time 2.5 h.

(2) The degradation rate of methyl orange was 98.71% when the $TiO_2$-Yb prepared by microwave hydrothermal method used for the degradation of the methyl orange solution in the ultraviolet irradiation for 50 min. The methyl orange was almost completely degraded when it was irradiated under the sun light for 4 h. This indicated that the $TiO_2$-Yb prepared by microwave hydrothermal method had higher photo-catalytic activity.

## References

[1] Y.Q. Hou, D.M. Zhuang and G. Zhang et al: Chemical Environmental Protection, Vol. 24 (2004) No.3, p.180. (In Chinese)

[2] Q.F. Zhou, S.H. Lv and Y.Y. Cui: Journal of Shanxi University of Science and Technology (NATURAL SCIENCE EDITION), Vol. 33 (2015) No.4, p.51. (In Chinese)

[3] C.X. Li, H.Z. Jin and Z.Z. Yang et al: Journal of Inorganic Materials, Vol. 32 (2017) No.4, p.357. (In Chinese)

[4] M.W. Li, M. Zhang and X.J. Bi: Chemistry Research, Vol. 24 (2015) No.1, p.57. (In Chinese)

[5] M. Zhang, Y.J. Lu and X.J. Bi. C. *Advances in Social Science Education and Humanities Research-Education, Management, Computer and Society.* (2016), p.1362.

[6] Y.J. Lu, X. Wang and X.J. Bi: Chemistry Research, Vol. 27 (2016) No.6, p.748. (In Chinese)

[7] S.H. Chen, Y. Xu and B.L. Lv et al: Chinese Journal of Physical Chemistry, Vol. 27 (2011) No.12, p.2933. (In Chinese)

[8] M. Zhang. *Preparation and Photo-catalytic Activity of Rare Earth Ytterbium and Erbium Doped $TiO_2$ Photo-catalysts* (MS., Yunnan Normal University, China 2016), p.25. (In Chinese)

[9] J.M. Zhou, X.H. Hu and J. Wang: Chemical Engineer, Vol. 255 (2016) No.12, p.76. (In Chinese)

[10] C.Y. Yan, H.L. Chen and Q. Chang et al: Journal of Environmental Science, Vol. 34 (2014) No.5, p.1220. (In Chinese)

[11] Z.L. He. *Morphology Control and Properties of Doped Nano Titania* (MS., Shanxi University of Science and Technology, China 2011), p.14. (In Chinese)

[12] J.H. Chen, Z.Q. Gong: Beijing: Science Press, (2006), p.5. (In Chinese)

[13] Z.H. Yuan, Y.C. Sun and Y.H. Wang et al: Journal of Chemical Engineering of Institutions of Higher Learning, Vol. 25 (2004) No.10, p.1875. (In Chinese)