

Preparation of Yb-Cu Co-doped TiO₂ Catalyst by Microwave Hydrothermal Method and Its Photocatalytic Activity

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Abstract. The Ytterbium and Copper co-doped TiO₂ catalyst TiO₂-Yb-Cu was prepared by microwave hydrothermal method, and the photocatalytic degradation activity of the catalyst was investigated. The optimum preparation conditions of the catalyst were obtained by optimizing the experimental conditions. The amount of ytterbium and copper doped was $n(\text{Yb}^{3+})/n(\text{Ti}^{4+}) = 0.16\%$ and $n(\text{Cu}^{2+})/n(\text{Ti}^{4+}) = 0.04\%$, the reaction temperature of microwave synthesis parallel synthesis apparatus 120°C, the reaction time 3 h, the microwave power 650 W, the calcination temperature of high temperature box type resistance furnace 600°C and the calcination time 5.5 h. The results of the TiO₂-Yb-Cu catalyst tested by SEM, BET, IR, XRD and Raman showed that it had the advantages of small size, high crystallinity and stable chemical properties when the catalyst was prepared by microwave hydrothermal method. The test results of photocatalytic degradation showed that the catalytic activity of copper and ytterbium co-doped preparing TiO₂-Yb-Cu catalyst had higher photocatalytic activity than single doped ytterbium or copper preparing TiO₂-Yb or TiO₂-Cu catalyst. The methyl orange almost could completely be degraded with the TiO₂-Yb-Cu catalyst used for photocatalytic degradation of the methyl orange solution under the UV irradiation at 50 min.

Introduction

With the rapid development of economy, people pay more and more attention to a series of environmental problems caused by economic development, hoping to develop the economy without destroying the environment. Semiconductor TiO₂ catalyst can catalyze the degradation of toxic pollutants to non toxic substances through its own photocatalytic activity, and TiO₂ catalyst itself has the characteristics of innocuity, stable chemical properties and low price. But the band gap of TiO₂ catalyst is narrow and the catalytic activity under visible light is low. In recent years, two elements have been used for co-doped to improve the photocatalytic degradation activity of TiO₂ catalyst. For example, Yuan et al[1] prepared Fe³⁺ and Zn²⁺ co-doped TiO₂ catalysts by sol-gel method. It was found that under the synergistic effect of two ions, the TiO₂ catalyst prepared by co-doped could significantly improve its photocatalytic activity under visible light. Xing Jinjuan et al[2] prepared S and N co-doped TiO₂ catalysts. It was found that the Ti-O-S and O-Ti-N bonds were formed in the TiO₂ lattice which changed the band structure of TiO₂ catalyst, and improved the decolorization rate of the catalyst for methyl orange. The previous work of our research group showed that two elements co-doped TiO₂ catalysts were prepared by sol-gel method had high photocatalytic activity, and more the microwave irradiation could significantly improve the degradation rate of methyl orange[3-7]. In this paper, the copper and ytterbium co-doped TiO₂ catalysts TiO₂-Yb-Cu were prepared by the microwave hydrothermal synthesis method. By optimizing the preparation condition of catalysts further improve the photocatalytic degradation activity of doped TiO₂ 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 tetrabutylorthotitanate according to $n(\text{Yb}^{3+})/n(\text{Ti}^{4+})=0.16\%$, copper nitrate and tetrabutylorthotitanate according to $n(\text{Cu}^{2+})/n(\text{Ti}^{4+})=0.04\%$ dissolved in 18 mL PH=2-3 dilute nitric acid to form A solution. Adding 17.5 mL ethanol into beaker after taking 3.4 mL tetrabutylorthotitanate, and stirring to form B solution. The A solution was added drop wise into B solution, and switched to PTFE high pressure reactor, then changing the microwave hydrothermal parallel synthesis of microwave power, hydrothermal reaction temperature and reaction time. Reaction, filtration, ultra pure water washing made white filter cake. Finally, the sample was fully grinded after the vacuum drying oven dried for 3 h. The Yb and Cu co-doped TiO_2 photocatalyst TiO_2 -Yb-Cu was prepared in a high temperature box type resistance furnace at different temperatures and placed in dryer.

Catalytic Activity Test of TiO_2 -Yb-Cu Catalyst.

The 0.5g TiO_2 -Yb-Cu catalyst was placed in the 50 mL concentration 10 mg/L methyl orange solution. The mixed solution was placed in a XH-300UL microwave combined catalytic synthesizer. After ultraviolet (UV) irradiation reaction after a certain period of time, the centrifugal separation of supernatant liquid with 722N spectrophotometer (the maximum absorption wavelength of 464 nm) was tested A. With the degradation rate of formula calculated the degradation rate of methyl orange: $\eta=(A_0-A)/A_0 \times 100\%$ (A_0 and A respectively before and after the absorbance of methyl orange degradation).

Results and Discussion

Effect of Doping Amount on the Photocatalytic Activity of TiO_2 -Yb-Cu.

In order to investigate the effect of copper doped amount on the photocatalytic activity of TiO_2 -Yb-Cu catalyst, the copper nitrate and tetrabutylorthotitanate molar ratio was changed by fixing $n(\text{Yb}^{3+})/n(\text{Ti}^{4+})=0.16\%$, microwave reaction parallel synthesis of temperature 120°C , reaction time 3h, microwave power 650W, high temperature box resistance furnace calcination temperature 600°C and the calcination time 5.5h. The result was shown in Figure 1. Similarly, the effect of ytterbium doped amount on the photocatalytic activity of TiO_2 -Yb-Cu catalyst was shown in Figure 2 by fixing $n(\text{Cu}^{2+})/n(\text{Ti}^{4+})=0.04\%$.

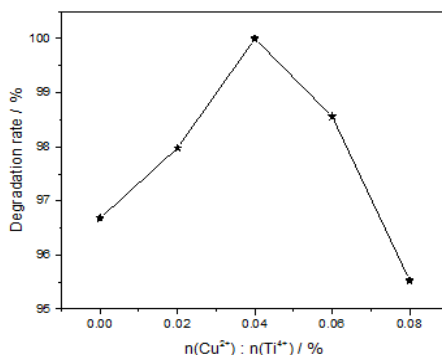


Figure. 1 Effect of copper doped amount on the photocatalytic activity of TiO_2 -Yb-Cu

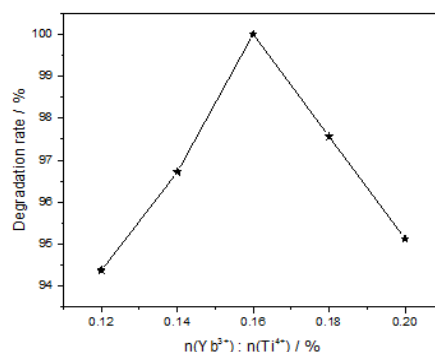


Figure. 2 Effect of ytterbium doped amount on the photocatalytic activity of $\text{TiO}_2\text{-Yb-Cu}$

The results from Figure 1 and Figure 2 showed that the degradation rate of methyl orange solution was increased with the increasing copper or ytterbium doped amount of $\text{TiO}_2\text{-Yb-Cu}$. The degradation rate of methyl orange had a maximum value when the $n(\text{Cu}^{2+})/n(\text{Ti}^{4+})$ was 0.04% or $n(\text{Yb}^{3+})/n(\text{Ti}^{4+})$ was 0.16%. Then the degradation rate gradually decreased with the increasing copper or ytterbium doped amount. Thus, the optimum doping amount of copper and ytterbium in the preparation of $\text{TiO}_2\text{-Yb-Cu}$ catalyst by microwave hydrothermal method was respectively $n(\text{Cu}^{2+})/n(\text{Ti}^{4+})=0.04\%$ and $n(\text{Yb}^{3+})/n(\text{Ti}^{4+})=0.16\%$.

Figure 3 was the infrared spectra of the $\text{TiO}_2\text{-Yb-Cu}$ and TiO_2 catalysts. The results from Figure 3 showed that the wide absorption band at 3400 nm was the stretching vibration peak of OH, 2800-3000 nm was the C-H stretching vibration peak of residual substances in the catalyst, the absorption peak at 1600 nm was the bending vibration absorption peak of OH, and the absorption peak of Ti-O was about 650 nm[8]. The result that the hydroxyl group peak of $\text{TiO}_2\text{-Yb-Cu}$ was obviously larger than that of pure TiO_2 on the surface of the catalyst could be obtained by stretching vibration peak at 3400 nm. Thus, the $\text{TiO}_2\text{-Yb-Cu}$ catalyst showed high photocatalytic activity with copper and ytterbium co-doped to improve the ability of adsorbing water[9].

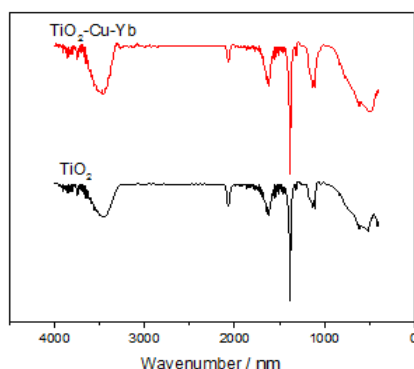


Figure. 3 The infrared spectra of $\text{TiO}_2\text{-Yb-Cu}$ and TiO_2 catalysts

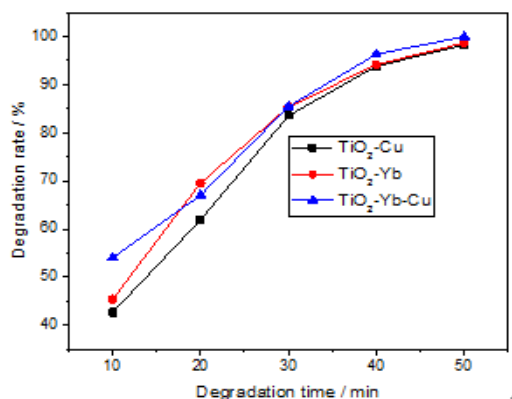


Figure. 4 The photocatalytic activity of $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-Yb}$ and $\text{TiO}_2\text{-Yb-Cu}$ catalysts

Photocatalytic Activity of Three Kinds of Doped Catalysts.

The catalytic activity of three kinds of doped catalysts $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-Yb}$ and $\text{TiO}_2\text{-Yb-Cu}$ in the degradation of methyl orange under UV irradiation was shown in Figure 4. The results from Figure 4 shown that the photocatalytic activity was increased with the reaction time gradually increased, but in the same degradation conditions the ytterbium and copper co-doped preparing $\text{TiO}_2\text{-Yb-Cu}$ catalyst for methyl orange degradation rate was higher than the single doped ytterbium or copper preparing $\text{TiO}_2\text{-Yb}$ or $\text{TiO}_2\text{-Cu}$ catalyst. The methyl orange almost could completely be degraded when the $\text{TiO}_2\text{-Yb-Cu}$ catalyst used to degrade the methyl orange solution for 50 min under the UV. The reason that the ytterbium and copper co-doped could improve the photocatalytic activity of $\text{TiO}_2\text{-Yb-Cu}$ was that the amount of Yb^{3+} incorporation on the crystallization of TiO_2 could inhibit the growth of particle size led to the catalyst had high specific surface area and the incorporation of small amounts of Cu^{2+} , due to the conduction band Cu^{2+} redox potential was higher than that of TiO_2 , so Cu^{2+} could inhibit the photogenerated electron recombination[10]. It is suggested that the ytterbium and copper co-doped could increase the photocatalytic activity of TiO_2 catalyst from the above two aspects.

The Effect of Calcining Temperature on the Photocatalytic Activity of $\text{TiO}_2\text{-Yb-Cu}$.

The effect of calcining temperature on the photocatalytic activity of $\text{TiO}_2\text{-Yb-Cu}$ was investigated under the optimum preparation conditions. The result was shown in Figure 5. The result from Figure 5 shown that the degradation rate of methyl orange increased with the calcination temperature increasing, the degradation rate reached a maximum value when the calcination temperature was 600°C , then it decreased with the calcination temperature increasing. The reason may be the non stoichiometry and lattice growth completely caused by lattice defects in lower temperature, but when the temperature was too high the catalyst caused phase transition phenomenon, these two situations could lead to a decline in the catalytic activity[11].

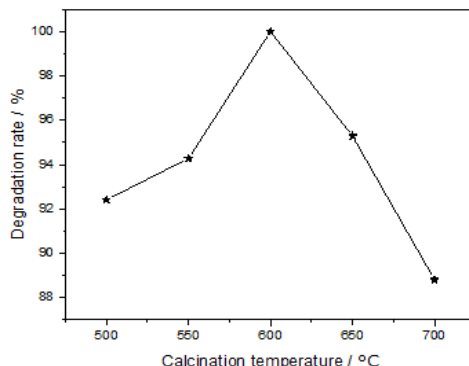


Figure. 5 The effect of calcining temperature on the photocatalytic activity of $\text{TiO}_2\text{-Yb-Cu}$

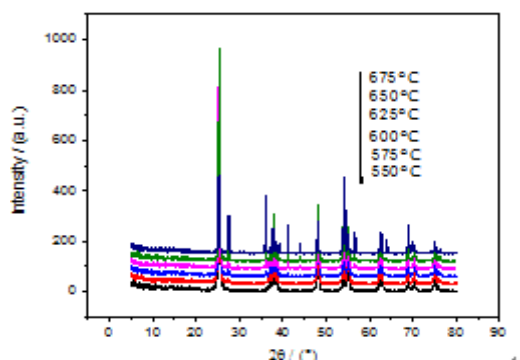


Figure. 6 XRD Spectrum of $\text{TiO}_2\text{-Yb-Cu}$ at different calcination temperatures

Figure 6 was the XRD spectrum of the $\text{TiO}_2\text{-Yb-Cu}$ catalyst at different calcination temperatures. From Figure 6, it could be seen that the phase of the catalyst was changed from anatase to rutile with the increase of calcining temperature. Jade6.5 analysis shown that the catalyst particle size was 22.41

nm and the crystallinity was 47.96 (1.42)% when the temperature was 550°C, the catalyst particle size was 24.64 nm and the crystallinity was 54.86 (1.51)% when the temperature was 575°C, the catalyst at two temperatures was only anatase phase without rutile phase. But the catalyst particle size was 23.93 nm and the crystallinity was 56.22 (1.27)% when the temperature reached 600°C, while the relative mass fraction of the anatase and rutile phase in the catalyst was respectively 99.4% and 0.60%. The diameters of the catalyst was 33.42, 40.26 and 61.41 nm, the crystallinity was 58.67 (1.44)% , 61.64 (1.33)% and 77.51 (2.21)% when the calcination temperature was respectively 625, 650 and 675°C, which the relative mass fraction of anatase and rutile phase was respectively 90.30% and 9.70%, 88.40% and 11.60% , 56.80% and 43.20%. These indicated that the catalyst had high photocatalytic activity when the mixture of anatase and rutile in TiO₂-Yb-Cu formed a mixed crystal in a certain proportion[12]. Which shown that the photocatalytic activity of the catalyst was low due to only anatase in catalyst when the calcination temperature was below 600°C. After that, the photocatalytic activity also increased with the increase of calcination temperature due to the effect of rutile. The TiO₂-Yb-Cu had high photocatalytic activity when the ratio of anatase and rutile achieved an optimal ratio. Then, the photocatalytic activity decreased with the rutile content too high.

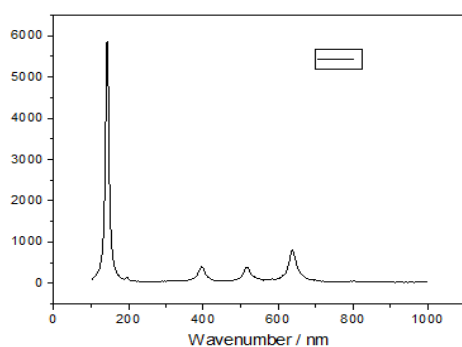


Figure. 7 Raman spectra of TiO₂-Yb-Cu catalyst

Raman Spectra of TiO₂-Yb-Cu Catalyst.

Figure 7 was the Raman spectrum of the TiO₂-Yb-Cu catalyst. The standard anatase TiO₂ catalyst belonged to the D4h point group, and its Raman spectra had active vibrational peaks respectively at 147, 198, 398, 515 and 637 nm. From Figure 7, it could be seen that the peak position of TiO₂-Yb-Cu was slightly displacement, and the peak broadening, this phenomenon was caused by the Yb³⁺ and Cu²⁺ doped TiO₂ catalyst lattice distortion and defects, so as to increase the number of surface OH. Because the OH number had an important influence on the photocatalytic activity of the catalyst, the photocatalytic activity of TiO₂-Yb-Cu increased with the number of surface OH increased.

Characterization of three kinds of doped catalyst SEM.

The SEM characterization of TiO₂-Cu, TiO₂-Yb and TiO₂-Yb-Cu was shown in Figure 8. From Figure 8, it could be seen that the particle size of TiO₂-Cu and TiO₂-Yb were not uniform and there were more obvious agglomeration (A and B), but the TiO₂-Yb-Cu had smaller particle size and particle size distribution, crystallization was higher, no obvious agglomeration (C). Therefore, the photocatalytic activity of TiO₂-Yb-Cu was higher than that of TiO₂-Cu or TiO₂-Yb[7,13].

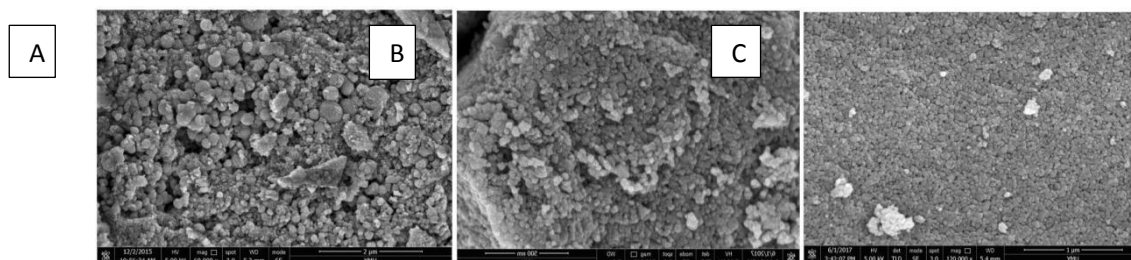


Figure. 8 SEM diagram of three doped TiO₂ catalysts

(A: TiO₂-Cu B: TiO₂-Yb C: TiO₂-Yb-Cu)

N2 Adsorption Desorption Analysis of Three Kinds of Doped Catalyst.

Table 1 was the specific surface area, pore volume and pore size data of TiO₂-Cu, TiO₂-Yb and TiO₂-Yb-Cu. From table 1, it could be found that the specific surface area, pore volume and pore size of the three kinds of doped catalysts were gradually increased, that is, TiO₂-Cu < TiO₂-Yb < TiO₂-Yb-Cu. The increase of the specific surface area, pore volume and pore size could increase the contact area of the catalyst with the pollutant, which the photocatalytic activity of the catalyst was improved. Therefore, the photocatalytic activity of TiO₂-Yb-Cu was higher than that of TiO₂-Cu or TiO₂-Yb.

| Sample | S _{BET} (m ² /g) | V _{BJH adsorption} (cm ³ /g) | V _{BJH desorption} (cm ³ /g) | D _{BJH adsorption} (Å) | D _{BJH desorption} (Å) |
|-------------------------|---|---|---|------------------------------------|------------------------------------|
| TiO ₂ -Cu | 14.8331 | 0.032997 | 0.052991 | 75.148 | 87.160 |
| TiO ₂ -Yb | 24.0657 | 0.124053 | 0.135151 | 152.835 | 126.999 |
| TiO ₂ -Yb-Cu | 27.5433 | 0.144943 | 0.151590 | 171.580 | 150.064 |

Conclusion

The best reaction conditions for preparing TiO₂-Yb-Cu catalyst by microwave hydrothermal method were n(Cu²⁺)/n(Ti⁴⁺)=0.04% and n(Yb³⁺)/n(Ti⁴⁺)=0.16%, microwave reaction temperature 120°C, reaction time 3 h, microwave power 650 W, calcination temperature 600°C, calcination time 5.5 h. The methyl orange almost could completely be degraded when the TiO₂-Yb-Cu catalyst used to degrade the methyl orange solution for 50 min under the UV.

The XRD spectrum analysis of TiO₂-Yb-Cu catalyst at different calcination temperatures showed that the catalyst had higher photocatalytic activity when the relative mass fraction of anatase phase and rutile phase was 99.4% and 0.60% respectively.

The results from the IR, SEM, XRD and Raman showed that the microwave hydrothermal preparation of TiO₂-Yb-Cu catalyst had the advantages that the particle sizes was smaller, the specific surface area, pore volume and pore size was larger, the number of surface OH was higher and the chemical properties was stable. Therefore, the photocatalytic activity of TiO₂-Yb-Cu was higher than that of TiO₂-Cu or TiO₂-Yb.

References

- [1] Z.H. Yuan, J.H. Jia and L.D. Zhang. Materials Chemistry & Physics, Vol.73 (2002) No.2, p.323
- [2] J.J. Xing, L.L. Peng and T. Lin, et al. materials science and engineering, Vol.35 (2017) No.2, p.274. (In Chinese)
- [3] J. Sun, W.J. Jiang and G.Q. Zhang, et al. molecules, Vol.27 (2013) No.6, p.566. (In Chinese)
- [4] G.Q. Zhang and X.J. Bi. chemistry, Vol.22 (2011) No.5, p.55. (In Chinese)
- [5] Y. Gong, W. Guo and G .Q. Zhang, et al. industrial catalysis, Vol.18 (2010) No.8, p.30. (In Chinese)
- [6] W.J. Jiang, J. Sun and X.J. Bi. Vol.21 (2013) No.9, p.32. (In Chinese)

- [7] M. Zhang. Preparation and Photo-catalytic Activity of Rare Earth Ytterbium and Erbium Doped TiO₂ Photo-catalysts (MS., Yunnan Normal University, China 2016), p.25. (In Chinese)
- [8] B.F. Gao, Y. Ma and Y.A. Cao, et al. chemical Acta, Vol.64 (2006) No.13, p.1329. (In Chinese)
- [9] J.H. Chen and Z.Q. Gong. Titanium dioxide semiconductor photocatalytic material ion doped. (Beijing: Science Press, China),p.5. (In Chinese)
- [10]H.Q. Jiang, P. Wang and H.Z. Xian. Journal of chemistry, Vol.64 (2006) No.2, p.145. (In Chinese)
- [11]Q.H. Zhang, L. Gao and J. Sun. Journal of inorganic materials, Vol.16 (2001) No.5, p.833. (In Chinese)
- [12]L. Chen, J. Zhu and Y.M. Liu, et al. Journal of Molecular Catalysis A Chemical, Vol.255 (2006) No.1, p.260.
- [13]Y.J. Lu, preparation of silver and SM doped TiO₂ photocatalysts and their photocatalytic activity by microwave hydrothermal method (MS., Yunnan Normal University, China 2017), p.25. (In Chinese)