

Preparation and Photocatalytic Properties of Cu-doped Nano-TiO₂/Microcrystal Muscovite Composites

Xiqiang Yuan^b, Kehui Qiu^a, Wenjian Tang^b, Qianchen Liu^b

Institute of Materials Science and Technology, Chengdu University of Technology, Chengdu 610059, P.R. China

^aqkh2188@163.com, ^byuanxi.qiang@163.com

Keywords: Microcrystal muscovite, Cu-doped, Nano-TiO₂, Photocatalytic degradation, Methylene blue.

Abstract. With microcrystal muscovite (MCM) as the carrier, butyl titanate as the source of titanium, acetic acid as the inhibitors, copper nitrate as dopant, Cu-doped nano-TiO₂/MCM composites were prepared by the sol-gel method. Then the composites were calcined at 500 °C for 2 hours. The samples were characterized by x-ray diffraction (XRD), scanning electron microscope (SEM) and DTA-TG methods. The photocatalytic activity of samples was evaluated by degradation of Methylene Blue (MB) under ultraviolet radiation (UV lamp 20 W, emission wavelength 340 nm). The experiment showed that the Cu-doped could enhance the photocatalytic degradation performance of the samples. Especially for the presence or absence of UV radiation conditions, we also researched the effect of muscovite, nano-TiO₂ and Cu-doped nano-TiO₂/MCM composites in MB solution. The results showed that the photocatalytic activity of Cu-doped nano-TiO₂/MCM composites have been significantly improved in MB solution. The degradation rate for MB solution (100 mL 5 mg/L) by Cu-doped nano-TiO₂/MCM (0.2 g, Cu/Ti molar ratios: 5%) is about 99% under UV radiation for about 6 hours at room temperature.

1. Introduction

In recent years, TiO₂ has been well known because of its nontoxicity, chemical inertness, high photocatalytic activity and low cost, and it has been widely investigated and used in many areas. TiO₂ has a significant degradation effect for organic and inorganic pollutants in the air and water, which has a broad prospect of application^[1, 2]. But the band gap of TiO₂ (E_g = 3.2 eV for anatase) is too wide, so the material is applied only under the UV light which wavelength is less than 387 nm^[3, 4]. While the absorption spectra of TiO₂ is in the UV region, so the principal deficiency is less utilization of the sun's rays. This also restricted its application in nature light condition^[5]. In order to enhance its absorption spectra in the visible light range, different elements (N, C, Cu, Fe, etc.) are employed in doping TiO₂. Now more and more people have been interested and began researching for this. Some researchers have shown that Cu-doped can lead to the absorption spectra red shift to visible light area and the catalyzer activity is enhanced^[6, 7]. Because of the price cheap, copper has great advantages in the photocatalyst modification and application.

Nano-TiO₂ particles reunion easily and have a poor dispersion during preparation and application, so it is very difficult to be separated with aqueous media after degradation^[8]. In order to improve its recycling and reuse, many researchers choose to load the nano-TiO₂ particles on various substrate, such as mica, graphite, glass, diatoms stone, fly-ash, etc^[9-12]. MCM is one kind of lamellar mineral which has high specific surface, strong adsorption and good chemical stability. All over the country, it is not only rich in mineral but also prepares processes easily^[13, 14]. So the application of MCM is more and more popular. Nowadays, it has been successfully used in the packing, paint and insulation materials^[15, 16]. The slice layer of MCM crystal can provide a smooth substrate for the nano-TiO₂ particles in this study.

2. Experimental

2.1 Materials.

The MCM used as the substrate was obtained from Sichuan xin ju Mining Co. (Chengdu, China). The diameter of the particles prepared ranged from 1-10 μm with a particle thickness less than 1 μm . The other materials used in the experiment were of analytical reagent grade. Butyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), acetic acid (CH_3COOH), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and methylene blue (MB) were obtained from Kelong Reagent Co. (Chengdu, China). All the chemicals was used without further purification. Deionized water was used throughout all the process of experiment.

2.2 Preparation of composites.

The Cu-doped nano- TiO_2/MCM were prepared by the sol-gel method. Firstly, 10 mL butyl titanate was added into 30 mL ethanol and 3 mL acetic acid used as the inhibitors under stirring for 20 min to stir evenly. Second, after mixing at room temperature, the solution that different molar ratios of copper nitrate (Cu/Ti molar ratios: 0~7%), 5 mL ethanol assembled and 2mL deionized water were added into it with a constant speed (1 mL/min) under continuous stirring. When the sol formed, MCM (TiO_2/MCM mass ratio: 50%) were added in this time. Then, it kept stirring until the formation of gel. After depositing for 24 hours, the gel were dried in the drying oven at 80°C and then ground into powers. The powers were calcined at different temperatures (450°C ~ 650°C) for 2 hours. After calcining, the Cu-doped nano- TiO_2/MCM photocatalyst was obtained.

Nano- TiO_2 and nano- TiO_2/MCM were prepared in a similar way except for adding copper nitrate or MCM.

2.3 Characterization of composites.

The crystal structure of the composites was determined by x-ray diffraction, using Cu $\text{K}\alpha$ radiation and operating at 40 kV/20 mA (DX-2700 dandong fangyuan, china); The surface morphology of MCM and Cu-doped nano- TiO_2/MCM were examined by field emission scanning electron microscope (Ultra 55, Carl Zeiss); The crystal structure transformation of nano- TiO_2 was presented by the DTA-TG (STA409PC, NETZSCH) with the heating rate of 10K/min and using air.

2.4 Photocatalytic activity of composites.

The photocatalytic reaction was conducted by the degradation of MB under UV radiation in a self-made instrument. The UV-light was provide by a 20 W UV lamp ($\lambda=340\text{ nm}$). MB was used as a target reactant. The 0.2 g photocatalyst were added into 100 mL MB (5 mg/L) under the magnetic stirring in the self-made instrument. At a specific time interval, 10 mL solution was taken out and centrifuged at 4000 r/min for 5 min. Then the photocatalysis effect for MB was tested by ultraviolet and visible spectrophotometer (UV-2100, Unico, China) at 665 nm. Comparative trials were carried out under the same condition by nano- TiO_2 and nano- TiO_2/MCM . The degradation ratio of the reactant can be calculated by Lambert-BeerLaw^[17]:

$$D = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where D is the degradation ratio, C_0 is the initial concentration and C_t is the concentration in different time.

3. Results and discussion

3.1 SEM analysis of composites.

The SEM micrographs (Fig.1) show the surface morphologies of unloaded MCM and Cu-doped nano- TiO_2/MCM composites. It can be seen from Fig.1a that the MCM has a layer structure and smooth surface. Fig1b shows that Cu-doped TiO_2 particles formed a dense coating on the surface of MCM. Most of the TiO_2 nanoparticles on the surface of MCM distribute relatively dispersion and

MCM provides a better carrier for Cu-doped TiO₂ nanoparticles. In addition, the main structure of MCM is kept perfectly after Cu-doped TiO₂ loaded. It can effectively suppresses the reunion of TiO₂ nanoparticles and improve photocatalytic performance.

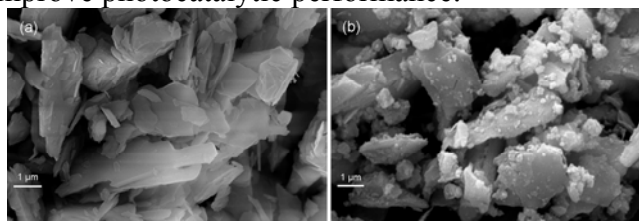


Fig.1. SEM micrographs of MCM and Cu-doped nano-TiO₂/MCM: (a) MCM, (b) Cu-doped nano-TiO₂/MCM.

3.2 DTA-TG analysis of TiO₂.

To investigate the crystalline phases of TiO₂, the test result is shown in Fig.2. Firstly, with the temperature increasing, there is a big slope in the TG curve. Because the adsorption water and residual organic begin to lose and decompose in this time. Second, when the temperature is above 400 °C, two peaks can be seen at 410.5 °C and 507.9 °C in the DTA curve. It may be that the TiO₂ begin to turn into anatase at 410.5 °C. At the same time, the TG curve tend to be stable. It proves that organic materials and adsorption of water has lost completely at this time. At 507.9 °C, the peak means that anatase starts to change into rutile. So the preparation temperature of the photocatalyst can be considered from 450 °C to 550 °C.

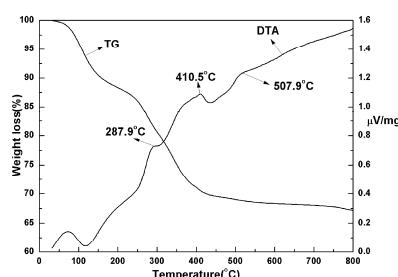


Fig.2. DTA-TG curves of nano-TiO₂.

3.3 XRD analysis of composites.

The XRD patterns of Cu-doped TiO₂/MCM composites after calcination at 450 °C~650 °C with the same amounts of dopant (Cu/Ti molar mass: 1%) are shown in Fig.3. In this study, the anatase has appeared peak ($2\theta = 25.48^\circ$) at 450 °C. It agrees with the peak at 410.5 °C in Fig.2 that the TiO₂ begin to turn into anatase. With the temperature increasing, the anatase grows more and more completely. At the same time, the anatase content and crystal size keep increasing. The XRD patterns at 500 °C have appeared a weak peak of the rutile, indicating that the parts of TiO₂ have transformed from anatase to rutile. The result is in good agreement with the report at 507.9 °C in Fig.2 analysis. More and more anatase change into rutile with the temperature rise. At 650 °C, the characteristic peak of rutile (27.6°) has become more obviously and the peak of anatase (25.48°) is going to disappear. In order to ensure the best temperature of the anatase, the photocatalytic performance of samples are tested at the following experiment.

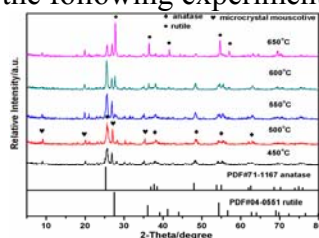


Fig.3. XRD patterns of composites with different temperatures.

3.4 Influence of temperature to Photocatalytic degradation.

Fig.4 shows photocatalytic degradation for MB by Cu-doped nano-TiO₂/MCM composites in different temperatures (450 °C~650 °C, Cu/Ti molar mass 1%). With the temperature increasing, the photocatalytic degradation rate is gradually rise. At 500 °C, it reaches the best (92.53%) in this experiment. When temperature less than 500 °C, the anatase growth is not complete. However, while temperature is over 500 °C, more anatase begins to turn into rutile. That also can be seen from the rutile percentage curve in Fig.4. The anatase and rutile phase content in crystalline TiO₂ powder are calculated using the integral area percentage of the (1 0 1) reflection and the (1 1 0) reflection of rutile in the XRD. From Fig.4, we also can see that the rutile phase content is increasing with the temperature rise. Some researchers have shown that photocatalytic degradation of anatase is better than rutile^[18]. In addition, Bin Wang and Fernanda Condi de Godoi have reported that TiO₂ synthesized in a relatively appropriate anatase/rutile mixing ratio of 90/10 can achieve the preferable photocatalytic efficiency^[19]. So according to the results of the Fig.2 and Fig.3, it can conclude the best temperature is 500 °C.

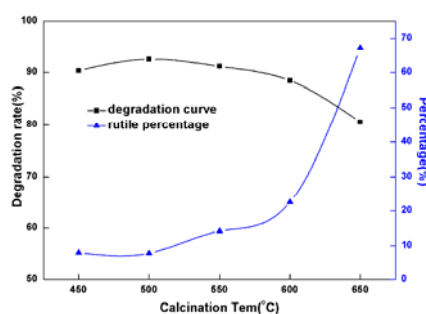


Fig.4. Photocatalytic degradation rate of Cu-doped nano-TiO₂/MCM in different temperatures and rutile percentage.

3.5 Influence of copper doping to Photocatalytic degradation.

According to the result of 3.4, we choose 500 °C calcined to analysis the influence of copper doping to photocatalytic degradation. Fig.5 shows the XRD patterns of Cu-doped nano-TiO₂/MCM with different doping amounts. With the concentration of Cu-doped increasing, the peak (1 0 1) of anatase is enhanced obviously. However, while the concentration is over 5%, the diffraction peaks broaden and peak intensities decline that is caused by the variation of interplanar distance. This shows that the copper doping can affect the crystallinity and growth of anatase. According to the JCPDS (71-1167) of anatase, the peak of anatase has a weak shift. Furthermore, it also can be seen that the interplanar distance (d) is gradually increased in the Table 1 (the lattice parameters are calculated using the Jade 5.0 software). It means that some copper ions come into the crystal lattice of anatase. Because Cu²⁺ ionic radius (0.087 nm) is bigger than that of Ti⁴⁺ (0.074 nm), which will cause the lattice distortion and the variation of interplanar distance. In addition, we can not find the peak of copper oxide. The reason also may be that many copper ions successfully incorporate into TiO₂ lattice or the Cu-doped amount is too low. Based on this analysis, it can know that the copper ions successfully infiltrate into TiO₂ lattice.

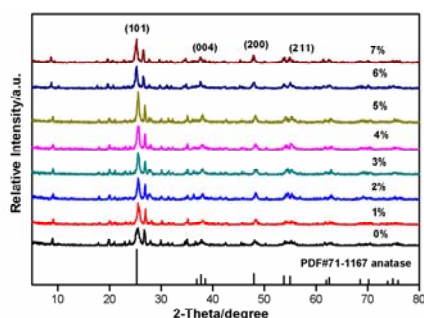


Fig.5. XRD patterns of Cu-doped nano-TiO₂/MCM with different doping amounts at 500 °C.

Table 1 Crystallographic data for Cu-doped nano-TiO₂/MCM with different doping amounts at 500 °C.

Doping content	Diffraction angle 2θ (1 0 1) / (°)	Interplanar distance (d)	Rutile percentage/%
0%	25.383	3.4830	10.5
1%	25.629	3.4832	9.01
2%	25.581	3.4833	9.56
3%	25.543	3.4836	10.23
4%	25.567	3.4838	9.64
5%	25.543	3.4896	9.06
6%	25.201	3.5130	9.95
7%	25.158	3.5374	10.36

Fig.6 shows the UV-vis absorption spectra of undoped and copper doped composites after being calcined at 500 °C. It can be seen that the absorption edge of copper doped composite red-shift to 415 nm. According to the equation: $\lambda_{\max} = hc/E_g$, the band gap energy of material can be calculated. The band gap energy of N-doped composites is 2.99 eV which is less than that of pure TiO₂ ($E_g = 3.2$ eV). The result means that copper ions may substitute lattice Ti⁴⁺ so that it causes the lattice distortion and suppress the recombination of electrons and holes. It obvious copper doping narrowed the band gaps of the composites. So copper doping can improve the photocatalytic activity of the samples.

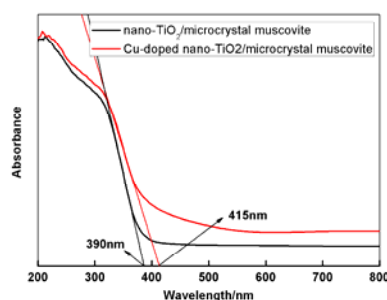


Fig.6. UV-vis absorption spectra of undoped and copper doped composites.

To investigated the influence of copper doping content (Cu/Ti molar mass: 0~7%) on the photocatalytic degradation rate, the result is shown in Fig.7. It can be seen that the photocatalytic degradation rate increases with copper concentration from 0% to 5%. Because the copper can accept the electron, it represses the electron-hole recombination. Therefore Cu-doped enhances the photocatalytic degradation of samples. However, when concentration is over 5%, the degradation rate begins to decrease. There may be that the Cu-doped amount is too high and redundant copper deposits the surface of the TiO₂. It can block the transfer of energy and affects electron-hole separation. The study has found that there is a optimal value about metal ion doping^[20]. From Fig.6, we also know that the relative content of anatase and rutile has not change much. So the Cu-doped do not affect the transform of between anatase and rutile. This can be sure that the optimal concentration is 5% in this study.

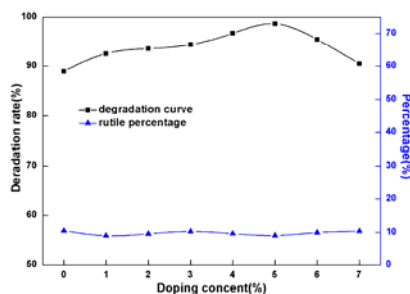


Fig.7. Photocatalytic degradation rate of Cu-doped nano-TiO₂/MCM with different doping amounts and rutile percentage.

3.6 Photocatalytic performance of Cu-doped TiO₂/MCM compared with other samples.

According to the conclusions in the 3.4 and 3.5, we choose the temperature 500 °C and molar mass 5% to compare with other samples, and the result is shown in Fig.8. It illustrates the influence of UV-light and MCM to degrade MB in Fig.8a and b. Among them, (a) indicates that UV-light on the degradation of MB solution has a certain effect. With the time going on, the degradation rate of MB increases weakly. At the 6 hours, it almost approaches 15%. In the (b), the MCM has a certain adsorption to the MB without UV radiation in the dark. Furthermore, the adsorption reaches balance about 2 hours and the saturated adsorption rate closes to 50%. In the Fig.8c and d, it shows the difference of the degradation rate by nano-TiO₂ and Cu-doped TiO₂/MCM composites with and without UV radiation. In the (c), it shows that both nano-TiO₂ and Cu-doped nano-TiO₂/MCM have the degradation for MB solution without UV radiation. Furthermore, the degradation rate of nano-TiO₂ is close to about 40% at 6 hours. However, due to the interactions between the degradation of nano-TiO₂ and MCM adsorption, the degradation rate by Cu-doped nano-TiO₂/MCM is more better than the nano-TiO₂' degradation rate. Compared with the degradation of nano-TiO₂, the adsorption of MCM for MB solution is as primary. From (d), we can see the degradation rate of MB by different samples with UV radiation. With the UV radiation, the degradation rate of them have been a significant improvement and the Cu-doped nano-TiO₂/MCM is especially evident. When the time is 6 hours, the degradation rate is almost 99% more than nano-TiO₂ (76.86%) and nano-TiO₂/MCM (88.95%). It means that the UV radiation greatly improved the photocatalytic activity of Cu-doped nano-TiO₂/MCM and the copper doping played a certain part in the degradation. The nano-TiO₂ can create pairs of electrons and holes under UV radiation. The hole in the valence band has a strong oxidation ability. The H₂O and OH⁻ on the surface of the TiO₂ can be oxidized to ·OH. Besides, electrons can combine with O₂ to make ·O₂⁻, and it produce OH⁻, ·OH and O₂ in final. So most of the organic matter in the MB can be rapidly decomposed into CO₂, H₂O and other nontoxic substances^[21]. Furthermore, copper ions can suppress the recombination of electrons and holes. This suggest that the UV radiation and copper doping increase greatly the degradation rate of samples for MB solution.

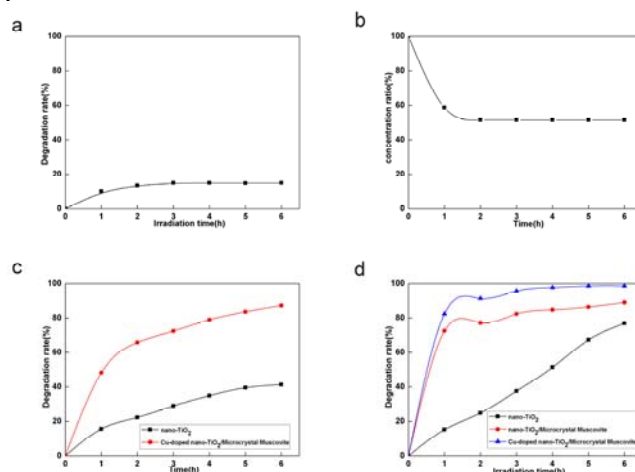


Fig.8. Adsorption and photocatalytic degradation for MB by the different samples

4. Conclusion

With MCM as the carrier, butyl titanate as the source of titanium, acetic acid as the inhibitors, copper nitrate as dopant, Cu-doped nano-TiO₂/MCM composites were prepared by the sol-gel method. The photocatalytic experimental results reveal that the materials obtained have an excellent photocatalytic activity for the degradation of MB. The doped copper ions can promote the photocatalytic activity of the sample. The copper ions can come into the crystal lattice to cause the lattice distortion and the variation of interplanar distance. MCM is a good carrier material for

nano-TiO₂ due to its slice layer structure, good adsorption and chemical stability. The Cu-doped nano-TiO₂/MCM may be a potential photocatalytic materials.

Acknowledgments

This work presented herein would not be possible without the Key Scientific and Technological Research and Development Program (Grant no. 2014GZ0089) in Sichuan Province, PR China. We would like to acknowledge them for the financial support.

References

- [1] X.B. Chen and S.S. Mao: Chemical Reviews. Vol. 107 (2007) No.7, p. 2891.
- [2] W. Mekprasart, W. Pecharapa: *Eco-Energy and Materials Science and Engineering Symposium*, Vol. 9, (2011) p. 509.
- [3] G.T. Yan, M. Zhang, J. Hou and J. J. Yang: Materials Chemistry and Physics. Vol. 129 (2011) p. 553.
- [4] S.Z. Hu, F.Y. Li and Z.P. Fan: Journal of Hazardous Materials. Vol. 196 (2011) p. 248.
- [5] M.M. Joshi, N.K. Labhsetwar, P.A. Mangrulkar, S.N. Tijare, S.P. Kamble and S.S. Rayalu: Applied Catalysis A: General. Vol. 357 (2009) p. 26.
- [6] Y Chen, L.L Sun and N.N Sun: Materials Review. Vol. 27 (2013) No.4, p. 135.
- [7] Jeon M K, Park J W and Kang M: Journal of Industrial and Engineering Chemistry. Vol. 13 (2007) p. 84 .
- [8] K.J. Xu, Z.Z. Yang and S.H. Dong: Journal of The Chinese Ceramic Society. Vol. 37 (2009) No.8, p. 1361
- [9] M.F. Huang, Z.X. Zheng and G.Q. Xu: Journal of The Chinese Ceramic Society. Vol. 12 (2007) No.1, p. 25 .
- [10] K.I. Shimizua, H.Murayamab, A.Nagaic and A.Shimada: Environmental. Vol. 55 (2005) p. 142.
- [11] P.W. Huo, Y.S. Yan, S.T. Li, H.M. Li and W.H. Huang: Applied Surface Science. Vol. 256 (2010) p. 3381 .
- [12] L.J. Wang, S.H. Zheng and W.J. Tian: Journal of The Chinese Ceramic Society. (2008) No.36, p. 1645.
- [13] Y.Y. Mao and L.M. Fan: Journal of Chengdu University of Technology. Vol. 27 (2000) No.suppl p. 98.
- [14] Y.Y. Mao and L.W. Hou: *J. China. Part*. Vol. 8 (2002) No.2, p. 42.
- [15] Petr Kalenda, Andréa Kalendová and Václav Štengl: Progress in Organic Coatings. Vol. 49 (2003) p. 138.
- [16] Z.M. Liang, W.J. Xu and Y.Y. Mao: China Non-Metallic Mining Industry Herald.(2003) No.4, p. 36.
- [17] T. Kondo, K. Shindo, M. Arakawa and Y. Sakurai: Journal of Alloys and Compounds. Vol. 375 (2004) p. 284.
- [18] W. Gao, F.Q. Wu and Z. Luo: Chemical Journal of Chinese Universities. Vol. 22 (2001) No.4, p. 660.
- [19] B.Wang, Fernanda Condi de Godoi, Z.M. Sun, Q.C. Zeng, S.L. Zheng, Ray L. Frost: Journal of Colloid and Interface Science. Vol. 438 (2015) p. 204.

- [20] Richardson PL and Perdigoto MLN: Applied catalysis B: Environmental. Vol. 126 (2012) p. 205.
- [21] K.H. Qiu, Y.M. Wang, P.C. Zhang and Y. Liu: Journal of Mineralogy and Petrology. Vol. 28 (2008) N0.4, p. 13.