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Preparation of Cu Doped TiO_2 Photo-catalyst by Microwave Hydrothermal Method and Study on Its Photo-catalytic Activity

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Abstract. The Cu doped TiO_2 photo-catalyst TiO_2-Cu was prepared by microwave hydrothermal method(MHM) and its photo-catalytic degradation activity in the microwave radiation and ultraviolet irradiation (MW-UV) was investigated. The best conditions of preparing TiO_2-Cu were obtained by optimizing the reactive condition. The structure of TiO_2-Cu was characterized by IR, XRD, SEM, AFM, RS and FS. The results showed that the MHM preparation of TiO_2-Cu had the structural characteristics of small particle size and lower fluorescence intensity which could effectively inhibit the recombination of photo-generated electron hole, thereby the TiO_2-Cu had higher photo-catalytic degradation activity. The methyl orange was almost degraded completely when the TiO_2-Cu prepared with the optimum condition was used to degrade methyl orange for 50 min under MW-UV.

Introduction

Semiconductor TiO_2 has been in the core position of photo-catalysis research and widely used in the field of photo-catalytic degradation of inorganic and organic pollutants because of its chemical stability, high catalytic activity, strong oxidation ability, non-toxic characteristics[1]. The research results show that the photo-catalytic activity of TiO_2 is not high under visible light, but doping can improve the photo-catalytic activity of TiO_2[2-4]. The doping of metal ions can inhibit the recombination of photo generated carriers, thus enhancing the photo-catalytic activity of TiO_2[5]. Cu^{2+} in TiO_2 can increase the photo-current under UV and capture the photo generated electrons, this process to improve the separation of photo generated carriers, reducing the recombination velocity of photo generated carrier. At the same time, this characteristic of Cu^{2+} enhances the generation of HO- in the solution, thus enhancing the photo-catalytic activity of TiO_2.

In our research group, the MHM was applied to the preparation of doped TiO_2 photo-catalyst in order to further improve its photo-catalytic activity[6-7]. The previous reported the photo-catalytic activity of TiO_2-Er prepared by the MHM[8]. Through a comparative study we found that it has larger surface area and pore volume, stimulated can emit strong fluorescence characteristics and higher photo-catalytic activity. In this paper, the based on research work of photo-catalytic activity for the TiO_2-Cu prepared by the sol-gel process, the catalyst prepared by the MHM is continually researched so as to further improve the catalytic performance of doped TiO_2 photo-catalyst. And more to explore the relationship between the catalyst structure and its photo-catalytic activity, the structure testing and characterization analysis are carried for TiO_2-Cu photo-catalyst.

Experimental Section

Experimental Reagents and Instruments. Concentrated nitric acid, anhydrous alcohol, titanic acid four butyl ester, copper nitrate, XH-800S microwave hydrothermal parallel synthesis, SX-4-10 high temperature box resistance furnace.

Preparation of TiO_2-Cu Catalyst. The copper nitrate with titanic acid four butyl ester according to n (Cu^{2+}) /n (Ti^{4+}) =0.08% dissolved in 18 ml PH solution of A in dilute nitric acid 2-3, Taking

17.5 ml of absolute ethanol, stirred 10 min, add 3.4 ml of titanic acid four butyl ester four n-butyl ester to form solution B, dropping the A solution into the B solution and stirred for 10 min. In the microwave water heat parallel synthesis instrument, after reaction for a period of time, washing, filtering, drying and drying in a high temperature box type resistance furnace, dried and calcined, the TiO_2-Cu catalyst is obtained.

Catalytic Activity Test of TiO_2-Cu Catalyst. The catalytic activity test methods for TiO_2-Cu catalysts refer to the references [9].

Results and Discussion

Effect of Copper Doping Content on Catalytic Activity. The ratio of copper to titanium is n (Cu^{2+}) /n (Ti^{4+}) =0.08%. The temperature of the parallel synthesizer is 160 ℃, the time is 3.5 h, the power is 600 W. The high temperature box type resistance furnace is set at 600 ℃ and the time is 3 h. The maximum degradation rate of 50 ml methyl orange (10 mg/L) is 98.26% for the TiO_2-Cu in UV. The IR is shown in Fig. 1 for the TiO_2-Cu prepared under the optimum conditions and compared with the pure TiO_2 catalyst.

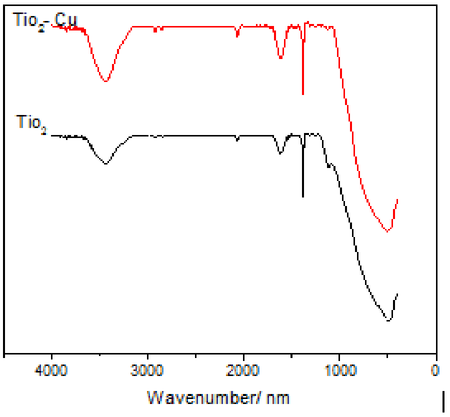

Fig. 1 IR of TiO_2-Cu and TiO_2

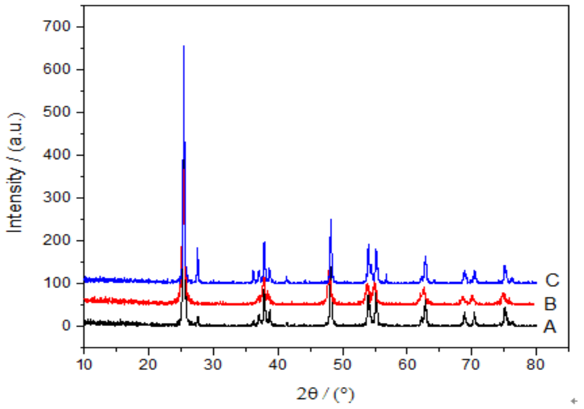

Fig. 2 XRD of TiO_2-Cu prepared by different calcination time（A: 2.5 h B: 3 h C: 3.5 h）

Effect of Calcination Time on Catalytic Activity. Fig. 2 shows the XRD spectra of TiO_2-Cu prepared at different calcination times. Through the analysis of the jade 6.5 TiO_2-Cu calcined 2.5 h containing anatase (PDF#: 83-2243) and rutile (PDF# 34-0180), whose diameter is 31.42 nm, the peak at 25.37 °as a amorphous phase, the crystallization degree is 54.16%, the relative content of anatase is 99.4%, the relative mass fraction of rutile is 0.60%. TiO_2-Cu calcined at 3.5 h, which contained anatase (PDF#: 83-2243) and rutile (PDF#: 87-0920), the particle size is 38.88 nm, the peak at 25.38 °as a amorphous phase, the crystallization degree is 56.58%, the relative content of anatase is 91.0%, the relative mass fraction of rutile is 9.0%. This can be obtained by the TiO_2-Cu prepared in the system when the relative mass fraction of rutile was between 0.60% ~ 9.0% and the relative mass fraction of anatase was between 91.0% ~ 99.4%, and more the TiO_2-Cu catalyst has a higher photo-catalytic activity.

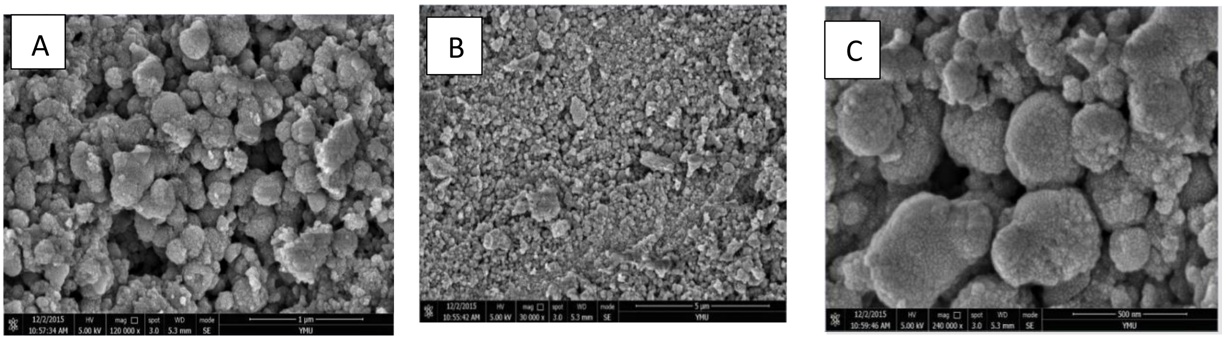

Fig. 3 SEM diagram of TiO_2-Cu（A:3000 B:12000 C:24000）

Scanning Electron Microscope. Fig. 3 shows SEM image of TiO_2-Cu catalyst in different magnification. By direct observation of the morphology of SEM TiO_2-Cu spherical catalyst has some agglomeration, which is due to grinding before sintering is not sufficient, calcination area is uneven and the heating rate leads to different [10]. However, the TiO_2-Cu catalyst is spherical or ellipsoidal in shape and smaller in size, increasing its specific surface area to make it more fully contact with methyl orange, thereby enhancing photo-catalytic activity.

Atomic Force Microscope. Fig. 4 shows TiO_2-Cu catalyst AFM. The TiO_2-Cu structure is observed by AFM diagram, and the structure is dominated by mutual torsion. Many small bulges appear on the surface, which is due to the smaller size of the TiO_2 particles and the loose and uniform distribution, which is consistent with the results of the SEM test. The particle size of the TiO_2-Cu is slightly smaller than the particle size calculated by XRD, probably due to the average particle size calculated by XRD, while AFM is only the apparent appearance of the sample[11]. This structural feature improved its stability in organic solvents, with smaller particle size and increased specific surface area. Therefore, its photo-catalytic activity was enhanced.

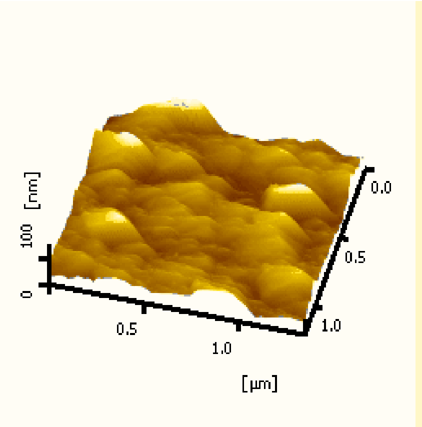

Fig. 4 AFM diagram of TiO_2-Cu

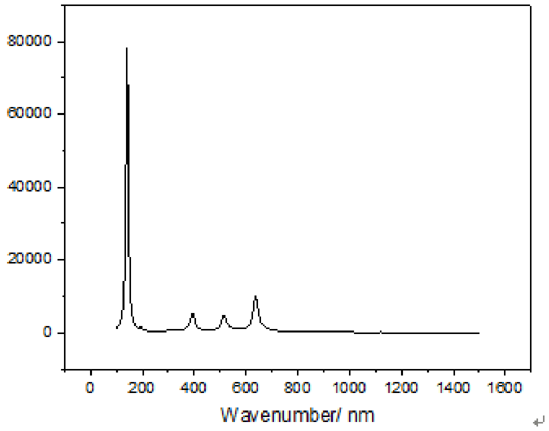

Fig. 5 Raman spectra of TiO_2-Cu

Raman Analysis. Fig. 5 shows the Raman spectrum of TiO_2-Cu catalyst. It can be clearly seen that the anatase peak of 150~200 nm and the rutile peak of 400~650 nm are especially obvious, and the peak height is very strong in TiO_2-Cu. The pure TiO_2 at about 700 ℃will be rutile[12], and TiO_2-Cu calcination temperature is 600 ℃, thus promote the copper doped TiO_2-Cu crystal to the transformation of rutile and have rutile at the low temperature. Because the structure of anatase and rutile is different, the presence of the two can lead to more defects, which is beneficial to the separation of photo generated electron hole, thus enhancing the photo-catalytic activity of TiO_2-Cu[13]. The strong absorption peaks in the visible region of 550 ~750 nm, which is due to the resonance absorption band of copper doped anatase TiO_2, and the absorption band in the UV region, that broaden the absorption range of copper doped TiO_2, so as to improve the catalytic activity of TiO_2 catalyst under visible light.

Fluorescence Spectrum Analysis. Fig.6 shows the fluorescence spectra of TiO_2-Cu and pure TiO_2 catalysts (excitation wavelength is 205 nm). From Fig. 6, we can see that between 250~600 nm, TiO_2 and TiO_2-Cu have a wide diffraction peak and similar shape, but the peak intensity of TiO_2-Cu is lower than TiO_2. This shows that copper doped does not cause new luminescence, mainly affecting the fluorescence intensity. In general, the lower the PL spectrum intensity, the lower the recombination probability of photo generated electron hole pairs. Therefore, the TiO_2-Cu catalyst inhibited the recombination of photo generated electron hole pairs, promoted the separation of electron hole and enhanced its photo-catalytic activity.

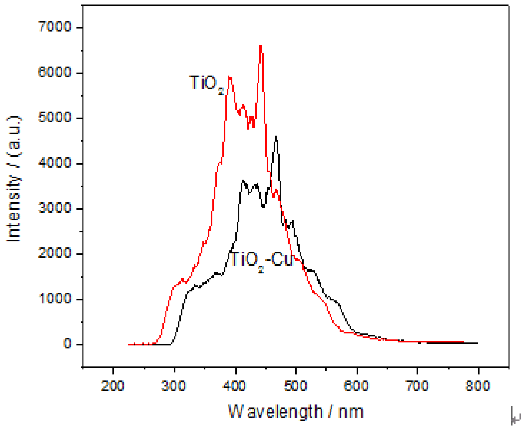

Fig. 6 Fluorescence spectra of pure TiO_2 and TiO_2-Cu

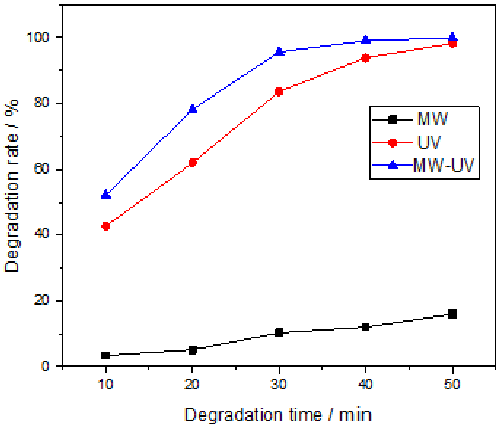

Fig. 7 Effect of degradation time on photo-catalytic activity of TiO_2-Cu under different conditions

MW, UV and MW-UV Degradation. Fig. 7 shows the influence of the degradation time on the photo-catalytic activity of TiO_2-Cu under the three conditions of MW, UV and MW-UV. It can be clearly seen that the degradation rate of TiO_2-Cu to methyl orange was only 15.98% at 50 min in the case of only MW and may reached 98.26% in 50 min by UV, but the degradation rate can reached almost 100% in 50 min with MW-UV. The research group reported the photo-catalytic activity of TiO_2-Cu prepared by sol-gel method, the degradation rates were respectively 3.78%, 92.98% and 98.39% under MW, UV and MW-UV when the degradation time is 2 h[9]. When the other degradation conditions are the same, by contrast, the degradation rate of methyl orange was respectively 15.98%, 98.26% and almost 100% for the TiO_2-Cu prepared by the MHM with MW, UV and MW-UV for 50 min. This shows that the TiO_2-Cu prepared by the MHM has higher photo-catalytic activity than the TiO_2-Cu prepared by sol-gel process, and more MHM does not need to join the ionic liquid as the reaction medium. Therefore, the MHM has the advantages of simple and fast operation, no pollution etc.

Conclusion

(1) TiO_2-Cu catalyst has higher photo-catalytic activity when it is prepared by the MHM. The optimum conditions of the MHM are copper and Ti molar ratio of n (Cu^{2+}) /n (Ti^{4+}) =0.08%, reaction temperature 160 ℃, reaction time 3.5 h, calcination temperature of 600 ℃, calcination time 3 h. The methyl orange almost completely degraded by MW-UV irradiation 50 min for TiO_2-Cu prepared under the best conditions.

(2) By IR, XRD, SEM, AFM, PL and RS characterization analysis of TiO_2-Cu prepared with the MHM, we find that it has smaller particle size, agglomeration decreased and increased the specific surface area and other characteristics, which can effectively inhibit the recombination of photo generated electron hole, as a result the photo-catalytic activity is higher.

(3) XRD data analysis shows that the photo-catalytic degradation activity of TiO_2-Cu catalyst is higher when the relative mass fraction of TiO_2-Cu catalyst rutile in 0.6% ~ 9.0%, the relative content of anatase in 9.0% ~ 99.4%.

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