

# Degradation of methyl orange using $\text{FeVO}_4\text{:Cu}^{2+}$ as photocatalyst

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**Abstract.** Nanosize Cu-doped  $\text{FeVO}_4$  was prepared by microwave-assisted method and was used as photocatalyst in the degradation of simulated wastewater like methyl orange. The effects of light intensity, amounts of  $\text{H}_2\text{O}_2$  and  $\text{FeVO}_4\text{:Cu}^{2+}$  on the degradation efficiency were studied. The result showed that under the optimized conditions, with an 800w xenon lamp, 0.09g of  $\text{FeVO}_4\text{:Cu}^{2+}$  and 0.3mL of 3% $\text{H}_2\text{O}_2$ , the degradation rate of methyl orange (30mL, 10mg/L) reached 94% after 180 min of viable light irradiation.

## 1. Introduction

Since 1972 when Fujishima and Honda first used  $\text{TiO}_2$  as photocatalyst in the decomposition of water[1], photocatalytic materials and technologies have attracted ever-increasing attention. The most commonly used  $\text{TiO}_2$  belongs to invisible UV light catalyst, which only takes advantage of 4% of the solar energy resources, while 43% of the visible light cannot be utilized[2]. Therefore, it is urgent for scientists to search ways to expand the spectral response of photocatalysts. Doping UV-responsible catalysts with different metal ions is one of the ways[3]. At the same time, people are taking more efforts in developing visible light catalysts. In recent years, many new narrow band gap catalysts have been studied, including  $\text{BiVO}_4$ [4],  $\text{Ag/AgBr}$ [5],  $\text{BiFeO}_3/\text{TiO}_2$ [6], etc.  $\text{FeVO}_4$  is a novel photocatalytic semiconductor for visible light response, which can be used for photodegradation of organic pollutants [7]. There are four types of crystal form for  $\text{FeVO}_4$ [8,9] : triclinic, orthogonal (I), orthogonal (II) and monocline, in which the triclinic type can be prepared under normal pressure, while the other three are prepared under high pressure conditions. The band gap of the triclinic  $\text{FeVO}_4$  is about 2.24eV, which is better for visible light response [10], however, its catalytic efficiency is not high enough.

In order to enhance the photocatalysis of  $\text{FeVO}_4$ ,  $\text{FeVO}_4$  and  $\text{Cu}_3(\text{VO}_4)_2$  were prepared by the microwave method, and mixed in certain proportion and calcined in high temperature to get Cu-doped  $\text{FeVO}_4$  ( $\text{FeVO}_4\text{:Cu}^{2+}$ ). Through the degradation of methyl orange, the photocatalytic performance of  $\text{FeVO}_4\text{:Cu}^{2+}$  was investigated, and the photocatalytic enhancement mechanism was analyzed.

## 2. Experimental

### 2.1. Reagents and Instruments

$\text{NH}_4\text{VO}_3$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , anhydrous ethanol, methyl orange and all other chemicals were of analytical grade and used without further purification.



The crystalline phases of the sample powders were analyzed by X-ray diffraction (TD-3500X XRD, China) with the diffraction angles ranging from  $10^\circ$  to  $70^\circ$ . The microstructural morphologies of the samples were analyzed by scanning electron microscopy (SU8010 FE-SEM, Hitachi, Japan). Diffuse reflectance spectra were obtained on a UV-Vis spectrophotometer (V-650 Jasco, Japan) equipped with a diffuse reflectance accessory.

## 2.2. Synthesis of $\text{FeVO}_4\cdot\text{Cu}^{2+}$ Photocatalysts

The Cu-doped  $\text{FeVO}_4$  samples were prepared as follows, 7.5 mmol  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  was dissolved in 25 mL deionized water to form solution A; 7.5 mmol  $\text{NH}_4\text{VO}_3$  was dissolved in 25 mL deionized water at  $70^\circ\text{C}$  to form solution B. Solution A was added slowly into solution B, and the mixture was vigorously stirred for 30 min until all the reagents were homogeneously dispersed. The mixture was transferred to a 100 mL three-necked flask, treated in a 600 Watt microwave oven at  $100^\circ\text{C}$  for 6 min. The precipitates were filtered, and washed repeatedly with deionized water and anhydrous ethanol, and dried at  $80^\circ\text{C}$  for 4h. Based on  $n(\text{Cu})/n(\text{V})=3:2$ ,  $\text{Cu}_3(\text{VO}_4)_2$  precursor was prepared according to the same preparation procedure as  $\text{FeVO}_4$ . Finally,  $\text{FeVO}_4$  and  $\text{Cu}_3(\text{VO}_4)_2$  precursors were mixed at a 10:1 weight ratio and calcined at  $550^\circ\text{C}$  for 2h to give  $\text{FeVO}_4\cdot\text{Cu}^{2+}$ .

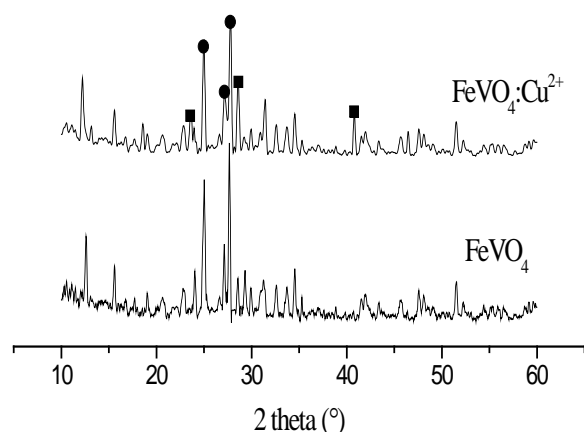
## 2.3. Degradation of Methyl Orange

The photocatalytic activities of the  $\text{FeVO}_4\cdot\text{Cu}^{2+}$  catalysts for methyl orange were evaluated under visible light irradiation using a 1000 W Xe lamp as the light source. The photocatalytic reaction were conducted as follows: 30 mL of 10 mg/L methyl orange was placed in a quartz tube, and mixed with 90 mg of  $\text{FeVO}_4\cdot\text{Cu}^{2+}$  and 0.3 mL of 3%  $\text{H}_2\text{O}_2$ . Before Xe lamp irradiation, the suspension was stirred in dark for 20 min to achieve the adsorption-desorption equilibrium between the catalyst and dye. 5 mL of the suspension was removed and centrifuged to remove the photocatalyst for analysis every 20min. The concentration of the remaining dye was determined by UV-Vis spectroscopy at 462 nm.

## 3. Results and Discussion

### 3.1. XRD Characterization

Figure 1 shows XRD patterns of  $\text{FeVO}_4$  and  $\text{FeVO}_4\cdot\text{Cu}^{2+}$  photocatalysts. As is seen, the strongest peaks of the as-prepared  $\text{FeVO}_4$  fully accord with JCPDS card No.38-1372, which is the characteristic XRD pattern of triclinic  $\text{FeVO}_4$ , and no other impurity peaks are found. The XRD pattern of  $\text{FeVO}_4\cdot\text{Cu}^{2+}$  is similar to that of  $\text{FeVO}_4$ , meaning the successful doping of Cu into the crystal of  $\text{FeVO}_4$ . Some new XRD peaks ascribe to  $\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$ , accounting for some impurity existed. Based on the calculation of Jade software, the average grain size of  $\text{FeVO}_4\cdot\text{Cu}^{2+}$  is 80.6 nm, which is larger than that of pure  $\text{FeVO}_4$ .

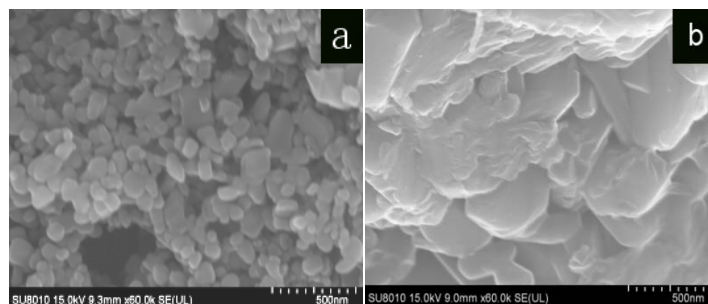


**Figure 1.** XRD patterns of pure  $\text{FeVO}_4$  and  $\text{FeVO}_4\cdot\text{Cu}^{2+}$

●  $\text{FeVO}_4$     ■  $\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$

### 3.2. SEM Characterization

Figure 2a shows the SEM image of  $\text{FeVO}_4$  photocatalyst. The  $\text{FeVO}_4$  particles are much uniform and compact, with an irregular shape and 50-100 nm of particle sizes. Figure 2b shows the SEM image of  $\text{FeVO}_4:\text{Cu}^{2+}$ . As is seen, the morphology of  $\text{FeVO}_4:\text{Cu}^{2+}$  is also irregular, but quite different from that of  $\text{FeVO}_4$ . The particles are accumulated into a kind of fluffy and honeycomb state. The grain size of  $\text{FeVO}_4:\text{Cu}^{2+}$  varies from 200 nm to 300 nm, larger than that of pure  $\text{FeVO}_4$ .

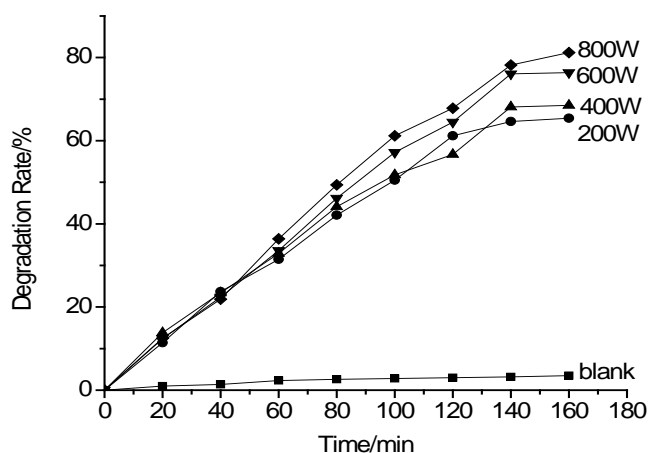


**Figure 2.** SEM images of  $\text{FeVO}_4$  and  $\text{FeVO}_4:\text{Cu}^{2+}$

(a)  $\text{FeVO}_4$  (b)  $\text{FeVO}_4:\text{Cu}^{2+}$

The band gaps ( $E_g$ ) of  $\text{FeVO}_4$  and  $\text{FeVO}_4:\text{Cu}^{2+}$  were obtained based on UV-Vis DRS spectra. The  $E_g$  of  $\text{FeVO}_4$  is about 2.24 eV, while the  $E_g$  of  $\text{FeVO}_4:\text{Cu}^{2+}$  is 2.01 eV, which is smaller than that of  $\text{FeVO}_4$ . Theoretically,  $\text{FeVO}_4:\text{Cu}^{2+}$  will absorb more visible light energy and produce more electron-hole pairs, which will probably improve the photocatalytic performance of  $\text{FeVO}_4:\text{Cu}^{2+}$ .

### 3.3. Degradation of Methyl Orange

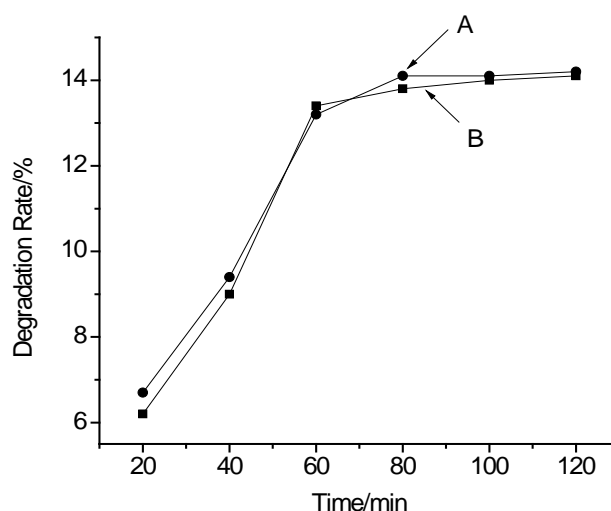


**Figure 3.** Effect of Xe lamp power on the degradation rate

**3.3.1. Light intensity effect.** Figure 3 shows the effect of Xenon lamp power on the degradation rate of methyl orange. As can be seen that the increase of Xe lamp power is beneficial to the improvement of the degradation efficiency of methyl orange. When the power of Xe lamp was set at 800 W, the degradation rate raised to 80%. With the light intensity increasing, more light quantum would reach the surface of the photocatalyst, making the stimulated semiconductor produce more electronic-hole pairs, which may be the main reason for the improvement of the degradation rate. Considering the power limit of the xenon lamp and energy consumption, the power of the xenon lamp will be set to

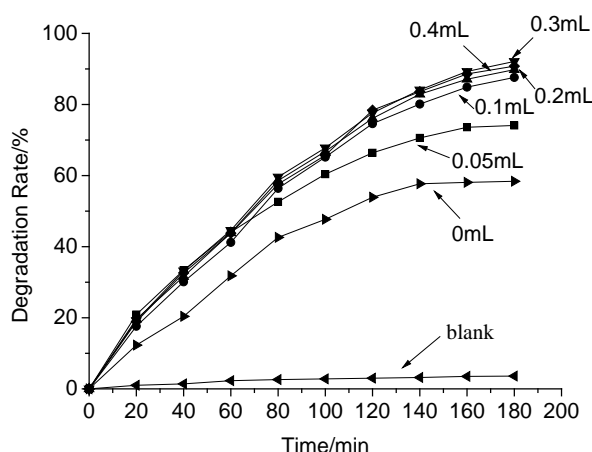
800 watts later.

**3.3.2.  $H_2O_2$  addition effect.** As an auxiliary agent, the addition amount of  $H_2O_2$  may affect the degradation of methyl orange. Therefore, a separate test was performed to determine the effect of  $H_2O_2$  on the degradation without addition of  $FeVO_4:Cu^{2+}$  photocatalyst. The figure 4 shows that without photocatalyst, light does not affect the degradation of methyl orange itself with only addition of  $H_2O_2$ . However, due to the oxidation of  $H_2O_2$ , there is a little degradation. In our case, the maximum degradation is about 14% within 80 min, which proves that  $H_2O_2$  does not degrade methyl orange significantly.



**Figure 4.** Degradation curve with  $H_2O_2$  but without catalyst

(A) light on (B) light off

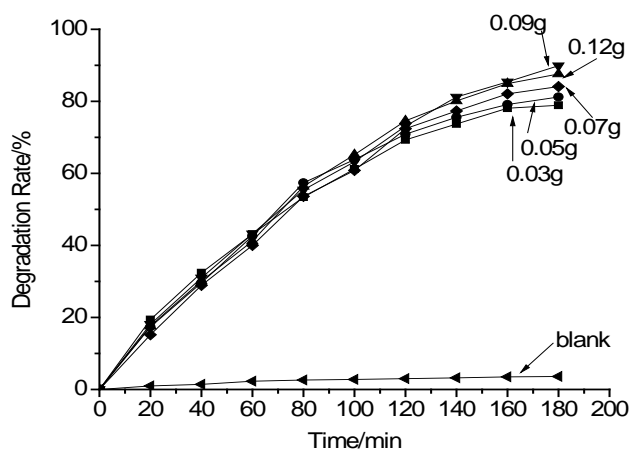


**Figure 5.** Degradation curves at different  $H_2O_2$  dosages

Under the same irradiation of 800 W Xe lamp, the same amount of catalyst was added in the same volume of methyl orange solution with different dosages of  $H_2O_2$ . Figure 5 shows the degradation curves of methyl orange at different  $H_2O_2$  dosages. It can be seen in figure 5 that with the addition of  $H_2O_2$  from 0mL to 0.2 mL, the degradation rate increases from 58% to 90%. The possible reason is that  $H_2O_2$  can be decomposed to form a large number of hydroxyl radicals with oxidative capacity,

improving the electron-hole active sites in the catalyst, and thus increasing the photocatalytic performance. When the amount of  $\text{H}_2\text{O}_2$  continued to increase, there was no further increase in degradation efficiency. Instead, the excessive  $\text{H}_2\text{O}_2$  would absorb the generated light quantum and reduce the degradation efficiency. So the addition of  $\text{H}_2\text{O}_2$  should be appropriate in the process of photodegradation.

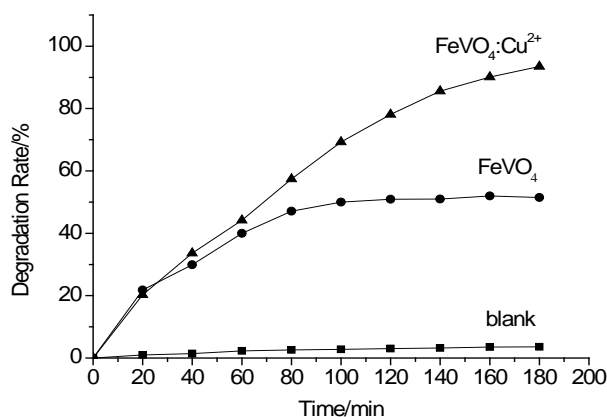
**3.3.3.  $\text{FeVO}_4\text{:Cu}^{2+}$  dosage effect.** In photocatalytic reaction, the amount of catalyst has a significant effect on the efficiency of the degradation of organic matter. Figure 6 shows the degradation curves for different  $\text{FeVO}_4\text{:Cu}^{2+}$  dosages. As shown in figure 6, with the increase of the amount of catalyst, the rate of photocatalytic degradation accelerated, from the 78% with 0.03 g catalyst to 89.9% with 0.09 g catalyst. However, when the amount of catalyst is too much, the catalyst particles will scatter light beams, which may weaken the effective light intensity and reduce the absorption of light.



**Figure 6.** Degradation curves for different dosages of  $\text{FeVO}_4\text{:Cu}^{2+}$

#### 3.4. Degradation of Methyl Orange under Optimized Conditions

The photocatalytic degradation curves of methyl orange under optimized condition are shown in figure 7. When exposed to 800 W Xe lamp for 180 min, with 0.09 g of  $\text{FeVO}_4$  and 0.3 mL of  $\text{H}_2\text{O}_2$  addition, the degradation efficiency of methyl orange was 51%. Under the same conditions, however, with  $\text{FeVO}_4\text{:Cu}^{2+}$  as the photocatalyst, the degradation rate reached 94%, indicating that doping of metal ions is a good way to improve photocatalytic efficiency. Figure 7 also shows that without any photocatalyst, degradation rate was only 3.6%, which may be owing to the adsorption only.



**Figure 7.** Degradation curves of methyl orange under optimized condition

#### 4. Conclusion

The nanosize  $\text{FeVO}_4\text{:Cu}^{2+}$  was prepared by a microwave method and was used as photocatalyst to degrade methyl orange in aqueous solution. After doping with  $\text{Cu}^{2+}$ , the band gap of  $\text{FeVO}_4\text{:Cu}^{2+}$  was reduced to 2.01 eV from the original 2.24 eV for  $\text{FeVO}_4$ , which increased the absorption of visible light. The photocatalytic degradation of methyl orange shows that with the 0.09 g of  $\text{FeVO}_4\text{:Cu}^{2+}$  and 0.3 mL of  $\text{H}_2\text{O}_2$  addition, and exposed to 800 W Xe lamp for 180 min, the degradation rate of methyl orange reached as high as 94%, indicating that photocatalytic degradation may be a good way to treat organic wastewater.

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