

# Microwave Synthesis of Cu, Fe-doped TiO<sub>2</sub> and Its Application for Photocatalytic Degradation of Organic Wastewater

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**Abstract.** In this paper, Cu<sup>2+</sup> and Fe<sup>3+</sup> co-doped titanium dioxide nanocomposite was prepared by iron nitrate, copper nitrate and titanium sulfate as raw materials and sodium dodecyl sulfate as surfactant under microwave irradiation. The x-ray diffraction (XRD) results show that as-prepared sample of direct adding doped copper and iron content were 1.0% and 0.5% of titanium sulfate amount of substance calcined at 500°C for 2 h is anatase. The SEM graph shows the morphology of the as-prepared samples is sheet structure composed of many particles. We also studied the photocatalytic activity of the as-prepared Fe<sup>3+</sup> and Cu<sup>2+</sup> co-doped TiO<sub>2</sub> nanocomposite by using degradation of methyl orange solution simulated organic wastewater. The effect conditions of photo-catalytic activities of the composite were investigated, such as different ratios of direct adding doped iron and copper content, different dosage of hydrogen peroxide, different pH value, and different dosage of nanocomposite. When the catalyst is 1.0 g/L, pH value is 4.3, C(H<sub>2</sub>O<sub>2</sub>) is 3 mL/L, the effect of the visible light catalytic activity was the best, in 30 min, the degradation rate of 20 mg/L methyl orange solution was more than 97%.

## Introduction

In recent years, with increasingly worsen problems of environmental pollutions, we have been in urgent need of improving our gradually deteriorated living conditions. The technology of photocatalytic degradation technology can not only effectively degrade organic and inorganic pollutions without the generating of new pollution, but also the process of catalysis does not need expensive oxidant, just sunlight could be brought about. Meanwhile photocatalyst also have advantages as can be regenerated and circularly used. Therefore, finding effective photocatalyst and catalytic materials has attracted researchers' intensive interest.

On one hand, as a kind of photocatalyst, TiO<sub>2</sub> can only be initiated by ultraviolet light, as it has a relatively broad energy band, of which the type of anatase is 3.2 eV and the type of rutile is 3.0 eV. It leads to a lower availability of sunlight[1]. On another hand, the photogenerated electrons and holes which has a high recombination ratio may cause a decline in the catalytic efficiency. In order to improve the photocatalytic efficiency and effectively inhibit the recombination of photogenerated charge carriers[2], so people adopt many kinds of method to improve its performance effectively, such as surface dye photosensitization, making use of semiconductors with different energy gap, coupling and doping by metal ion and so on. The method of ion doping which is easier, better in improving its quality and more propitious to the enhance the rate of photocatalysis among such methods, is paid more attention[3-4].

The doping metallic ion in the TiO<sub>2</sub> crystal lattice may introduce flaw or the change crystallinity, thus influence the recombination of electron/ hole[5]. After doped metal ion, the energy gap structure of TiO<sub>2</sub> crystal lattice may be altered so the metallic ion energy gap has been possible to accept on the TiO<sub>2</sub> valence band the excitation electron; but also might absorb the photon to cause the electron transition to on the conduction band of TiO<sub>2</sub>. Doping energy level which is in the forbidden band make photons with long wavelength can also be absorbed, which broaden the absorption spectrum of TiO<sub>2</sub>. Meanwhile photogenerated electrons and holes respectively from

conduction band and valence band can also be captured by impurity energy levels and separating the electrons and holes, which lead to a decreasing of rate of their recombination, increase the lifetime of carriers and increase the number of carriers in per unit time and per unit volume. At last, it may bring about an increasing in the probability for carriers to transmit to interface to carry out an oxidation-reduction, thus enhance the efficiency of photocatalysis of TiO<sub>2</sub>[6-8]. Single ion doping has a certain effect, but the photocatalytic effect is not the best[9]. So we try to modify two ion doping, there may be synergistic effect, the photocatalytic effect has been improved significantly

In this paper, Fe<sup>3+</sup> and Cu<sup>2+</sup> co-doped titanium dioxide nanocomposite was synthesized through direct feeding by microwave, characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and observed its photocatalytic activity by catalytic degradation of methyl orange. The x-ray diffraction (XRD) results show that as-prepared sample of direct adding doped iron and copper content were 0.5% and 1.0% of titanium sulfate amount of substance calcined at 500°C for 2 h is anatase. When the catalyst was 1.0 g/L, pH value was 4.3, C(H<sub>2</sub>O<sub>2</sub>) was 3 mL/L, it reached the best catalytic performance.

## Experimental Section

### Instruments and Reagents

Microwave oven with 650W (Sanle general electric corp. Nanjing, China) with refluxing system was used. Powder XRD was used to characterize the sample. Data were collected on a Shimadzu XRD-6100 X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda=0.15406$  nm). The morphology and size were determined by SEM. The SEM images were recorded on a JSM-5510LV scanning electron microscope (Japanese electronics). Lambda10 UV-vis spectrometer (Perkin-Elme Corp, USA) was used for monitoring the absorption spectra of photo-degradation of methyl orange.

All the reagents used were of analytical purity. Doubly distilled water was used throughout the experiments.

### The Microwave Synthesis of Fe<sup>3+</sup> and Cu<sup>2+</sup> Co-doped Titanium Dioxide Nanocomposite

The mixture solution about 100 ml including 1.0 g SDS, 2.4 g Ti(SO<sub>4</sub>)<sub>2</sub> and a certain quantity of Cu(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>3</sub> was placed in a microwave refluxing system to react for 20 min with a power of 40% and cool down naturally to room temperature. Then the precipitate was centrifuged, washed with the distilled water and dried at 60 °C in vacuum for 4 h, the sample was sintered at 500 °C for 2h. The final product in white was collected for characterization.

### The Photocatalytic Degradation Experiment of Fe<sup>3+</sup> and Cu<sup>2+</sup> Co-doped Titanium Dioxide Nanocomposite

The photocatalytic degradation of the aqueous solution of methyl orange (20 mg/L) with the as-prepared catalyst (1g/L) dispersed by ultrasonic vibration, some H<sub>2</sub>O<sub>2</sub> and dilute nitric acid adjusting to a certain pH value was investigated. Then the mixture solutions were placed in a glass beaker, and exposed to visible light irradiation at room temperature. Every 10 min, the solution of the surface in the glass beaker was centrifuged and determined by the UV spectrophotometer. The photocatalysis reaction was last until the discoloration of the solution was fulfilled or stopped. The formula of degradation rate is as follow:  $D_t\% = (A_0 - A_t) / A_0 \times 100\%$ . In the formula:  $D_t$  is the methyl orange degradation rate by visible light irradiation for the time of  $t$  in the presence of catalyst,  $A_0$  shows the absorbance of methyl orange solution after adding catalysts but without the sunlight irradiation,  $A_t$  is the absorbance of the methyl orange solution filled with catalyst under sunlight irradiation for the time  $t$

## Results and Discussion

Figure 1 is the XRD patterns of as-prepared samples of 1.0% Cu and 0.5% Fe co-doped TiO<sub>2</sub> sintered at 500°C for 2 h. The XRD patterns showed in Fig.1A(peak  $2\theta$ :25.15, 37.66, 47.80, 54.17,

62.45 ) demonstrate that's of anatase-type  $\text{TiO}_2$  (JCPDS No.1: 21-1272). The Cu and Fe doping amount almost has no effect on the  $\text{TiO}_2$  crystal structure

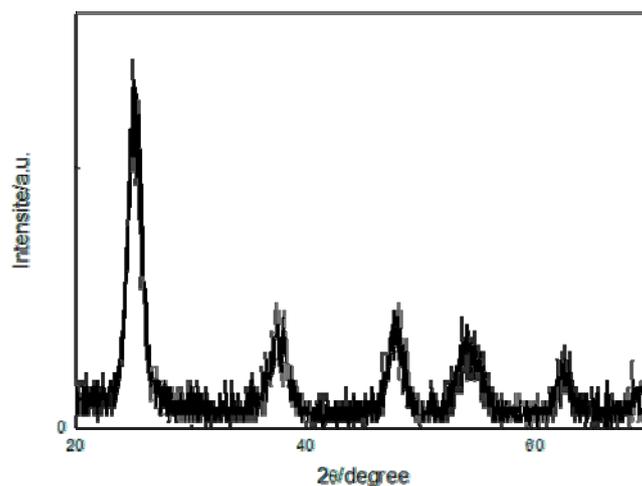


Fig.1 X-ray diffraction patterns of as-prepared samples

The SEM graph (Fig.2) shows the morphology of the as-prepared samples is sheet structure composed of many particles. It seems obvious massing which is owing to tremendous surface energy of nanoparticles.

Figure 3 is the typical visible absorption spectra of photo-degradation of methyl orange. Add 1.0 g / L 1.0% Cu and 0.5% Fe co-doped  $\text{TiO}_2$  photocatalyst into 100 mL 20 mg/L methyl orange solution, adjust pH to 4.3 and add 0.3 mL  $\text{H}_2\text{O}_2$ , then degradation under the visible light. It can be seen that with the photocatalytic degradation, the absorbance of the solution decreases gradually. After 30 minutes of irradiation, the solution in the range of visible light has almost no absorption, indicating that the methyl orange has been degraded thoroughly.

We also studied the influence factors of the photocatalytic performance, such as heat treatment temperature of the catalyst, the dosage of the catalyst, the pH value of the solution, the dosage of the  $\text{H}_2\text{O}_2$ . The results showed the best photocatalytic effect, when the heat treatment temperature is 500 °C, the dosage of the  $\text{H}_2\text{O}_2$  is 3 mL/L, the pH value of the solution is 2.5, the dosage of the catalyst is 1.0 g/L.

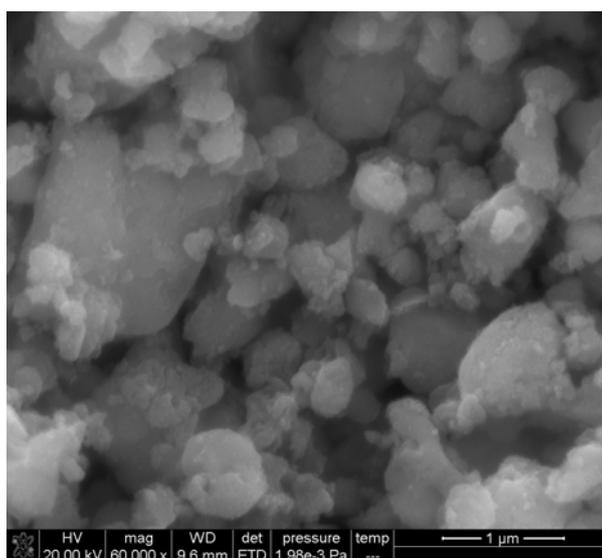


Fig.2 The scanning electron micrograph of as-prepared samples

Mechanism of through microwave synthesis may be that in the surfactant SDS one is a long chain of carbon-based water-repellent and the other is a charge of the hydrophilic group. It forms micelles

in aqueous solution.  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  co-doped nano- $\text{TiO}_2$  will grow around the micelle surface precipitation. Washed products and part of SDS was wiped clean; further heat-treated SDS ash residue decomposition. They form a spherical porous structure which aggregate by many small particles. It can be seen clearly from the SEM images. Porous structure can be increased the specific surface area in photocatalyst. Bigger surface area is advantageous for the adsorption of oxygen on the particle-surface to accept electronic high probability. Thereby it lowered the electronic / hole composite probability and prolonged the life of electron and hole. So it enhanced the catalytic properties.

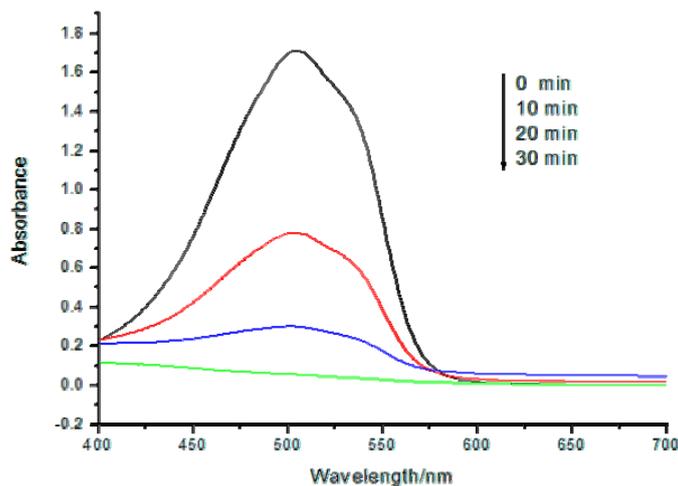


Fig.3 Visible absorption spectra of photo-degradation of methyl orange

At the same time, copper dioxide and Iron oxide may distribute evenly in the titanium dioxide crystal after  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  mixed evenly. But the ion radius of  $\text{Cu}^{2+}$  is 72 pm, the ion radius of  $\text{Fe}^{3+}$  is 64 pm, the ion radius of  $\text{Ti}^{4+}$  is 68 pm, they are similar in size.  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  are easier to destroy the original crystal lattice of  $\text{TiO}_2$  which causes the crystal lattice to have the distortion and enhances the catalyzed efficiency. Expecting  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  co-doped  $\text{TiO}_2$  nanocomposites can extend photo-carrier lifetime to raise catalytic properties effectively.

When Cu and Fe doping content is too large or too little, the catalytic properties are not too good. This may be due to that when the doping amount is less than the optimum amount, with the increase of dopant concentration, the number of the doped ion trap provides increased, enhance the inhibition ability of electron/hole recombination and the photocatalytic performance improves. When the doping amount is greater than the optimum value, as the decrease of the distance of trapped carrier, doping ions form electron-hole recombination center, and the excess doping concentration may reach saturation and produce kaintype, reduce  $\text{TiO}_2$  effective surface area, thus reduce the photocatalytic efficiency.

## Conclusions

In this paper, the Cu and Fe co-doped nano- $\text{TiO}_2$  is prepared through direct feeding microwave radiation. The method of direct feeding microwave radiation is very simple. The samples of 1.0% Cu and 0.5% Fe doped  $\text{TiO}_2$  sintered at  $500^\circ\text{C}$  for 2 h, XRD patterns show that the crystal is anatase and SEM pictures show the morphology is small grain of sheet structure.

A certain amount of Cu and Fe doping can improve the photocatalytic efficiency of  $\text{TiO}_2$ , catalyst dosage has little effect on the final degradation in a certain range, but have effects on the degradation time. The proper amount of  $\text{H}_2\text{O}_2$  can improve the visible light photocatalytic efficiency of as-prepared photocatalyst, acidity of solution in the acidic range affects little on the degradation efficiency, but also has effect on degradation time. It turns out that it reach the best efficiency on degradation when catalyst is 1.0 g/L, pH value is 4.3 and adding  $\text{H}_2\text{O}_2$  is 3 mL/L under the visible light. The as-prepared photocatalyst is an excellent photocatalysts, it is expected to

be used in photocatalytic degradation of organic wastewater to improve the deteriorating environmental problems.

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