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The Microwave Synthesis and Photocatalytic Activity of W^{6+}-Doped TiO_2 Nanocomposite

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Abstract

W^{6+}-doped TiO_2 was prepared by sodium tungsten (VI) and titanium sulfate with sodium dodecyl sulfate as surfactant under microwave irradiation. The samples were characterized by X-ray diffraction (XRD) and Scanning electron micrograph (SEM). The results showed that the as-prepared nanocomposite of inventory molar ratio of 2% calcined at 500˚C for 2 h was anatase. The SEM showed that the majority of the catalyst was a relatively flake structure, and some fine particles attached to it. We also studied the photocatalytic activity of the as-prepared samples by using degradation of methyl orange. The factors including inventory molar ratio and concentration of W^{6+}-doped, calcined temperature, amount of hydrogen peroxide and acidity of solution were investigated. When the catalyst was 1.0 g/L, pH was 2, C(H_2O_2) was 3 mL/L, the degradation rate of TiO_2 for methyl orange of 20 mg/L reached 79.63% in 40 min.

Keywords

W^{6+}-Doping, Titanium Dioxide, Microwave Synthesis, Photocatalysis, Methyl Orange

1. Introduction

With the development of science and technology, a variety of new organics are emerging, many of them are difficult to handle by traditional physical and chemical methods, biochemical methods also have very little effect. Therefore, it requires us to find an effective method to deal with the refractory organics [1].

TiO_2 is an economic, environmental and inexpensive semiconductor photocatalyst and widely used in the degradation of organic pollutants. TiO_2 has special physical and chemical properties and electronic band structure, high photocatalytic activity. It is widely used in the research field of environmental protection and pollution

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control as photocatalyst [2].

On one hand, as a kind of the photocatalyst, TiO_2 can only be initiated by the ultraviolet light as it has a relative 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 [3]. On the other hand, the photogenerated electrons and holes with 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 photoproduction charge carriers [4], the researchers adopt many kinds of methods to improve its performance effectively [5]-[7], and the method of ion doping is reported most [8]-[11].

In this paper, W-doped nano-TiO_2 was synthesized through direct feeding by the microwave. Its photocatalytic activity was observed by the catalytic degradation of the methyl orange, and the factors including inventory molar ratio and concentration of W^{6+}-doped, calcined temperature, amount of hydrogen peroxide and acidity of solution were investigated. When the catalyst was 1.0 g/L, pH was 2, $C(H_2O_2)$ was 3 mL/L, the degradation rate of TiO_2 for methyl orange of 20 mg/L reached 79.63% in 40 min.

2. Experiment

2.1. Instruments and Reagents

Microwave oven with 650W (Sanle General Electric Corp., Nanjing, China) with refluxing system was used. Powder X-ray diffraction (XRD) was used to characterize the sample. Data were collected on a Shimadzu XRD-6100 X-ray diffractometer (Cu Kα radiation, λ = 0.15418 nm). The morphology and size were determined by SEM. The SEM images were recorded on a Quanta 200 FEG field emission scanning electron microscope. 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.

2.2. Microwave Synthesis of W^{6+}-Doped TiO_2 Nanoparticles

The mixture solution including 100 mL pure water, 1.0 g sodium dodecyl sulfate, 2.4 g $Ti(SO_4)_2$, a certain quantity of urea and $Na_2WO_4{\cdot}2H_2O$ was placed in a microwave refluxing system to react for 20 min with a power microwave radiation of 40% and cool down naturally to the room temperature. Then the precipitate was centrifuged, washed with the distilled water and dried at 60˚C in the vacuum for 4 h, the powder was sintered at 500˚C for 2 h. The final product in white was collected for the characterization.

2.3. Photocatalytic Degradation Experiment of W^{6+}-Doped TiO_2

The photocatalytic degradation of the aqueous solution of the methyl orange (20 mg/L) with the as-prepared catalyst dispersed by the ultrasonic vibration, some H_2O_2 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 the visible light irradiation at the room temperature. Every 10 min, the surface solution in the glass beaker was centrifuged and determined by the UV-visible absorption spectrometer. The photocatalysis reaction lasted until the discoloration of the solution was fulfilled or stopped. The formula of the degradation ratio is as follow

$$D_t\% = \frac{(A_0 - A_t)}{A_0} \times 100\%$$

where D_t is the methyl orange degradation rate by the visible light irradiation for the time of t in the presence of the catalyst, A_0 shows the absorbance of the methyl orange solution after adding catalysts without the sunlight irradiation, A_t is the absorbance of the methyl orange solution filled with catalyst under the sunlight irradiation for the time of t.

3. Results and Discussion

3.1. XRD, SEM Analysis of W^{6+}-Doped TiO_2

Figure 1 shows the XRD pattern graph of as-prepared sample of 2% W-doped TiO_2 sintered at 500˚C for 2 h. The XRD pattern (peak 2θ: 25.2, 37.8, 47.99, 54.9) showed that the product was anatase-type TiO_2 (JCPDS File

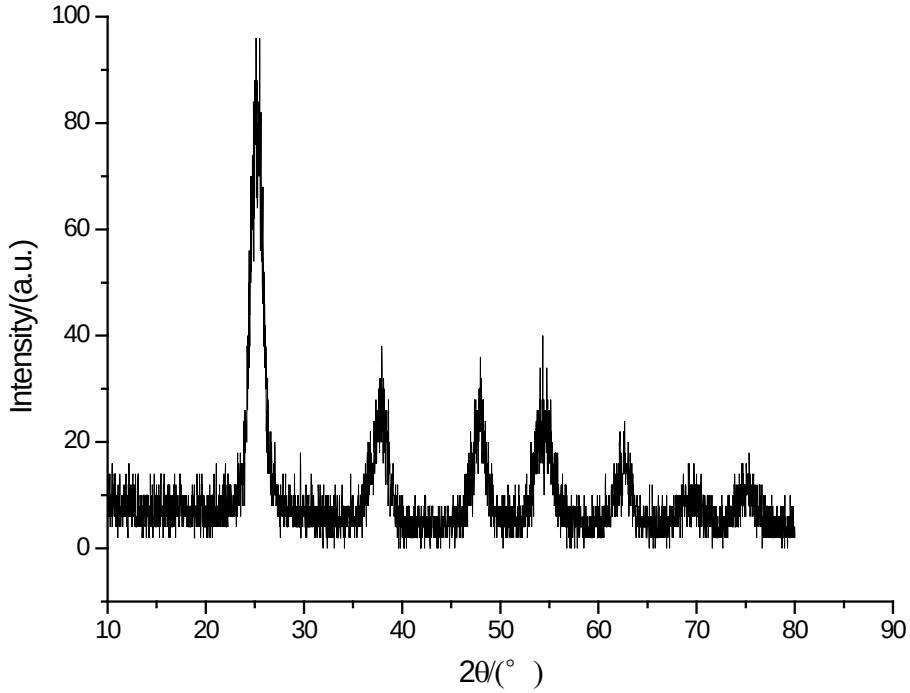

Figure 1. X-ray diffraction pattern of as-prepared sample (the nanocomposite of inventory molar percentage of 2%).

No. 21-1272). The W doping amount almost has no effect on the TiO_2 crystal structure. Adopted Scherrer equation, we can estimate the size of the crystal. The average size of as-prepared sample is 6 nm.

Figure 2 shows the SEM pattern graph of as-prepared sample of 2% W-doped TiO_2 sintered at 500˚C for 2 h. It shows that the majority of the catalyst is a relatively flake structure, and some particles attached to it. The size of most of the flakes is 50 to 500 nm.

3.2. Photocatalytic Activity of W^{6+}-Doped TiO_2 Nanocomposite

Figure 3 shows the typical visible absorption spectra of the photo-degradation for the methyl orange. It can be seen that with the photocatalytic degradation, the absorbance of the solution decreases gradually. After 10, 20, 30, 40 min of the irradiation, the degradation rate of TiO_2 for methyl orange of 20 mg/L reached 35%, 65%, 75%, 79.63%, respectively. After 40 min of the irradiation, the solution in the range of the visible light has almost no absorption, indicating that the methyl orange has been degraded thoroughly. When the methyl orange solution is directly put under the illumination without the catalyst, the results show that the solution does not fade by continuous illumination for 2 h, and the detection by the UV-visible absorption spectrometer finds that the absorbance does not change.

3.3. The Mechanism of Reaction

The mechanism of the microwave synthesis may be that at one side of the surfactant sodium dodecyl sulfate is a long chain of carbon-based water-repellent, and at the other side is the hydrophilic group with the charge. It forms micelles in the aqueous solution. W^{6+}-doped nano-TiO_2 will grow around the micelle surface precipitation. Washed products and some parts of sodium dodecyl sulfate were wiped clean and further heat-treated, sodium dodecyl sulfate ash residue decomposes and forms a spherical porous structure which is aggregated by many small particles. It can be seen clearly from the SEM images, the majority of the catalyst is a relatively regular structure. It can increase the specific surface area in the photocatalyst. Larger surface area is advantageous for the adsorption of oxygen on the particle-surface, and enhances the acceptable probability of the electrons. Thereby it reduces the electron and hole composite probability, and prolongs the life of the electron and hole. So it improves the catalytic properties [12].

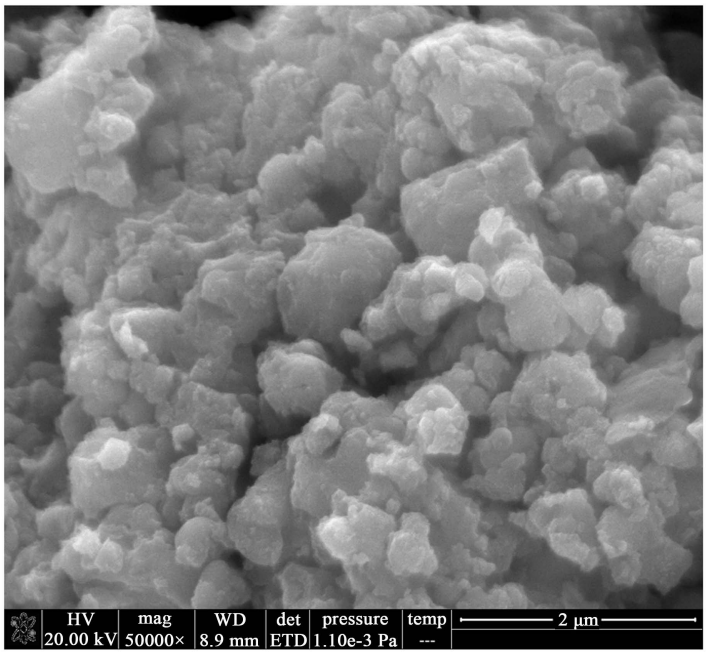

Figure 2. Scanning electron micrograph of as-prepared sample.

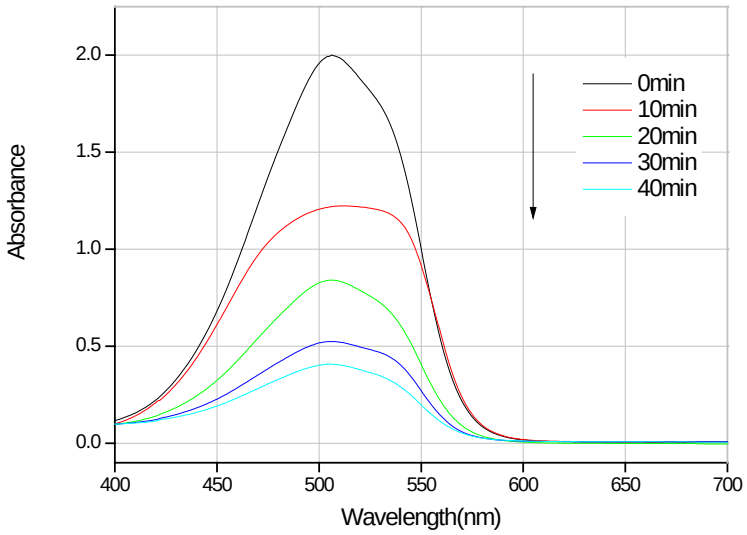

Figure 3. Visible absorption spectra of photocatalytic degradation of methyl orange. (1.0 g/L of the nanocomposite of inventory molar percentage of 2%, pH was 2, C(H_2O_2) was 3 mL/L, 20 mg/L of methyl orange).

At the same time, sodium tungstate may distribute evenly in the titanium dioxide crystal after W^{6+} and Ti^{4+} mixed evenly. W belongs to the d areas element. But the ion radius of W^{6+} is 68 pm, ion radius of Ti^{4+} is 68 pm. W^{6+} is easier to destroy the original crystal lattice of TiO_2, which brings the distortion to the crystal lattice and enhances the catalyzed efficiency. Expecting W^{6+}-doped TiO_2 nanocomposites can extend the photo-carrier life-time to raise catalytic properties effectively.

When W doping content is too large or too small, the catalytic properties are not so good. When the doping amount is greater than the optimum value, as the decrease of the distance of the trapped carrier, doping ions

form the electron-hole recombination center, and the excess doping concentration may reach saturation, produce kainotype and reduce TiO_2 effective surface area, thus reduce the photocatalytic efficiency.

Calcined temperature can stabilize the crystalline form of the synthesized product, but too large or too low will affect the catalytic properties. The product is irregular polygon block when the temperature is too low. And when the temperature is too high, it can cause further growth of nano particles by sintering or crystal, increased particle size, decreased photocatalyst specific surface area, and eventually it can lead to the decrease in the photocatalytic efficiency.

4. Conclusions

In this paper, the W^{6+}-doped nano-TiO_2 was synthesized through direct feeding microwave radiation. The method of direct feeding microwave radiation is very simple. The sample of 2% W-doped TiO_2 is sintered at 500˚C for 2 h. XRD patterns show that the crystal is anatase, and SEM pictures show that the majority of the catalyst is a relatively flake structure, and some fine particles attach to it.

A certain amount of W doping and calcined temperature can improve the photocatalytic efficiency of TiO_2, the proper amount of H_2O_2 can improve the visible light photocatalytic efficiency of the W-doped nanosized composite, the acidity of the solution in the acidic range affects little on the degradation efficiency, but also has effects on the degradation time. It turns out that the best efficiency is obtained on the degradation when the catalyst of 2% W-doped TiO_2 sintered at 500˚C for 2 h is 1.0 g/L, pH is 2, and H_2O_2 with the volume fraction of 0.003 under the visible light is added. The as-prepared photocatalyst is an excellent photocatalyst.

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