Preparation and Photocatalytical of $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ Composite Materials by Hydrothermal Method

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Abstract—working with waste water contain dyes presents challenges, so to find some photocatalyst artificial synthesized is a fascinating research job. Using Na_2WO_4•$2H_2O$, $Zn(NO_3)_2$•$6H_2O$, $Bi(NO_3)_3$•$6H_2O$ and HF as raw materials, three different mole ratio of photocatalyst of $Bi_2WO_{6-x}F_{2x}$ / $ZnWO_4$ have been successfully synthesized by hydrothermal method. The catalysts were characterized by powder X-ray diffraction (XRD) and diffuse reflectance spectrum (DRS). The sample has been made visible light photocatalytic performance test for RhB solution which concentration is 10 mg/L. The experimental results show that the legal system have $ZnWO_4$ and different mole ratio of the Bi_2WO_6 / $ZnWO_4$ and $Bi_2WO_{6-x}F_{2x}$ / $ZnWO_4$ by hydrothermal method, $Bi_2WO_{6-x}F_{2x}$ / $ZnWO_4$ composite nano powder have been got after the doped of fluorine ion in Bi_2WO_6 and $ZnWO_4$.In photocatalytic experiment which the best photocatalytic effect of $Bi_2WO_{6-x}F_{2x}$ / $ZnWO_4$ is 0.10/1 as Bi_2WO_6 / $ZnWO_4$ mole ratio, this conclusion is consistent in the diffuse reflection spectrum.

***Keywords-** $ZnWO_4$; $Bi_2WO_{6-x}F_{2x}$; hydrothermal method; RhB; photocatalytic*

I. INTRODUCTION

In 1972 Fujishima and Honda [1] found that under UV irradiation water on the TiO_2 electrode can be broken down into H_2 and O_2. Their research achievements of the landmark were released and people have found many efficient photocatalyst,(and)marked the beginning of photocatalytic area. In 1976, Carey[2] et al. reported under the irradiation of ultraviolet light, such as polychlorinated biphenyls (PCBS), chlorinated paraffin, etc in the water can found in the presence of TiO_2 light catalyst under the condition of effective dechlorination reaction, this research found that make people aware of the semiconductor photocatalyst for the prospects of the photocatalytic degradation of organic pollutant. But as a result of anatase type TiO_2 degree of wide band gap of 3.2 eV, TiO_2 can only respond to below 400 nm UV light and the sunlight spectrum accounted for most of the visible light utilization efficiency is too low to limit the development of industrial application of nanometer TiO_2. Therefore, to develop efficient visible light induced photocatalyst has far-reaching significance. In recent years, scientific studies have found that using fluorine ions on TiO_2 surface treatment can greatly improve the photocatalytic performance of the film. Fluorine doped TiO_2 thin film in the ultraviolet photocatalytic activity has improved significantly and chemical adsorption to the fluorine ion on the surface of the TiO_2 particles, can promote the generation of hydroxyl radicals under UV irradiation, which can improve the degradation of organic pollutants, for example, the phenol and acid orange. Light to hydrophilic test results show that the surface of fluoride can increase TiO_2 thin film under UV irradiation surface water contact angle of the lower rate. As a result, people try to generate fluorine doped TiO_2 thin film. Hattori etc. [3] applied trifluoroacetic acid fluorine source using sol-gel method for fluorine doped TiO_2 thin film. Yaling Su[4] and others got NH_4F as fluorine source using chemical vapor deposition method to fluorine doping of TiO_2 nanotubes, and it is concluded that fluorine doped TiO_2 nanotubes to visible light catalytic reduction slack activity of methyl orange was obviously higher than that of without doping of TiO_2 nanotubes. Recently, some non-doped fluorine ion TiO_2 catalyst showed a similar improvement of photocatalytic activity.

Fluorine doping $ZnWO_4$ clearance has been reported. Fluorine ion may increase $ZnWO_4$ crystal WO_6 octahedral W atoms in the surrounding coordination layer, and cause WO_6 octahedral deformation [5], leading to increased photoproduction electron transfer rate, more electrons transfer to the photocatalyst surface to improve the ability of photocatalytic degradation of RhB. At the same time, the fluoride Bi_2WO_6 presented to improve the photocatalytic degradation of RhB, which may be due to surface synergistic effect caused by fluoride and fluorine ions doped into the crystal lattice. According to these results, regardless of the fluorine doping approach, the introduction of fluorine can really improve the photocatalytic activity of semiconductor [6]. Moreover, rather than using a single light catalyst, and other semiconductor optical coupling, metal or molecular catalyst heterostructure formation, these structures have been found to significantly improve the photocatalytic activity [7]. Heterostructure Bi_2WO_6/TiO_2 light photocatalytic performance is higher than the titanium dioxide, which is because it has higher charge carrier separation efficiency [8]. $Bi_2WO_6/ZnWO_4$ composite photocatalytic activity has been proven to improve the properties of $ZnWO_4$ [9-10].

In all, designed to fluorine and $ZnWO_4$ form again after doping Bi_2WO_6 composite photocatalyst, through a series of hydrothermal method with $Bi_2WO_{6-x}F_{2x}/ZnWO_4$, and compares the three different ratios (0.05, 0.10, 0.15) of the sample effect on the degradation of RhB.

II. EXPERIMENTAL AND CHARACTERIZATION

This experiment mainly chemical reagent is as follows: 30% HF, NaOH, Na_2WO_4•$2H_2O$, $Bi(NO_3)_3$•$2H_2O$, $Zn(NO_3)_2$•$6H_2O$, Ethylene glycol(EG), Anhydrous ethanol, RhB etc., Chemically pure. The X-ray diffractgrams of the samples were recorded by a PuXi Perking powder diffractometer. The diffraction patterns were recorded at room temperature by using Co K radiation. A scanning speed of 4 deg/min and a chart speed of 13 mm/deg were generally employed. The scanning electron micrographs were recorded by S3400N (Hitachi Company) with electron microscope operating at accelerating voltage of 15 or 20KV. The UV–vis absorption spectra of RhB solution and UV–vis reflectant spectra for powder were obtained using Thermo Scientific Evolution 220 (Thermo Fisher Scientific).

A. *Preparation of $ZnWO_4$ nanorods*

This experiment should be made $ZnWO_4$ nanorods, modified concrete practice references[9].

B. *Preparation of Bi2WO6-xF2x/ ZnWO4*

Preparation of $Bi_2WO_{6-x}F_{2x}$ adding a certain amount of $ZnWO_4$ nanorods (Bi_2WO_6 / $ZnWO_4$ mole ratio: 0.05, 0.10 and 0.15, respectively) and strong mixing. After 30 minutes, the suspension was transferred into a reaction kettle, and reaction temperature was 120 °C for 15 hours. The collected sediment with ethanol was washed with water several times. After the samples was washed with ethanol and deionized water several times, dried in 50 °C 4 hours, finally $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ photocatalysts was got.

C. *Photocatalytic experiment*

For example: using analytical balance accurately said 20 mg samples and clean small beaker, take 10 mL solution simulated wastewater by the pipette (RhB) join the small beaker. Put small beaker at 2 min during the ultrasonic instrument, and the sample powder evenly dispersed in solution. Add magnetron, puts a beaker has preheat half an hour to 150 W magnetic stirring under visible light (no more change after speed setting) for photocatalytic degradation experiment. After a certain time, 30, 60, 90, 120, 90 min, remove the beaker, transfer the solution to a clean, dry 10 mL centrifuge tube, less than 10 mL with deionized water supplement, centrifugal separation of solution for 20 min, centrifuge speed is set to 4000 r/min. After the centrifugal, take the supernatant fluid

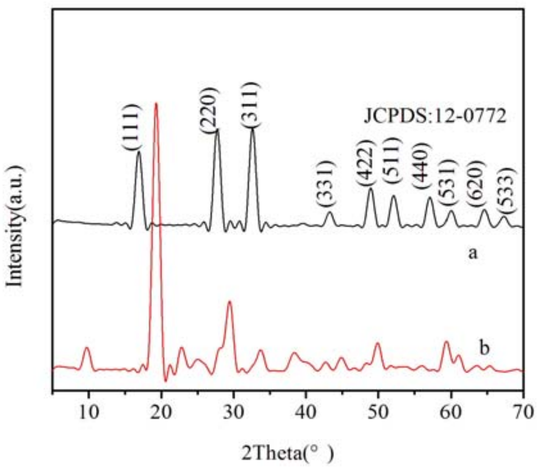

Figure 1. XRD patterns fluoride of Na_2WO_4 crystal before and after doping.(a.pure Na_2WO_4 ,b.$Na_2WO_{4-x}F_{2x}$)

type in Thermo Scientific Evolution 220 UV-vis spectrophotometer (RhB_{Max} = 554 nm) on the absorbance measurement. According to the formula to calculate the sample rate of the degradation of RhB solution, the degradation rate of RhB solution to characterize the photocatalytic degradation performance of the sample.

III. RESULTS AND DISCUSSION

A. *Influence of fluorine doping on the crystal structure*

Fig. 3-1 shows the fluorine element before and after doping of Na_2WO_4 crystal XRD spectrum, for pure Na_2WO_4 standard XRD patterns, a standard JCPDS card is No. 12-0772, and marked with its main crystal indices, b for after fluoride to replace the $Na_2WO_{4-x}F_{2x}$.The figure shows that after replaced by fluorine Na_2WO_4 obvious changes have taken place in crystal type. It is clearly that there are elements of fluorine in 2theta= 20^o~30^o. But due to the limited reaction conditions and analysis method, we can't clearly identify into Na_2WO_4 how much is the amount of fluoride in the concrete, so it have to be for the $Na_2WO_{4-x}F_{2x}$.

As shown in Fig. 2 was three different mole ratio of $Bi_2WO_6/ZnWO_4$, Bi_2WO_6 JCPDS standard card number was 39-0256, and $ZnWO_4$ was 15-0774. When the molar ratio of $Bi_2WO_6/ZnWO_4$ increased from 0.05 to 0.15, were just Bi_2WO_6 the intensity of the diffraction peak had increased gradually, and the intensity of the diffraction peak of $ZnWO_4$ was lower. It found that there was not impurity peak and show that composite material was a kind of two-phase composition: Bi_2WO_6 and $ZnWO_4$. As shown in Fig. 3 fluorine doping Bi_2WO_6 and $ZnWO_4$ again after the different molar ratio of compound, after $Bi_2WO_{6-x}F_{2x}/ZnWO_4$, shown in Fig. 1 in fluorine doping Na_2WO_4 as similar as $Bi_2WO_{4-x}F_{2x}$ with the increase of mole ratio of $ZnWO_4$, in 20° to 30° and at 30°to 35°.

B. *Photocatalytic performance analysis*

The effect of doped fluorine element before and after different mole ratio of $Bi_2WO_6/ZnWO_4$ composite photocatalyst need test on the catalytic degradation of RhB solution. It was shown in Fig. 4 samples of visible light RhB degradation rate of 10 mg/L line diagram along

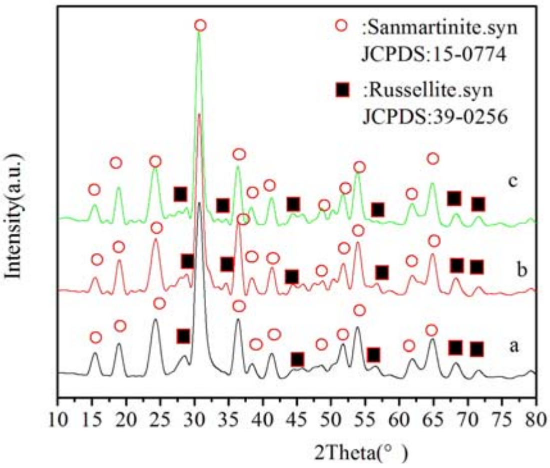

Figure 2. . XRD patterns of different mole ratio of Bi_2WO_6 / $ZnWO_4$. (a.0.05 ; b.0.10 ; c.0.15).

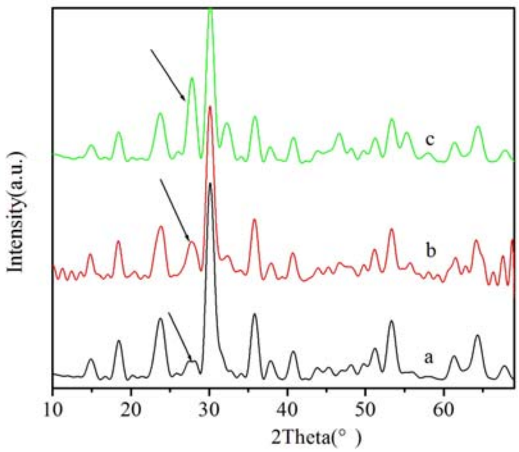

Figure 3. XRD patterns of different mole ratio of $Bi_2WO_{6-x}F_{2x}$ and $ZnWO_4$ (a: 0.05; b: 0.10; c: 0.15).

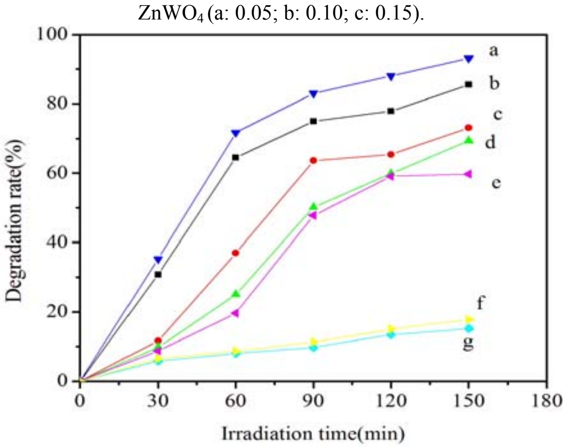

Figure 4. Samples of visible light RhB degradation rate of 10 mg/L change over time(a: $0.10Bi_2WO_{6-x}F_{2x}/ZnWO_4$, b:0.10 $Bi_2WO_6/ZnWO_4$, c: 0.15 $Bi_2WO_{6-x}F_{2x}/ZnWO_4$, d: 0.05 $Bi_2WO_{6-x}F_{2x}/ZnWO_4$,e:0.05 $Bi_2WO_6/ZnWO_4$, f: 0.15 $Bi_2WO_6/ZnWO_4$, g: $ZnWO_4$).

with the change of time, the figure can be concluded that 0.1/1 $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ to 10 mg/L of the degradation of RhB rate was the highest, followed by 0.1 $Bi_2WO_6/ZnWO_4$.When samples without introducing fluorine element, $Bi_2WO_6/ZnWO_4$, fluoride after doping, for the degradation of RhB rate is not as the molar ratio of Bi_2WO_6 and $ZnWO_4$ increases, but the order of 0.10 > 0.05 > 0.15.When the fluorine element doping, $Bi_2WO_6/ZnWO_4$ nor for the degradation of RhB rate as $Bi_2WO_{6-x}F_{2x}$ and $ZnWO_4$ mole ratio increases, and the order of 0.10 > 0.05 > 0.15. And samples doped with fluorine than no fluorine is generally better on photocatalytic performance.

Pure $ZnWO_4$ and $ZnWO_4/Bi_2WO_6$ composite had some different in photocatalytic activity. The $ZnWO_4$ /Bi_2WO_6 composite, the photocatalytic activity of $Bi_2WO_6/ZnWO_4$ is better than single $ZnWO_4$, and when the introduction of Bi_2WO_6 and $ZnWO_4$ mole ratio was 0.10, the compound after $Bi_2WO_6/ZnWO_4$ photocatalytic effect is best. That means in composite Bi_2WO_6 than column is limited, only when no more than a mole ratio, $ZnWO_4$ photocatalytic performance can be improved better.

The photocatalytic activity of $Bi_2WO_6/ZnWO_4$ and $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ was different. At the same when the mole ratio of $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ on the catalytic effect of RhB is stronger than the $Bi_2WO_6/ZnWO_4$, illustrates the introduction of fluorine element to improve the ability to respond to visible light, fluoride WO_6 structure of oxygen was replaced, make W element around the chemical environment changes, thus affecting the photocatalytic performance of the sample.

C. Fluorine doping amount and different mole ratio on the diffuse reflection effect of the sample

As shown in Fig. 5 was the UV-Vis diffuse spectrums of the sample. According to the energy band theory and the principle of semiconductor photocatalysis, as sample price bring electron by ultraviolet or visible light irradiation, their price bring electronic will be challenged, has a highly active light living a hole - electron pair, so that the sample under the light conditions with good photocatalytic activity, to the catalytic degradation of organic pollutants, etc. By Fig.5, you can see that although the maximum absorption wavelength of $ZnWO_4$ samples is larger, but low absorbance in UV-Vis scale; and maximum absorption of $Bi_2WO_6/ZnWO_4$wavelength change is not big, absorbance increase is more obvious. Much more fluorine elements added into $Bi_2WO_{6-x}F_{2x}/ZnWO_4$, much more significant on photocatalytic activity. Absorption peak area is larger, photocatalytic effect is better.

IV. CONCLUSIONS

Three different mole ratio of $Bi_2WO_{6-x}F_{2x}$/ $ZnWO_4$ photo catalysts have been successfully synthesized by hydrothermal method with Na_2WO_4•$2H_2O$, $Zn(NO_3)_2$•$6H_2O$, $Bi(NO_3)_3$•$6H_2O$ and HF as the raw materials. Catalysts were characterized with XRD and DRS, respectively. The morphology of $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ is used for enhancing photocatalytic effect in RhB degradation under UV light. The main conclusions are as follows: (1) adopted a series of water got $ZnWO_4$ bounding into the legal system and the different mole ratio of $Bi_2WO_6/ZnWO_4$ and $Bi_2WO_{6-x}F_{2x}/ZnWO_4$, showed by XRD spectrum in the $Bi_2WO_6/ZnWO_4$ composite nano-materials, founded no impurity peak shows that composite

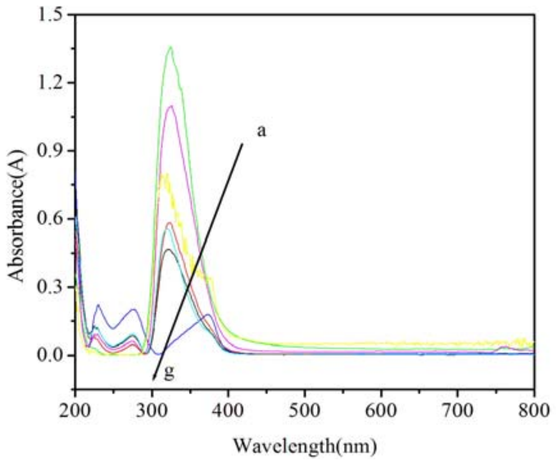

Figure 5. DRS spectrum of samples (a:0.15 $Bi_2WO_{6-x}F_{2x}/ZnWO_4$; b:0.15 $Bi_2WO_6/ZnWO_4$; c:0.10 $Bi_2WO_6/ZnWO_4$; d:0.05 $Bi_2WO_6/ZnWO_4$; e:0.10 $Bi_2WO_{6-x}F_{2x}/ZnWO_4$; f:0.05 $Bi_2WO_6/ZnWO_4$; g:$ZnWO_4$)

material is composed of Bi_2WO_6 and $ZnWO_4$ two phase composition. So introducing fluorine ion with $ZnWO_4$ can get Bi_2WO_6 $Bi_2WO_{6-x}F_{2x}/ZnWO_4$ composite nano powder. (2) For Bi_2WO_6 and $ZnWO_4$ composite with different mole ratio of the sample, by contrast, the photocatalytic effect is best in 0.10 which to participate in the quantities of Bi_2WO_6 composite at this time is the best. (3) For $Bi_2WO_{6-x}F_{2x}$/ $ZnWO_4$ is as same as the $Bi_2WO_6/ZnWO_4$ mole ratio, it was also found that 0.10 $Bi_2WO_{6-x}F_{2x}$/ $ZnWO_4$ photocatalytic effect is best.

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