Synthesis of Monoclinic scheelite $BiVO_4$ by Simple Precipitation Method and Photocatalytic Performance under Visible-light Irradiation

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Abstract: Visible-light responsive photocatalyst BiVO4 were synthesized by simple precipitation method, following by calcination process. The phase structure, morphology, specific surface area and optical absorption properties of as-synthesized BiVO4 were characterized by XRD, SEM, BET, UV-Vis DRS and FTIR, respectively. Acid Black 10B was used as simulated dye wastewater to investigate the photocatalytic activity of BiVO4. The results indicate that the samples obtained under different calcination temperature are all monoclinic phase BiVO4. The band gap energy of BiVO4 calcined at 500 °C, 600 °C, 700 °C are 2.50 eV, 2.45 eV and 2.37 eV, respectively. BiVO4 calcinated at 500 °C or 600 °C show excellent photocatalytic activity, and the particles are spherical-like in shape. When the concerntration of dye is 20 mg/L, the dosage of BiVO4 is 200 mg/50 mL, visible light is used as irradiation source and reaction time is 60 min, the degradation rate of the dye can reach to about 100%. The degradation process can be considered as the first-order reaction kinetics.

1 Introduction

Nowadays, with the development of chemical, papermaking, textile and metallurgical industries, water pollution has been a major concern among the environmental issues in modern society. Especially, dyeing wastewater has the characters of high toxicity, high colority, complicated composition, so the treatment technology is complex and difficult. Since Fujishima firstly used TiO_2 as a catalyst to decompose water under the sun light in 1972[1], the dyeing wastewater treatment technique based on semi-conductor photocatalysts has got widespread interest[2,3]. Among the semiconductor photocatalysts, monoclinic scheelite $BiVO_4$ has drawn considerable attention because it has narrow band gap(2.4 eV) and its Bi-O polyhedron is more distorted which leading to better efficient separation of photo-generated electrons and holes.

$BiVO_4$ can be synthesized by many methods, such as hydrothermal method[4], sonochemical method[5], wet-chemical processes[6]. These methods have some disadvantages, such as complicated equipments, or various additives, and the product usually exists in monoclinic and tetragonal mixed-phase state. Against this background, in this present work, a simple and easy-control synthesis route, i.e., liquid-phase precipitation method followed by calcination process was developed to synthesize single-phase monoclinic scheelite $BiVO_4$. Its optical absorption properties photocatalytic activity were investigated. Moreover, the kinetics of photocatalytic reaction were studied, and the possible mechanism of photocatalytic degradation was proposed.

2 Experimental

2.1 Synthesis of the Samples

All the raw materials are analytical-reagent grade and water used in the synthesis is deionized water. Liquid-phase precipitation method was developed to prepare $BiVO_4$. Firstly, 0.58 g NH_4VO_3 was dissolved in 100mL hot water, then cooled to room temperature and the resultant solution was marked as solution A. 2.42 g $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 3 mL concentrated nitric acid and a little water, then the water was added to dilute the solution to 100 mL and the resultant solution was

marked as solution B. Secondly, solution B was added into solution A dropwise under ultrasonic vibration. After that, the pH value was adjusted to 4 with concentrated ammonia. The suspension was stirred for 8 h in 90 °C water bath. Then, the obtained suspension was aged for 24 h. The precipitate was collected by centrifugation, washed with distilled water and absolute alcohol, and then dried at 80 °C. Finally, the primary product was calcined to get final product with a higher degree of crystallization.

2.2 Photocatalytic Test

Photocatalytic activities of the as-synthesized samples were evaluated by the degradation of Acid Black 10B under Metal Halide Lamp irradiation (simulation of visible light). Specific process: 50 mL, 20 mg/L Acid Black 10B solution was taken into quartz reactor tube, adding 200 mg sample. Then, the mixture was stirred for a certain time in BL-GHX-V photochemical reaction instrument under the visible light irradiation. Then the mixture solution was centrifuged to remove the photocatalyst. Absorption spectra of the centrifuged solution were recorded with TU-1801 UV-Vis spectrophotometer. Finally, the decolorization rate (De) of dye solution could be calculated by the equation: De = $(A_0-A)/A_0\times100\%$, here, A is the final absorbance and A_0 is the initial absorbance of the dye solution at the maximum absorption wavelength (λ = 618 nm).

2.3 Characterization

The phase structure of the samples were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray powder diffractometer with Cu-Kα radiation source (λ=0.15406 nm, 40 kV×40 mA). The morphology and size of the samples were tested on the Phenom ProX Desktop scanning electron microscope (SEM) and the UV-Vis diffuse reflectance absorption spectra (DRS) were recorded by a TU-1901 UV-Vis Spectorphotometer. Brunauer-Emmett-Teller (BET) specific surface areas of the samples were analyzed using TristaarⅡ3020 apparatus. Fourier transform infrared spectra (FTIR) were acquired with a Thermo Nicolet 380 FTIR spectrometer.

3 Results and Discussion

3.1 X-ray Diffraction Analysis

It is known that $BiVO_4$ exists in three crystalline phases: monoclinic scheelite, tetragonal zircon and tetragonal scheelite structures. Among them, the photocatalytic activity of $BiVO_4$ with monoclinic scheelite structure is much higher than that of the other two[7]. Therefore, the phase structure is an important factor to the photocatalytic performance.

In order to confirm the phase structure of as-synthesized samples, the XRD patterns were measured and shown in Fig.1. It can be seen that the initial product without calcination only shows a small bulge near 28.9°, which indicats that the sample is amorphous. After calcined at 500 °C, the sample shows strong diffraction peaks and all the diffraction peaks can be indexed to the monoclinic scheelite structure $BiVO_4$ (JCPDS No.14-0688) with unit cell parameters a=0.5195 nm, b=1.1701 nm, c=0.5092 nm, β=90.38°. Moreover, it can be seen that the intensity of diffraction peaks increases gradually with the increase of calcination temperature, indicating that the crystallinity of sample is improved gradually. Thus, the samples prepared by this method not only have pure phase, but also have good crystallinity.

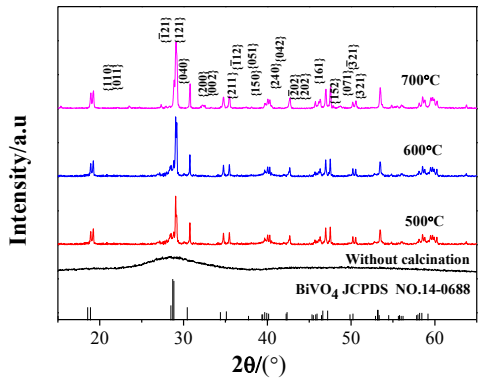

Fig.1 XRD patterns of $BiVO_4$ samples synthesized under different calcination temperature

3.2 Morphology Analysis

Fig.2 shows the SEM photographs of $BiVO_4$ samples obtained under different calcination temperature. It can be observed that the $BiVO_4$ without calcination presents flocculent morphology. $BiVO_4$ sample calcinated at 500 °C consists of spherical-like particles with the average diameter of 143nm. For the sample obtained at 600 °C, the particle size is raised to about 580nm. When the temperature is increased to 700°C, the morphology of the product varies greatly, developing from spherical-like particles to irregular-shaped blocks. As shown in Fig.2(d), the hard agglomeration phenomenon is very serious, and the particle size increases further to 7-8μm. The surface areas of $BiVO_4$ samples calcined at 500°C, 600 °C and 700 °C are 4.6209 m^2/g, 0.1397 m^2/g and 0.0717 m^2/g, respectively. According to the above analysis results, it can be concluded that the increase of calcination temperature will result in the increase of grain size, decrease of surface area and obvious hard agglomeration. This is mainly due to that with the increase of calcination temperature, atomic diffusion of $BiVO_4$ particles became more active, allowing for the reapportion of atoms to lower chemical potential status and generating agglomeration to lower the interfacial energy[8].

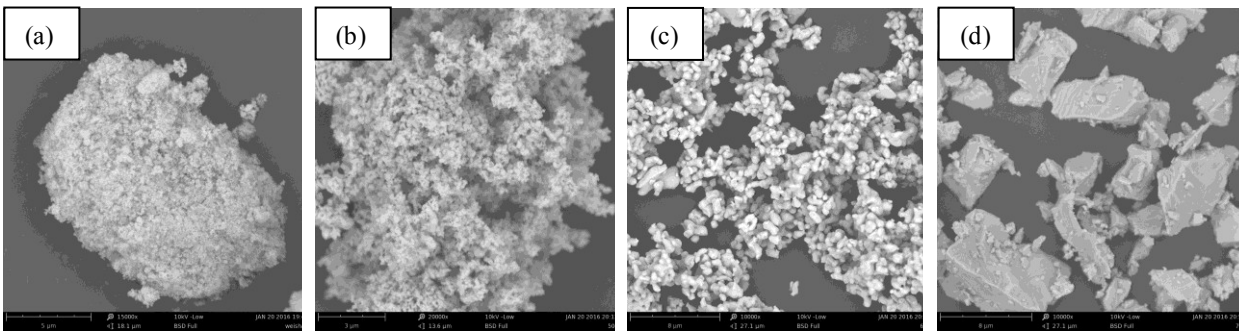

Fig.2 SEM images of $BiVO_4$ samples obtained at different calcination temperature

(a) without calcination, (b) 500 °C, (c) 600 °C, (d) 700°C

3.3 Optical Absorption Properties

Fig.3 shows the UV-Vis diffuse reflectance spectra of $BiVO_4$ samples calcined at different temperatures. It can be observed that all the samples have a broad and strong absorption in the range of 300 - 550 nm, suggesting that the synthesized samples not only can absorb the ultraviolet light, but also can absorb the visible light. So, it can be inferred that the samples are potentially good photocatalysts for sunlight-driven applications. The band gap energy (*Eg*) is a key parameter to the photocatalyst. As shown in Fig. 3, *Eg* can be estimated from the UV-Vis diffuse reflectance spectra using Tauc equation [9], $a(v)hv=K(hv-Eg)^{n/2}$, where $\alpha(v)$ is the optical absorption coefficient, hv is

the energy of the incident photon, K is an empirical constant. Therefore, by plotting the curve of $(ahv)^2$ versus hv (shown in the insets (d)-(f)) and extrapolating the curve to zero absorption coefficient, Eg can be obtained. From the insets, it can be observed that the Eg is 2.50 eV, 2.45 eV and 2.37 eV, respectively for $BiVO_4$ samples calcined at 500 °C, 600 °C and 700°C.These values are consistent with the result(2.47 eV) reported in the literature[10].

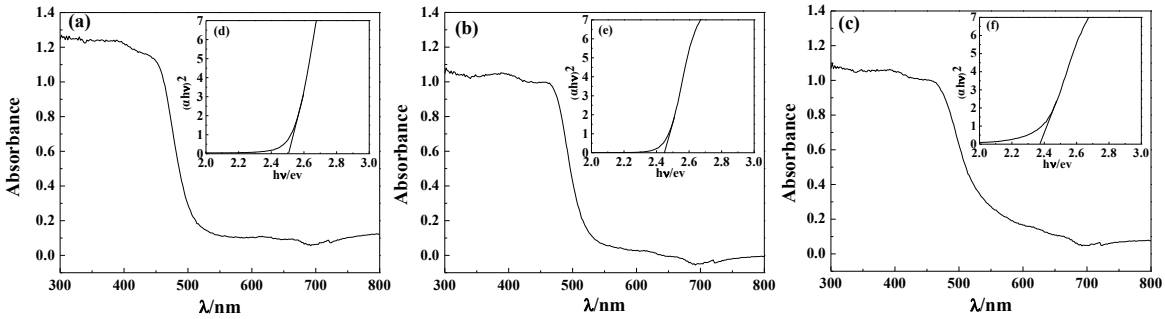

Fig.3 UV-Vis diffuse reflectance spectra of $BiVO_4$ samples calcined at (a)500°C, (b)600°C, (c)700°C; Inset(d)-(f): plot of $(\alpha hv)^2$ versus incident photon energy (hv)

3.4 Photocatalytic Activity

In order to contrast the photocatalytic activity of $BiVO_4$ samples calcined at different temperature, UV-Vis spectra of the solution after degrading reaction (60 min irradiation under visible light) were measured and compared with that of initial Acid Black 10B solution. In Fig.4, for the initial dye Acid Black 10B solution, the absorption peak at 618nm is caused by Azo bond conjugation system and the one at 320nm is caused by benzene and naphthalene ring structure[11]. When $BiVO_4$ calcined at 500 °C or 600 °C is used as photocatalyst, the characteristic absorption peaks of the dye solution are almost disappeared and the degradation rate (De) is nearly 100% (shown in inset). While $BiVO_4$ calcined at 700 °C as photocatalyst, the absorption peaks of the dye solution is decreased obviously, but still remains. In this situation, the decolorization rate is only 73.5%. Therefore, $BiVO_4$ calcined at 500 °C and 600 °C exhibit high photocatalytic activity. Further increasing calcination temperature will decrease the photocatalytic activity. This is mainly due to the increased particle size and decreased surface area with calcination temperature increasing.

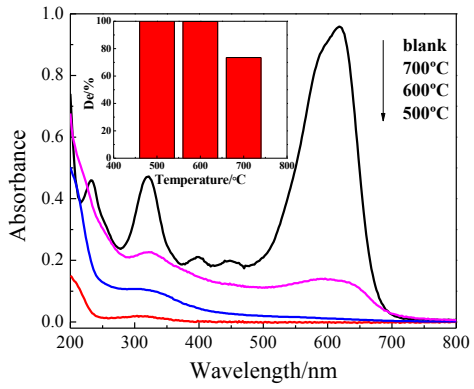

Fig.4 UV-Vis spectra of the solutions after degradation using samples calcined at different temperature as photocatalyst. Inset: Relationship between calcination temperature and De

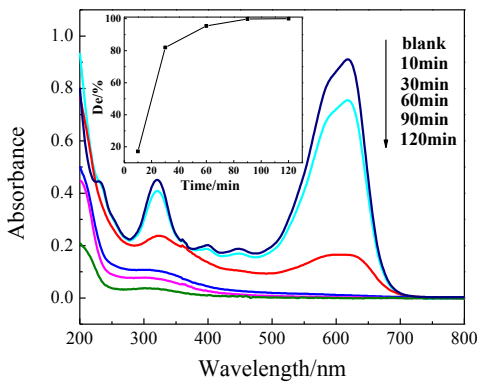

Fig.5 UV-Vis spectra of the dye solutions under different photocatalytic reaction time. Inset: Relationship between photocatalytic reaction time and De

Photocatalytic reaction time is also an important factor affecting the degradation rate (De) of the dye. Fig.5 represents UV-Vis spectra of the dye solution under different photocatalytic reaction time and the degradation rate (shown in inset). It can be seen that the absorption peaks of the dye solution are decreased gradually with the prolong of photocatalytic reaction time. When the irradiation time is 10 min, the degradation rate of Acid Black 10B solution is 17.1%; for 30 min, the degradation rate is improved to 82.9%; when the time is prolonged to 60 min, the degradation rate can reach to 99.9%. At this point, the UV-Vis absorption curve of the solution is very flat and the characteristic absorption peaks of the dye is almost disappeared, which indicates that the molecular structure of Acid Black 10B has almost been completely destroyed. After that, the degradation rates are all close to 100%. So, in order to save the time, the photocatalytic time is confirmed to 60 min.

3.5 Reaction Kinetics for Degradation of Acid Black 10B

As shown in Fig.6, there is a approximate linear relationship between $\ln(C_t/C_0)$ and t, here, C_0 and C_t are the initial concentration of dye solution and the concentration at time t during the degradation reaction, respectively. It can be inferred that the degradation reaction accords with one order reaction kinetics equation. The apparent rate constant is 0.0795 min^{-1}, which is obtained from the slope of the plot of $\ln(C_t/C_0)$ versus reaction time.

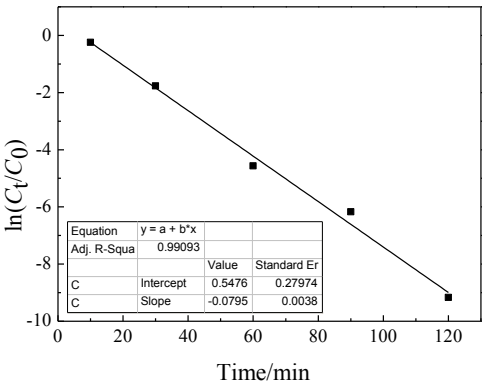

Fig.6 Kinetic plot of photodegradation reaction of Acid Black 10B

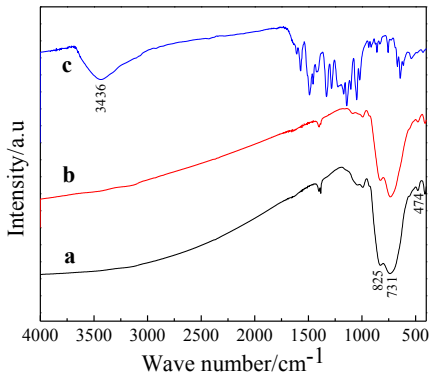

Fig.7 IR spectra of (a) $BiVO_4$, (b)the solid sample after degrading reaction,(c)Acid Black 10B

3.6 Mechanism of the Photocatalytic Reaction

In order to explore the mechanism of the photocatalytic reaction, the FTIR spectra of samples before and after photocatalytic reaction and Acid Black 10B (solid) are measured and shown in Fig.7. For the sample before photocatalytic reaction (Curve a in Fig.7), the peak at 474 cm^{-1} is ascribed to Bi-O vibration, the peaks at 731 cm^{-1} and 825 cm^{-1} can be assigned to symmetric and antisymmetric stretching vibration of V-O in the monoclinic phase $BiVO_4$[4], respectively. In Curve b, the position and shape of the peaks are bascially same as those in Curve a, no characteristic peaks of the dye can be found, and the color of the sample is still bright yellow, which indicates that the crystal structure of the sample has not been changed after photocatalytic reaction. Thus, the decolorization of dye solution is a result of photocatalytic degradation rather than absorption.

In $BiVO_4$ with monoclinic scheelite structure , the Bi^{3+} 6s and O 2p orbits hybridize to form the valence band. Due to its narrow band gap (~2.4 eV), under visible light irradiation, electrons in the valence band can be excited to the conduction band, leaving holes in the valence band and generating electron-hole pairs in $BiVO_4$ particle. The holes (h^+) as a kind of good oxidants can react with H_2O and OH^- adsorbed on the surface of $BiVO_4$ particles to produce highly active hydroxyl radicals (·OH). The photogenerated electrons(e^-) transfer to the surface of $BiVO_4$ particles to interact with O_2 to generate highly active $\cdot O_2^-$ and $HO_2\cdot$ radicals[12]. These highly active radicals (·OH, h^+ , $\cdot O_2^-$ and $HO_2\cdot$) attack the dye molecules, and then make them degrade into inorganic small molecules through a series of oxidation-reeeduction reactions.

4 Conclusion

$BiVO_4$ with single-phase monoclinic scheelite structure was synthesized by simple precipitation method followed with calcination process. The band gap energy of as-synthesized $BiVO_4$ is 2.37~2.50 eV and the UV-Vis absorption band is very broad, extending from 300 nm to 550 nm. It is found that the increase of calcination temperature will result in the increase of particle size and the morphology developing from spherical-like particles to irregular-shaped blocks. $BiVO_4$ samples obtained at 500~600 °C show excellent visible-light photocatalytic activity. The process of degradation reaction accords with one order reaction kinetics equation. The photocatalytic mechanism is presumed as follows: under visible light irradiation, the photogenerated holes (h^+) react with H_2O and OH^- adsorbed on the surface of $BiVO_4$ particles to produce highly active ·OH, and the photogenerated electrons (e^-) interact with O_2 to generate highly active $\cdot O_2^-$ and $HO_2\cdot$. Then these highly active radicals attack the dye molecule to achieve photodegradation.

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