Hydrothermal preparation and visible-light photocatalytic activity of bismuth layer structure Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ nanoplates

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Abstract. Nanoparticles of bismuth-layered ferroelectric and photocatalytic material, Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ have been prepared by hydrothermal method synthesis, the raw materials include Bi(NO$_3$)$_3$, NaOH and Nb$_2$O$_5$. The phases and morphologies of the samples are characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic performance of the Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ powders were evaluated by degradation of methylene blue (MB) molecules ($\lambda$>400 nm). The results show that the phases of Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ particle is pure orthorhombic bismuth layer structure at 160°C and 10 h. The morphology of the sample is flake-like, the thickness size is 25 nm, and the edge size is 200 nm. Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ sample has excellent light response performance in the ultraviolet-visible wavelength range, with a band gap of 2.55 eV, and it exhibits photocatalytic performance for photocatalytic decomposition of MB under ultraviolet-visible light irradiation. As novel of visible-light-driven photocatalysts, Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ with a two-layer Aurivillius structure has a great potentially application in environment-protection field.

1. Introduction

Currently, the increasing pollution problem has attracted more and more attention, semiconductor photocatalysis is one of the most promising technologies, it provide “green” environmental protection technology to eliminate all kinds of pollutants from the source[1-8], particularly water pollutants caused by the industries organic pollutants. Since TiO$_2$ was discovered to be used for photocatalytic water splitting, photocatalysis based on semiconductor materials has attracted widespread attention [3]. In recent years, The research on photocatalytic materials in the visible light range has become the focus because they respond to solar energy more effectively than traditional wide-band gap light catalysts, e.g., TiO$_2$[3-4]. Aurivillius type bismuth layer structured compounds consists of alternating (Bi$_2$O$_3$)$^{2+}$ layers and (A$_{n-1}$B$_n$O$_{3n+1}$)$^{2-}$ octahedral layers, with normal formula Bi$_2$A$_{n-1}$B$_n$O$_{3n+3}$(A=K, Na, Ca, Sr, Ba, Bi, Pb and B=Ti, Zr, Nb, Ta, W, Mo, Fe). This type compounds normal have layered structure and peculiar performance, such as ferroelectricity, piezoelectric properties, catalytic properties and dielectric responsiveness[5-7]. Recently, much attention has been focused on bismuth layer structured compounds as photocatalytic decomposition photocatalysts, with exhibiting excellent photocatalytic performance for the degradation of organic pollutants under visible light irradiation, for example, Bi$_2$WO$_6$[2-8], Bi$_2$W$_2$O$_{12}$[8], Bi$_2$MoO$_6$[9], BiVO$_4$[10], BiNbO$_4$[11], BiTaO$_4$[11], CaBi$_2$O$_4$[12], Bi$_2$Ti$_2$O$_7$[13], Pb$_2$Bi$_2$Nb$_2$O$_{15}$[14], SrBi$_2$Nb$_2$O$_9$[15] and Bi$_4$Ti$_3$O$_{12}$[16]. Studies have shown that the...
Aurivillius metal oxide materials with $d^0$ electronic structure, such as Nb$^{5+}$[11], Ta$^{5+}$[11] and Ti$^{4+}$[16] are efficient photocatalysts for overall water splitting with high quantum yields[14]. Sodium bismuth niobate oxide, Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ (hereafter NBNO) is a $n=2$ of the Aurivillius type. The unit cell of NBNO belongs to the structure of the orthogonal space group $A2\bar{1}m$ and is divided into two molecular formula units, namely (Bi$_2$O$_2$)$^{2+}$and(Na$_{0.5}$Bi$_{1.5}$Nb$_2$O$_7$)$^{2-}$ layers. As we all know, the ferroelectric material of the NBNO sample has been studied for its high Curie temperature $T_c$ (~780 °C) and good performance[2,7,9]. Nevertheless, the photocatalytic activity of bismuth layer structure NBNO have not been researched yet, studying the material size effect of photocatalytic performance is extremely important for the basic research and engineering application of optoelectronics[2,7,9].

In this work, NBNO was synthesized by hydrothermal method, and its photo-electronic properties were studied. In addition, the performance study of NBNO photocatalytic decomposition of methylene blue (MB) was also carried out.

2. Experimental

2.1. Preparation of the NBNO powders by hydrothermal method

The reagents used in this study were all analytical grade which were purchased from the Shanghai Chemical Company. Deionized water was used throughout the experimental process. Weighing Bi(NO$_3$)$_3$·5H$_2$O (0.2425 g, 0.5 mmol), Nb$_2$O$_5$(0.1027 g, 0.4 mmol), NaOH(0.4000 g, 0.1 mmol as reaction material. In the preparation experiment, Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 25 mL water of was added 3 mL of HNO$_3$ (3 M), magnetic stirring for 5 min, then add Nb$_2$O$_5$ with vigorous stirring for 10 min to get solution A, 10 mL water dissolve NaOH to get NaOH solution and denoted as the solution B. The solution A and the solution B is stirred and mixed with each other, the NH$_3$·H$_2$O was then added to adjust the pH value to 8, this mixture was stirred for an additional 20 min to get precursor. Then it was transferred to a 50 mL Teflon-lined stainless autoclave. It is placed in an oven, keep heating at 140-180 °C for 8-12 h, and then cooled to room temperature with the furnace. The yellow precipitate was rinsed with deionized water and absolute ethanol for 3-5 times, respectively. The sample was dried at 80°C[1-4,8,9,14].

2.2. Performance characterization

An X-ray diffractometer with Cu Ka radiation was used to determine the phase structure of the sample, the model is Bruker D8 Advance. Use a scanning electron microscope(SEM) to observe the morphology of the obtained powder under an accelerating voltage of 20 kV. The instrument model is SEM, JSM-5610LV. The sample was dry pressed into a disc shape, and the UV-Vis absorption spectrum of the obtained powder was tested with an ultraviolet-visible spectrophotometer, the instrument model is Cary 100, Varian, USA, and BaSO$_4$ was used as the reflectance standard in the experiment[8,14,15].

2.3. Photocatalytic decomposition of MB

The performance of NBNO powder as a photocatalyst is evaluated by degrading MB under simulated sunlight. The light source uses a 500WXe lamp and the 400 nm cut-off filter. The simulation experiment was carried out in a sealed black box at room temperature. The reaction beaker was placed in the black box, the top light source was turned on and the cut-off filter was placed to achieve visible light irradiation. The initial concentration of MB is 10 mg/L, and the content of catalyst is 0.1 g/L. The sample is first dispersed in an ultrasonic bath for 10 minutes, then the solution is stirred for 30 minutes and exposed to visible light. The catalytic decomposition reaction of MB under the light condition was tested by detecting the ultraviolet-visible absorption spectrum of the solution every 15 minutes. Theoretically, the concentration of MB should be proportional to the maximum absorption intensity of the absorption spectrum[8,14,15].
3. Results and discussion

3.1 Phase Structure of Samples

Fig. 1 is the XRD patterns of the NBNO samples after difference temperature on hydrothermal reaction at 140, 160 and 180 °C for 10 h. XRD patterns showing all samples were pure bismuth layer structure Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ (NBNO) with the orthorhombic space group A$_{2}$$\alpha$m, The strongest diffraction peak of the powder corresponds to the (115) crystal plane of the standard card, corresponding well to the orthorhombic phase of NBNO(JCPDS No.42-0397). This is also consistent with the characteristic peak of bismuth layered materials reported in the previous literature as $(112n+1)$ [3,18]. The intensity of diffraction peak at 140 °C is relatively weaker, due to the low reaction temperature, grain is not developed, the degree of crystallization is small. The intensity of diffraction peak become sharper at 160 °C, the diffraction peaks at 180 °C is similar to the peak at 160 °C with increased peak heights, the peaks becomes sharper, and the sharp diffraction of X-ray diffraction (XRD) indicate the formation of well-developed NBNO, It may be that the higher temperature can provide larger energy to overcome the energy barrier of phase transition and reaction temperature accelerated the crystallization process of the product. The experiment selected 160 °C as optimum temperature for hydrothermal method from the angle of economizing energy, compared with the conventional solid state reaction should be prepared NBNO powder at 860 °C, the hydrothermal method proceeds at lower temperature[3,17,18].

Fig. 2 is the XRD patterns of the NBNO samples after difference time on hydrothermal reaction method for 8, 10 and 12 h. With the increase of reaction time, the intensity of diffraction of the NBNO phase increased gradually. The figure shows that the crystal structure of NBNO does not change much with the extension of the reaction time, which means that the reaction time has little effect on the crystal crystallization process of NBNO. From the reaction condition and economic considerations, we select the 10 h reaction time[3,17,18].

3.2 The micromorphology of NBNO

Fig. 3a-d is the SEM morphology of samples at reaction temperatures of 140 °C, 160 °C and 180 °C for difference reaction temperature. Fig. 3a is the morphology of powder prepared at 140 °C for 10 h, the morphology of most NBNO sample is ellipsoidal particles[1-3,8,9,10]. Fig. 3b shows the NBNO morphology of synthesized at 160 °C for 10h. The grains layered growth along the a-b plane and without hard aggregate. The sample is flake-like, the thickness size is 25 nm, and the edge size is 200 nm. The flakes morphology of samples is determined by the bismuth layer structure characteristics of the inherent[1-3,8,9,10]. Fig. 3c shows the morphology of the powder synthesized at the same temperature but the reaction time prolongs to 12 h, the sample further grow up, some grains extraordinarily grow[1-3,8,9,10]. Fig. 3d shows the morphology of the sample synthesized at 180 °C for 10 h, the morphology of most sample is plate shaped, some particles interconnected with each
there is a small amount of hard aggregate particles and interfused to the bigger particles[1-3,8,9,10].

Fig. 3 Representative SEM morphology of NBNO. 3 (a) 140 °C for 10h, 3(b) 160 °C for 10h, 3 (c) 160 °C for 12h and 3(d) 180 °C for 10h.

3.3 Photophysical and photocatalytic properties

The photo-electric response characteristics of semiconductors are considered to be a key factor in determining their photocatalytic activity, which is closely related to the electronic structure of the material[2,15]. The photoelectric response characteristics of NBNO is measured by using an ultraviolet-visible spectrometer, and its diffuse reflectance spectrum is shown in Fig. 4. According to its spectrum, NBNO sample exhibits photoelectric response characteristics from ultraviolet light region to visible light shorter than 487 nm, which is consistent with the yellow color of its powder.

According to the crystal semiconductor band gap theory, the photo-electric response performance near the band edge can be expressed by the formula $a h \nu = A(h \nu - E_g)^{n/2}$, where $a$, $h$, $\nu$, $E_g$ and $A$ correspond to the photo-electric response coefficient, Planck Constant, optical frequency, band gap and constant, respectively[2,3,19,20]. The last parameter $n$ depends on the characteristics of the photo-electron transition in the semiconductor. For materials with direct photo-electron transition, $n=1$, and for materials with indirect photo-electron transition, $n=4$. The absorption coefficient of the full emission spectrum is directly proportional to the absorbance. Experiments have proved that this transformation of bismuth-based oxides is straightforward. The band gap energy value of the material is estimated by the tangent intercept of the abscissa on the graph $(A h \nu)^{1/2} = f(h \nu)$[2,19], and the experiment shows that the measured band gap of NBNO is 2.55 eV.

The catalytic performance of the sample under light conditions was tested and evaluated by the degradation degree of MB in the aqueous solution. The amount of MB adsorption of NBNO nanosheets and the changes in the spectrum over time during the decomposition process under light conditions are shown in Fig. 5. As shown in Fig. 5, under visible light irradiation, the time change of MB concentration is monitored and evaluated by checking the change of the maximum absorption peak. In the ultraviolet-visible spectrum, the absorption peak intensity of MB at 663 nm is the largest, which is considered to be its characteristic peak. During the decomposition reaction process under light conditions, it can be concluded that the absorption intensity of MB at 207 and 507 nm decreases.
rapidly, indicating that MB decomposes rapidly under visible light conditions, the absorption peaks has disappeared after 90 min of irradiation, its absorption curve is very flat, solution clear transparent, and without new absorption peak, which showed that the molecular structure of MB under the effect of photocatalyst has been completely destroyed and degraded. The variation curve of MB concentration with the catalytic reaction time under light conditions is shown in the inset of Fig.5. Under visible light irradiation, the photocatalytic degradation rate of NBNO nanosheets within 90 minutes is $\sim 97.3\%$. It can be seen that the bismuth-layered NBNO nanoplates shows good photocatalytic response activity for degradation of organic dyes of MB.

4. Discussion

The bismuth layer structured compounds exhibits the highest catalytic response characteristics under light irradiation due to three possible mechanisms. First, The influence of material molecular structure characteristics and inherent semiconductor energy band structure on photocatalytic performance. Studies have shown that it is due to the bismuth element. Bismuth (Bi) is a p-zone metal element with $d^{10}$ configuration. The $6s$ of Bi can be hybridized with the $2p$ energy level of O to form a preferred hybrid valence band (VB), which is beneficial to increase the photo-generated holes in the band gap. The mobility of Bi$^{3+}$ is conducive to the enhancement of the photocatalytic performance of Bi$^{3+}$-based oxide[18]. Previous studies have proposed this possible factor[18,19]. The absorption band edge of orthorhombic system bismuth layer structured NBNO appears in the visible wavelength range, the suitable energy band help for absorption of sunlight. The second possible mechanism is intrinsic layered structure. The $(A_{m-1}B_mO_{3m+1})^2$ structure of the distortion and BO$_6$ octahedral dipole moment of gigantic effectively stimulate the creation of photogenerated electron-hole pairs. Excited electrons leave holes in the valence band. At the same time, the layered structure able to take advantage of layered space as the appropriate response and reduced the electron-hole recombine, increase the reaction efficiency. The third is NBNO nanoplates with smaller particle size and large specific surface area. The photoresponse characteristics of photocatalytic materials are closely related to the particle size, specific surface area and geometry of the particles, etc[14-16]. Compared with the hydrothermal method that reacts at low temperature, it is easier to prepare particles with a smaller particle size. Therefore, NBNO samples can more effectively sense the energy of incident light, thereby improving catalytic performance.

5. Conclusion

The NBNO nanoplates photocatalysts were successfully synthesized by a hydrothermal method. The NBNO nanoplate was found to be a novel and promising visible light driven photocatalysts, with $2.55\text{ eV}$ of a narrowed band gap. At an optimal reaction condition at 160 °C and 10 h, the sample has the
best photocatalytic response to the MB dye photocatalytic decomposition reaction under simulated sunlight, and after 90 min of irradiation, the MB was removed 97.3%. It exhibited a notable visible light induced photocatalytic capability due to its bismuth layer structured, appropriate band gap, the smaller particle size and large specific surface area. The experimental results show that NBNO nanosheets are a novel type of high-efficiency photocatalyst with a very wide range of application prospects, this research provides a new strategy for the design of nanostructured photocatalysts with excellent performance.

Acknowledgments
This research was supported by the fund of Natural Science Basic Research Program of Shanxi, China (Program No. 2019JZ-40), the National Natural Science Foundation of China (21471159).

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