Preparation and photocatalytic property of sunlight-driven photocatalyst $Bi_{38}ZnO_{58}$

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Abstract

Sunlight-driven photocatalyst $Bi_{38}ZnO_{58}$ was synthesized by a solid-state reaction method. The synthesized product was characterized physically by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The photocatalytic degradation of methylene blue was evaluated by spectrophotometric analysis; meanwhile, the possible pathway of the photocatalytic reaction also has been studied. In addition, the band edge position of $Bi_{38}ZnO_{58}$ was roughly calculated according to the electronegativity of the constituent atoms, and the calculation result further confirms the strong oxidative property of the photocatalyst under the sunlight irradiation.
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1. Introduction

Photocatalytical1y decomposing organic pollutants by utilizing an oxide semiconductor to generate clean environment has been a dream of humankind for several decades [1–5]. To date, many organics have been found to be decomposed on TiO_2 that is strongly responsive to ultraviolet light (UV) occupying merely ca. 4% of whole solar energy, which makes it impossible to futherly wider application. Therefore, it is indispensable and urgent to develop a particular photocatalyst sensitive to sunlight [4,5] for wastewater treatment.

The desired effect in the process for decomposition of organic contaminants is that photogenerated holes in a semiconductor photocatalyst oxidize the organic pollutants via intermediate products to inorganic substances, such as Cl^-, SO_4^{2-}, NO_3^-, and so on [6]. This process involves: (1) photogenerated electrons in the conduction band (CB) are trapped by a recipient (such as oxygen); (2) photogenerated holes in the valence band (VB) are consumed by donors (such as organics) [7]. The higher the mobility of the photogenerated carriers (including holes and electrons), the better the performance of the photocatalyst [8–10]. In addition, the VB position of a semiconductor also plays an important role in deciding the photocatalytic activity of the semiconductor. The deeper the VB of a semiconductor, the stronger its oxidative activity, and the higher the photocatalytic property of the material for decomposition of the organics. Therefore, in order to develop a sunlight sensitive photocatalyst with a narrow band gap, it is also a useful way to control the position of the VB [7].

Based on the above overviews, in this paper, we prepared the new photocatalyst, $Bi_{38}ZnO_{58}$, whose photocatalytic property was investigated based on methylene blue as decomposed substance. Methylene blue was completely decomposed within only 5 h under sunlight irradiation, which demonstrated that $Bi_{38}ZnO_{58}$ owned good photocatalytic activity. Meanwhile, its photocatalytic mechanism and band edge potential were studied in detail.

2. Experimental

2.1. Preparation of $Bi_{38}ZnO_{58}$

$Bi_{38}ZnO_{58}$ semiconductor was prepared by solid-state reaction method. $Bi(NO_3)_3 \cdot 5H_2O$, $ZnCl_2$, NaOH and PEG 400 were used as the starting materials, which were all of analytic reagent grade. $Bi(NO_3)_3 \cdot 5H_2O$, $ZnCl_2$ and NaOH were weighed in the

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stoichiometric proportion of $Bi_{38}ZnO_{58}$, and milled carefully, respectively. Then $Bi(NO_3)_3 \cdot 5H_2O$ and $ZnCl_2$ were mixed with addition of 20 ml PEG 400 solution. The mixture was ground for 1 h, and then the needed amount solid powder of NaOH was added into the former mixture with very vigorous grindings for 30 min. The sample was kept for several days at 60 °C in order to ensure that the reaction was thoroughly completed, then reground and sintered at 700 °C for 2 h in air.

2.2. Characterization of $Bi_{38}ZnO_{58}$

X-ray diffraction study was carried out using an X-ray diffractometer (XRD, Max 18^{XCE}, Japan) using a Cu Kα source ($\lambda = 0.154056$ nm). The image of the sample was examined by Scanning electron microscopy (SEM, LEO 1403VP, Germany) and transmission electronic microscopy (TEM, Hitachi-600, Japan). To determine the band gap energy of the photocatalyst, UV–vis diffuse reflectance spectra was carried out, in the wavelength range of 200–600 nm, using a Hitachi U-3010 spectrophotometer. The pure powdered Al_2O_3 was used as a reference sample.

2.3. Photocatalytic activity measurements

The photocatalytic activity of $Bi_{38}ZnO_{58}$ photocatalyst was evaluated by photodegradation of methylene blue aqueous solution. All photocatalytic reaction was performed under sunlight irradiation and maintained constant magnetic stirring, and 100 ml of methylene blue solution (5×10^{-5} mol/l) was mixed with 0.1 g as-prepared photocatalyst in a beaker. The methylene blue solution was taken 6 ml away every certain minute during the whole irradiation. The concentrations of methylene blue solution were determinded by UV–vis spectrophotometer (UV-2450, Japan and adsorption at $\lambda_{max} = 664$ nm for methylene blue).

3. Results and discussion

3.1. Phase of $Bi_{38}ZnO_{58}$

The crystalline structure of the as-prepared $Bi_{38}ZnO_{58}$ was characterized by using an X-ray diffractometer. As shown in

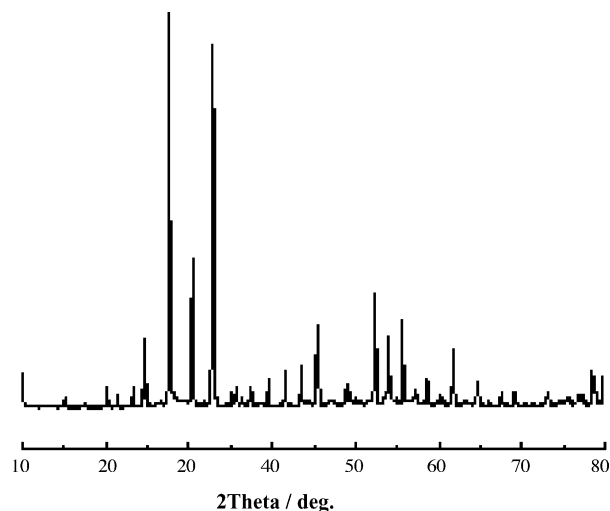Fig. 1. The XRD pattern of $Bi_{38}ZnO_{58}$.

Fig. 1, all these diffraction peaks of the synthesized $Bi_{38}ZnO_{58}$, including not only the peak position but also their relative intensities, can be indexed into the cubic crystalline structure, which is in line with the standard spectrum (JCPDS, card no. 42–0183).

3.2. SEM and TEM of $Bi_{38}ZnO_{58}$

The SEM and TEM images of $Bi_{38}ZnO_{58}$ are shown in Fig. 2(a) and (b), respectively. From the images, it can be seen that the sample are nanorodes with relatively uniform size. The diameter of nanorodes is about 70 nm, and the length of short nanorodes is ranged from 200 to 500 nm. However, there also exists a little agglomeration, which probably attributes to the heat treatment under the high temperature of 700 °C.

3.3. UV–vis diffuse reflectance spectrum and band energy

The room temperature UV–vis diffuse reflectance spectrum of $Bi_{38}ZnO_{58}$ is shown in Fig. 3. As seen in Fig. 3, $Bi_{38}ZnO_{58}$ shows a strong photoabsorption property in the UV region, moreover, it can absorb visible light shorter than 582 nm. As to the

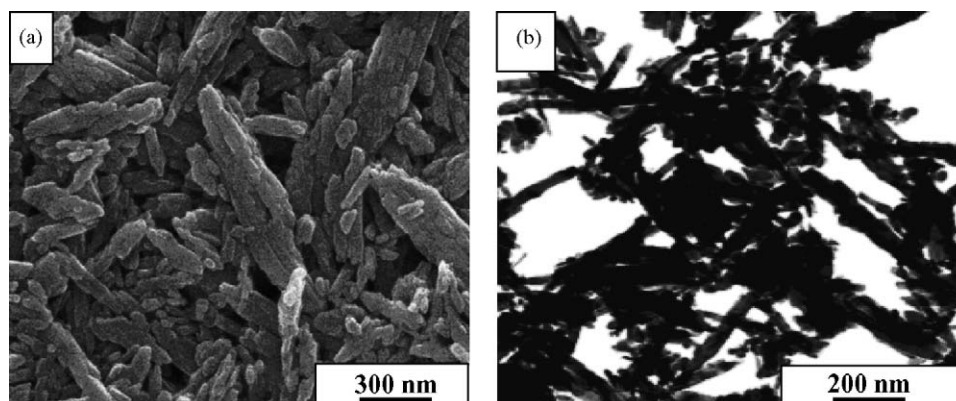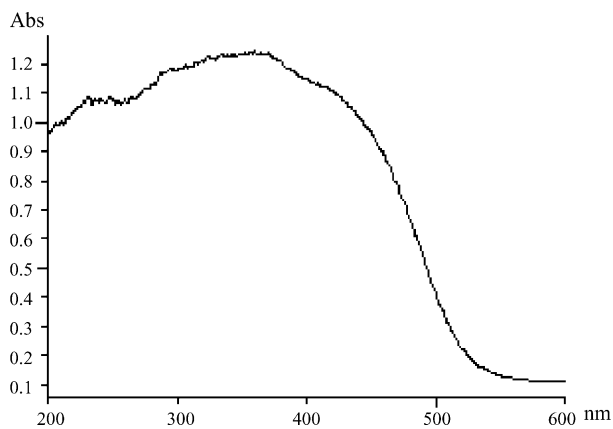Fig. 2. SEM (a) and TEM (b) images of $Bi_{38}ZnO_{58}$.

Fig. 3. UV–vis diffuse reflectance spectrum of $Bi_{38}ZnO_{58}$.

Fig. 5. Wavelength dependence of degradation rate of methylene blue solution over $Bi_{38}ZnO_{58}$ photocatalyst with different cut-off filters after light irradiation for 1 h.

wavelengths of absorption edges, they are determined by extrapolating the horizontal and sharply rising portions of the curves and defining the edge as the wavelength of the intersection. The band gap absorption edge of $Bi_{38}ZnO_{58}$ is determined to be 582 nm in the visible region [11–13], from which the optical band gap of $Bi_{38}ZnO_{58}$ can be calculated as ca. 2.13 eV.

3.4. Photocatalytic activity

For the purpose of comparison, experiments of the degradation of methylene blue in the presence and absence of $Bi_{38}ZnO_{58}$ under sunlight irradiation have been both done, respectively. It can be seen from Fig. 4 that the methylene blue solution is stable and cannot yet be decomposed under sunlight irradiation in the absence of $Bi_{38}ZnO_{58}$, which is in consistent with the Ref. [6]. However, methylene blue can be completely decomposed just after only 5 h sunlight irradiation in the presence of $Bi_{38}ZnO_{58}$.

3.5. Wavelength dependence and degradation mechanism

In order to confirm that the photocatalytic reaction is really driven by light, we further obtained the wavelength dependence of the photocatalytic activity of $Bi_{38}ZnO_{58}$ with the different

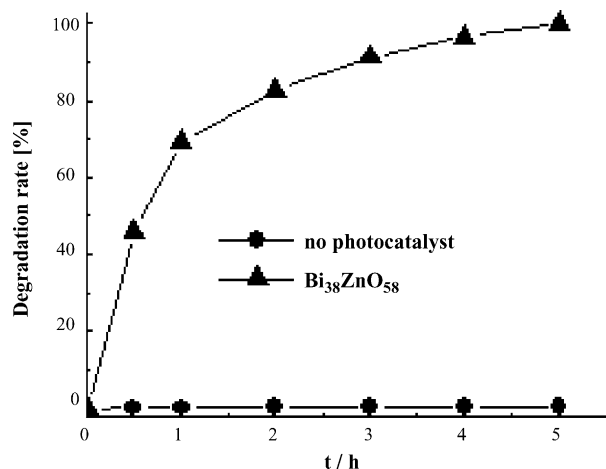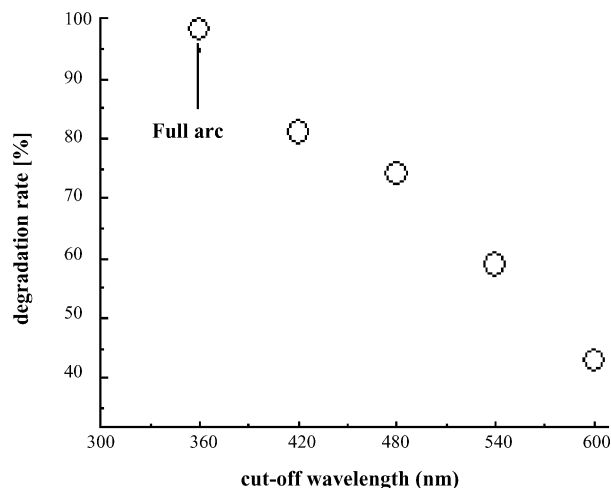Fig. 4. The photocatalytic activity of $Bi_{38}ZnO_{58}$.

optical cutoff filters, which were from full arc (without filter) to $\lambda = 600$ nm, under near 1 h light illumination. The results are plotted in Fig. 5. If a reaction is really driven by light, the variation of the light wavelength will affect directly the amount of photons entering the reaction system and then affect the photocatalytic properties [14,15]. From Fig. 5, it can be seen that the variation of the photocatalytic properties over $Bi_{38}ZnO_{58}$ is closely relevant to that of light wavelength, indicating that methylene blue catalytic degradation over $Bi_{38}ZnO_{58}$ was truly driven by light. Meanwhile, $Bi_{38}ZnO_{58}$ showed not only high photocatalytic activity in the UV light region, but also in the visible light region. The photocatalytic activity decreased with increasing wavelength λ in the visible light region. However, the photocatalyst still kept a high activity, Even when the cut-off filter of $\lambda = 600$ nm was employed, indicating that the catalyst is active in a wide wavelength range.

To get some information about the degradation mechanism of methylene blue over $Bi_{38}ZnO_{58}$, possible pathway of the photoelectrons transfer excited by sunlight illumination was systematically investigated. It can be seen from Fig. 3 that $Bi_{38}ZnO_{58}$ showed the ability of absorbing visible light shorter than 582 nm, which could cause the transition of the electrons from the valence band (VB) to the conduction band (CB) in the $Bi_{38}ZnO_{58}$, as shown in the process 1 in Fig. 6. Then the electrons in the conduction band were captured by O_2 dissolved in water, correspondingly the holes in the valence band react with OH^- or H_2O, which were adsorbed on the surface of $Bi_{38}ZnO_{58}$, to give the hydroxyl radical [16]. And it has been reported that the produced hydroxyl radical initiates various oxidation reactions [17,18]. That is to say, methylene blue can be photocatalytically degraded when the wavelength is shorter than 582 nm. Simultaneously, $Bi_{38}ZnO_{58}$ also showed certain photocatalytic activity when the light wavelength was much longer than 582 nm. It is known to all that methylene blue dye can absorb the whole range of visible light, which is attributed to the ground state and the excited state of the dye [6]. Therefore, methylene blue and $Bi_{38}ZnO_{58}$ were both the materials absorbing light irradiation in the present study.
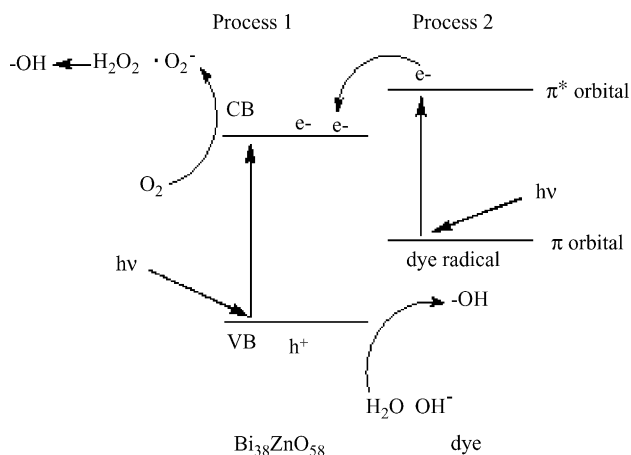
Fig. 6. Photocatalytic mechanism for $Bi_{38}ZnO_{58}$.

However, in the case of $\lambda \geq 582$ nm, methylene blue was the main material absorbing light irradiation. From the methylene blue photolysis it can be seen that the methylene blue solution is stable and cannot yet be degraded under sunlight irradiation in the absence of photocatalyst. Therefore, $Bi_{38}ZnO_{58}$ played an important role in the photocatalytic decomposition of methylene blue, even if the light wavelength was longer than 582 nm. When $\lambda \geq 582$ nm, methylene blue dye absorbed the incident photon flux, and the photogenerated electrons were transferred to the excited state from the ground state of the dye owing to the intramolecular π–π^* transition, then the photoelectrons of the excited state were immediately injected into the conduction band (CB) of $Bi_{38}ZnO_{58}$. Subsequently, the photoelectrons in the conduction band (CB) were captured by O_2 dissolved in the water and the oxidized dyes were degraded via several intermediates, as shown in process 2 in Fig. 6. To sum up, the photocatalytic degradation of methylene blue was the joint effort of $Bi_{38}ZnO_{58}$ photocatalyst and dye itself in the present work.

3.6. Calculation of the VB position of $Bi_{38}ZnO_{58}$

For the sake of knowing about the VB position of $Bi_{38}ZnO_{58}$, we also calculated theoretically the band edge position of $Bi_{38}ZnO_{58}$ according to the concepts of electronegativity. Up to now, many chemists have calculated band potentials for oxide semiconductors using the atomic electronegativities of the constituent atoms [19,21]. The electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy [20], other than the common-defined term. The CB edge position of a semiconductor at the point of zero charge can be expressed empirically by [19,20].

$$E_{CB} = X - E^e - 0.5E_g$$

Where E_{CB} is the CB edge potential, X the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, E^e the energy of free

electrons on the hydrogen scale (≈ 4.5 eV), and E_g is the band gap energy of the semiconductor. According to this empirical expression, the CB edge energy of $Bi_{38}ZnO_{58}$ is roughly calculated. Subsequently the edge position of the VB of the photocatalyst is determined as 2.6 eV based on its band gap energy. Compared with strong oxidants such as H_2O_2 and O_3, whose oxidative potential 1.77 eV (H_2O_2) and 2.07 eV (O_3), respectively, $Bi_{38}ZnO_{58}$ photocatalyst has a much stronger oxidative activity.

4. Conclusion

$Bi_{38}ZnO_{58}$ photocatalyst has been successfully synthesized by means of solid-state reaction method and its photocatalytic property also has been systemically investigated. Methylene blue, as a considerable stable organic pollutant, can be nearly entirely degraded within 5 h under sunlight irradiation and its degradation mechanism was also studied. Moreover, the test of wavelength dependence revealed that the photocatalytic property of $Bi_{38}ZnO_{58}$ was closely associated with its optical absorption and the calculation of band edge potential further proved its considerably high oxidative activity. In short, the present work synthesized a promising photocatalyst sensitive to sunlight for wastewater treatment.

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