Novel Template-Free Solvothermal Synthesis of Bi_2WO_6 Micro/Nano-Structures with pH-Controlled Shapes

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Abstract. A novel Bi_2WO_6 micro/nano-structures with pH-controlled shapes were synthesized by Novel template-free solvothermal synthesis method. Multiple technologies were applied to characterize the as-synthesized samples including X-ray powder diffraction(XRD), field emission scanning electron microscopy(FE-SEM), UV-vis diffuse reflectance spectrum(UV-vis), nitrogen absorption/desorption isotherm. The photocatalytic activity of the samples was evaluated by degrading ciprofloxacin simultaneously.It is demonstrated that the morphologies of composites were controllable with pH of reactant solution .The result showed that nearly 90% of all the target antibiotics were degraded within 180min utilizing the Bi_2WO_6 synthesized under pH of 7.

1. Introduction

Antibiotics have increasingly aroused attention due to their ubiquitious occurrence in water environment.Trace level of antibiotics has been detected in water environment compromising ground water, surface water even drinking water[1-4]. It has become a matter of concern as emerging pollutants among the public. These chemicals pose potential risks and hazards to human health and ecological sustainability. It is of great significance to degrade and eliminate the antibiotics by performing a green and economical technology.

Semiconductor photocatalysts have gained tremendous attention due to their wide applications in water purification by degrading antibiotics under visible light irradiation recently[5-6]. Bi_2WO_6 is one of newly developed visible-light-driven photocatalysts, and its photocatalytic performance is seriously dependent on its structure, morphology and components[7-8]. Shape-controlled synthesis of semiconductor micro- and nano-materials has been considered as an important fundamental scientific subject due to their variety of shape- and size-dependent electrical and optical properties, which would open a new domain of theoretical and technological application[9-12]. Owing to photocatalysts properties depending greatly on their orientations of the active constituents, the design of organized photocatalysts with novel structure has been an important active research direction. Here, we developed a method to obtain Bi_2WO_6 micro/nano-structures with pH-controlled shapes via template-free solvothermal synthesis. The resulting Bi_2WO_6 micro/nano-structures had a flowerlike end composed of thousands of Bi_2WO_6 nanowires. The as-prepared nanomaterials are suitable to be used as sensors to detect chemical materials due to their special morphology and large surface area.

2. Experimental Procedure

All the chemicals used were of analytical grade without any purification. In a typical procedure, 5mM of sodium tungstate($Na_2WO_4 \cdot 2H_2O$) was dissolved in 40mL deionized water to form solution A and 10mM of bismuth nitrate($Bi(NO)_3 \cdot 5H_2O$) was dissolved in 40mL deionized water to form solution B. Both solutions were ultrasonicated for 30 min in order to disperse the compounds in the solvent sufficiently. A mixed solution was obtained by adding solution A to solution B dropwise followed by magnetic stirring at room temperature for 1h. The pH of the mixture solution was adjusted by adding 1%HNO_3 or 2mol/L NaOH to 1, 3, 5, 7, 9 and 11. Subsequently, the final

mixture solution was transferred into a 100mL Teflon-lined autoclave up to 80% of the total volume. Then the autoclave was sealed in a stainless steel tank and heated at 120°C for 18h. After cooling to room temperature, the as-synthesized precipitates was separated by centrifugation, then washed with distilled water and absolute ethanol three times respectively. Finally the samples were dried at 100°C for 6h for further investigation and application.

X-ray powder diffraction(XRD) patterns of as-synthesized samples were recorded on a D/max-2550 PC (RIGAKU, Japan) X-ray diffractometer using monochromatized Cu Kα(λ=1.54056Å) radiation under 40kV and 200 mA and with 2 ranging from 10°-60°. The field emission scanning electron microscopy images (FE-SEM) of the Bi_2WO_6 powders were observed by a JEOL JSM-6335F scanning electron microscope with an accelerating voltage of 20kV. UV-visible diffuse reflectance spectra(DRS) of Bi_2WO_6 powders were obtained for the dry-pressed disk samples using a UV-vis spectrometer (Lambda 35, America PerkinElmer), and $BaSO_4$ was used as a reflectance standard in the UV-vis diffuse reflectance experiment. Nitrogen adsorption/desorption isotherms were measured at -196°C in a TRISTAR-3020 automated gaseous adsorption system. The surface area and pore distribution of the samples was calculated based on Brunauer-Emmett-Teler (BET) nitrogen adsorption theroy.

Photocatalytic activities of the samples were evaluated by decomposition of three typical antibiotics ciprofloxacin, erythromycin and tetracycline simultaneously in aqueous solutions under visible light irradiation of 500W Xe lamp at ambient temperature. 200mg of as-synthesized Bi_2WO_6 was suspended in a 50mL of 20μg/mL solution of the mixture of the three antibiotics. Then the mixed solution was magnetically stirred for 30min in the dark to achieve the adsorption-desorption equilibrium of target compounds on the surface of the photocatalysts. Then the Xe lamp was turned on to activitate the photocatalysis. For every additional 30min, about 1mL suspensions were collected and centrifuged followed by filtering through 0.22μm organic membrane for further quantification utilizing established HPLC-MS/MS method. Based on the equation below to calculate the degradation ratio.

3. Results and discussion

The morphologies of the as-synthesized Bi_2WO_6 can be observed by FE-SEM as shown in Fig.2. At the pH values of 1, the product consisted of a large quantity of hierarchical nest-like structure with diameter of 1-2μm, the nest-like hierarchical structure was constructed dimensionally by nanoplate layers with length of about 500nm and thickness about 10nm. At the pH values from 3 to7, the structures of the product were similar to the one at the pH values of 1. However, at the pH values of 9, the sample was consisted of two structures including the nanoplate of the broken nest-like structure and regular hexahedron indicating the transforming of the structure of the product at the pH of 9, while when the pH was 11, the structure was totally regular octahedron. We could summarize that the pH value played an important role in the morphology of the product Bi_2WO_6.

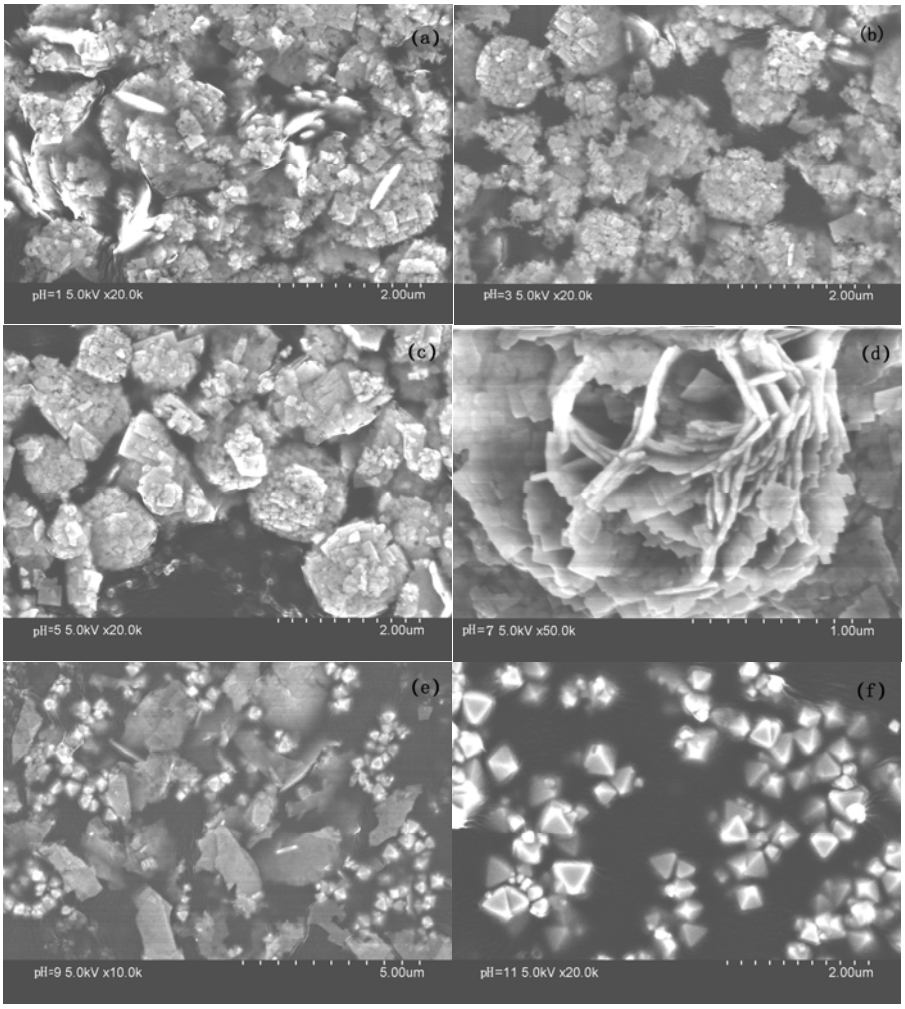

Fig.1 FE-SEM images of the synthesized Bi_2WO_6 at different pH values:(a)pH=1,(b)pH=3, (c)pH=5,(d)pH=7,(e)pH=9,(f)pH=11

In Fig.2, the XRD patterns of Bi_2WO_6 synthesized in the precursor solution under the pH values from 1 to 11 by the 120°C low temperature and 18h hydrothermal process was presented. As shown in the figure, we can conclude that the samples synthesized under the pH from 1 to 7 were indexed to the pure russellite phase of orthorhombic Bi_2WO_6 according to the database of JCPDS NO.39-0256[16]. Perfect peak was gained when the pH values was 7, indicating that its crystallinity was better than other samples. No other characteristic peaks of other impurities were observed. The diffraction peaks of the obtained samples were determined at 2θ =28.54°, 33.10°, 47.38°, 56.19°, 58.79°, indexing to the (131), (200), (202), (331) and (262) crystallographic planes of the samples respectively. However, the powder synthesized samples under the pH of 9-11 showed another two characteristic peaks at 2θ = 32.45°, 46.42° indexing to crystalline structure of the pure cubic Bi_2O_3 corresponding to the Miller indices of the (200), (220). Bi_2O_3 was gained under high pH values. The generation of Bi_2O_3 can be explained based on following chemical formation.

$$7Bi_2O_2(OH)NO_3+2WO_4^{2-} + 3OH^- \rightarrow Bi_{14}W_2O_{27} + 7NO_3^- + 5H_2O \qquad (1)$$

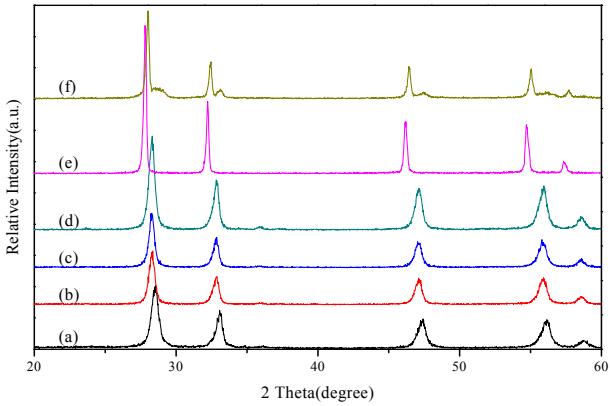

Fig.2 XRD patterns of the synthesized Bi_2WO_6 under (a) pH=1, (b) pH=3, (c) pH=5, (d) pH=7, (e) pH=9, (f) pH=11.

When the precursor solution pH > 8, by-product $Bi_{14}W_2O_{27}$ was obtained which existed as Bi_2O_3. We can summarize that appropriate pH values can promote the formation of pure orthorhombic Bi_2WO_6 under pH of 1-7, while the alkalinity could suppress the formation of Bi_2WO_6 and accelerate the formation of Bi_2O_3 phase.

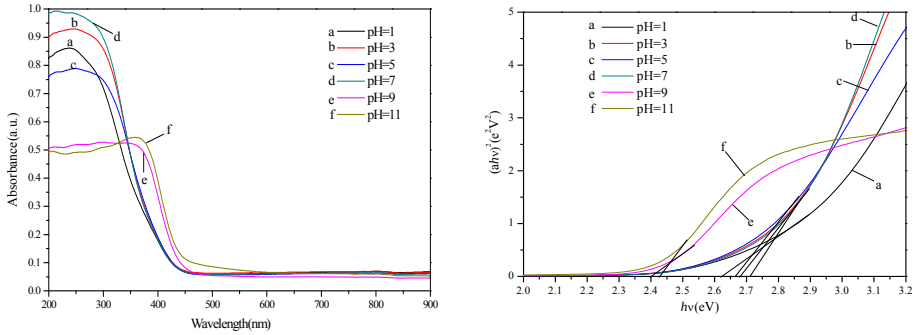

Fig.3 UV-vis diffuse reflectance spectra and Plots of the $(ah\nu)^2(e^2V^2)$ versus $h\nu$(eV)of Bi_2WO_6 synthesized at different pH values

To have a better understanding of the impact of pH values on the electronic properties of the samples, UV-vis diffused reflectance spectra of the as-prepared samples were displayed in Fig.3. Based on the data of the experiment, the absorption spectrum was drawn. As can be seen the light absorption edge of the Bi_2WO_6 synthesized under the pH values from 1 to 7 is from 200-450nm. Pure Bi_2WO_6 have strong absorption in the UV and visible light region. However, for the samples synthesized with pH =9.0 and 11.0, the absorption response becomes weaker and blue left occurs indicating their poor absorption in UV and visible light region. The band gaps of the six samples are calculated based on the formula below:

$$\alpha h\nu = A\,(h\nu - E_g)^{n/2} \qquad (2)$$

Where α, h, ν, A, E_g and n are the absorption coefficient, the Planck constant, the light frequency, the gap band energy and a constant, the constant for Bi_2WO_6 is set 1. A spectra can be drawn which the X axis and Y axis represent the $h\nu$(eV) and $(\alpha h\nu)^2$ (e^2V^2) based on the UV-vis diffuse reflectance spectra of the as-prepared samples. The result shows that the band gaps are different, the values were 2.87eV, 2.83eV, 2.73eV, 2.81eV, 2.45eV, 2.42eV respectively. Due to the generation of Bi_2O_3 with the pH =9.0 and 11.0, we just consider the samples synthesized with the pH values from 1 to 7. The smaller band gap might improve the photocatalytic activity of Bi_2WO_6. The

Bi_2WO_6 synthesized with pH =5.0 and 7.0 exhibited good performance during the photodegradation procedure.

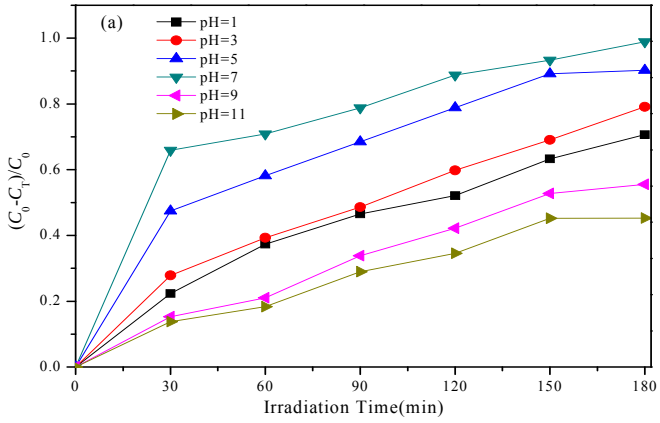

Fig.4 Degradation of the Ciprofloxacin over Bi_2WO_6 synthesized under different pH values

The photocatalytic activity of the as-synthesized Bi_2WO_6 under different synthesized pH was evaluated by simultaneously degradation of ciprofloxacin in aqueous solutions under visible light irradiation. In the degradation procedure, an HPLC-MS/MS method was utilized to determine the accurate concentration of the target drugs simultaneously, and this method was more sensitive and rapid than single HPLC method. The 40mL mixture of the three antibiotics with the concentration of 20μg/mL was added to six tubes with the volume of 50mL. Then 0.2g Bi_2WO_6 was added into the solution. The tubes were then settled in the photocatalysis instrument and magnetically stirred in the dark for 30min to obtain a desorption-adsorption equilibrium. 500W Xe lamp was then turned on to activate the photocatalytic procedure. 1mL sample was achieved at the interval of 30min followed by analyzed via HPLC-MS/MS based on established method. As can be seen in Fig.4, as for ciprofloxacin, 95% of the ciprofloxacin was photodegraded in 180min with the assistance of Bi_2WO_6 synthesized under pH of 7. Whereas, the samples synthesized under alkaline condition showed low photocatalytic ability. In conclusion, the Bi_2WO_6 synthesized under pH of approximately 7 had a high photocatalytic activity. This was in accordance with the high surface area 25.89m^2/g, low band gap of the Bi_2WO_6 when the solution pH was 7.

4. Conclusions

In summary, Bi_2WO_6 micro/nano-structures have been successfully prepared via a facile hydrothermal synthesis using template-free solvothermal synthesis method. The results indicated that the pH of reactant solution affected the growth rate of the particles, leading to various morphologies such as side spindle-like, bundle-like, laminar and egg-like during the growing process. The synthesizing mechanism and the morphological evolution were also proposed. This approach is a generalized process that can be used to synthesize different hybrid structures through controlled incorporation of inorganic particles into the cystine matrix, which should have outstanding potential in providing development of hybrid structures with desired morphologies for biosensor and drug delivery. In a summary, pH value plays an important role in the synthesis progress of Bi_2WO_6 resulting the differernce in morphology, crystallinity, optical properties, electronic properties, surface area as discussed above. When removing the organic pollutants ciprofloxacin, the as-prepared samples exhibit different photocatalytic performance.

Acknowledgments

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