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Controllable topological transformation from BiOCl hierarchical microspheres to Bi_2WO_6 superstructures in the Bi–W–Cl–O system

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ABSTRACT

In this work, three-dimensional (3D) Bi_2WO_6 superstructures assembled by nanosheets were prepared using the topological transformation of BiOCl hierarchical microspheres via a facile one-pot solvothermal method. Interestingly, it was found that the transformation process experienced three stages including BiOCl, BiOCl/Bi_2WO_6 composites and Bi_2WO_6 with increasing solvothermal time at 150 °C, which was confirmed by X-Ray Diffraction (XRD), Raman spectrometer and Transmission Electron Microscopy (TEM) results. Importantly, the crystal growth of Bi_2WO_6 superstructures occurred at the exposed (001) facets of BiOCl nanosheets with WO_6^{6-} units replacing the interlaminar Cl atoms. Also, the growth mechanism was revealed and discussed in the thermodynamic and kinetic dynamic aspects. Compared with BiOCl superstructures, the BiOCl/Bi_2WO_6 composites and Bi_2WO_6 superstructures showed better photocatalytic activity in the degradation of benzene gases under visible-light irradiation owing to the existence of visible-light-active Bi_2WO_6. This topological transformation by regulating the solvothermal synthetic conditions may provide a new insight into the controllable synthesis of other 3D compounds.

1. Introduction

Semiconductor photocatalysis has attracted extensive attention due to its great potential applications in solar energy conversion and environmental purification [1–3]. Among various photocatalysts, BiOCl has been widely studied for its outstanding photocatalytic activity [4–7]. Unfortunately, BiOCl with large intrinsic band gap (3.4 eV) can only adsorb UV light (less than 5% of the whole solar light) [8]. On the other hand, Bi_2WO_6 is a smaller band-gap (2.6–2.8 eV) semiconductor which can capture visible light ($420 < \lambda < 470$ nm) of sunlight and is a well-known visible-light-driven photocatalyst for degradation of organic dyes [9–11]. But its application remains limited because of its high electron-hole recombination rate in photocatalytic process. To overcome the intrinsic limitations of single metal oxide, these two semiconductors are usually coupled. In this sense, BiOCl/Bi_2WO_6 composites are widely synthesized and their properties are investigated [12,13]. These works are mainly focused on their photocatalytic performance but the effect of BiOCl/Bi_2WO_6 coupling on the photocatalytic activity is still contradictory [12]. When the properties of BiOCl, BiOCl/Bi_2WO_6 composites and Bi_2WO_6 are studied in comparison, these photocatalysts should be prepared at the same system and exhibit the similar size and shape. However, the formation mechanism of BiOCl, BiOCl/Bi_2WO_6 composites, Bi_2WO_6, especially their superstructures at the same system has been reported rarely and is still unclear. Thus, it is of great significance to synthesize BiOCl, BiOCl/Bi_2WO_6 composites and Bi_2WO_6, respectively with similar morphology at the same system. Also, the controllable formation mechanism should be revealed in detail. To keep their similar morphology, it is better that these three photocatalysts can be topological transferred to each other [14]. However, it is difficult to realize the topological transformation from one to another because they always exhibit complicated superstructures composed of nanocrystals due to their lower surface energy [11,12,15–17]. Therefore, it is still a great challenge to realize the topological transformation from BiOCl superstructures to Bi_2WO_6 superstructures.

In this work, we employed a simple one-pot solvothermal method to synthesize BiOCl/Bi_2WO_6 and Bi_2WO_6 superstructures through topological transformation process by regulating solvothermal temperature and time. XRD, Raman and HRTEM

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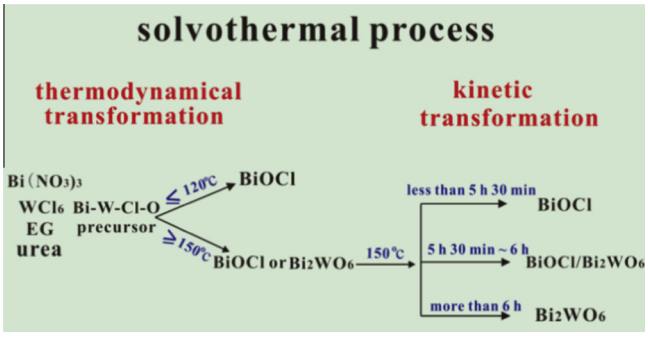
results confirmed this controllable topological transformation from BiOCl superstructures to Bi_2WO_6 superstructures. Especially, HRTEM images showed (001) facets of BiOCl and (010) facets of Bi_2WO_6 in the transformation process, which were high active planes and can favor the topological transformation. Furthermore, the obtained BiOCl/Bi_2WO_6 composites exhibited a red shift in the optical adsorption spectra compared with BiOCl. Furthermore, the formation mechanism of Bi_2WO_6 nanoflower as a kind of superstructure was revealed for the first time to occur at the exposed (001) facets of BiOCl nanosheets with WO_6^{6-} units replacing interlaminar Cl atoms in the Bi–W–Cl–O system. Also, the topological transformation by regulating the solvothermal synthetic conditions may provide a new insight into the controllable synthesis of other 3D compounds. In addition, the optical and photocatalytic properties of the obtained BiOCl, BiOCl/Bi_2WO_6 composites and Bi_2WO_6 superstructures were investigated in comparison.

2. Experimental

2.1. Chemicals and synthesis

All the chemical reagents used in the experiments were obtained from commercial sources as analytical grade reagents and used without further purification. In a typical experiment, 1 mmol of Tungsten hexachloride (WCl_6) (0.3966 g) was dissolved in ethylene glycol (50 ml) with ultrasonicated and vigorous stirring. Subsequently, 2 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ (0.9701 g) was added into the solution under ultrasonicated and vigorous stirring to form a transparent mixture solution. Then, 20 mmol of urea (1.2 g) was added and magnetically stirred until it was dissolved completely. The resulting precursor solution was finally transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was solvothermally treated at a certain temperature for certain time, then allowed to cool naturally to room temperature. The products were obtained by centrifugation and washed several times with distilled water and absolute alcohol, dried at 80 °C for 12 h subsequently. The solvothermal temperature and time were selected as the experimental variables for the preparation of the samples. Situation1: the solvothermal temperature was 90 °C, 120 °C, 150 °C, 180 °C for 30 h respectively. Situation 2: the solvothermal temperature was 150 °C for 5.5 h, 5.67 h, 5.83 h, and 6 h respectively.



Scheme 1. Schematic illustration for the synthesis process of Bi-based compounds via solvothermal strategy.

2.2. Characterization

The crystal structures of the as-synthesized products were characterized by X-Ray Diffraction (XRD; Philips X'pert X-ray diffractometer) in the 2θ range from 10° to 80° with a rate of 2°/min using Cu Kα1 radiation ($\lambda = 1.5406$ Å). Field-emission scanning electron microscopy (FESEM) observations were carried out with a FEI Sirion 200 microscope (FEI Company, Eindhoven, the Netherlands), operated at an acceleration voltage of 20.0 kV. Raman spectra were acquired with laser excitation at 488 nm using a Raman spectromicroscope (HORIBA Jobin Yvon Lab RAM HR) scanning from 100 cm^{-1} to 1000 cm^{-1} at room temperature in air. Lattice structure was observed by high-resolution Transmission Electron Microscopy (HRTEM) (JEM2010FEF from JEOL Company) with an acceleration voltage of 200 kV. UV/Vis measurements were made using a PerkinElmer Lambda 35 spectrophotometer in diffuse reflectance mode and employing $BaSO_4$ as a background for the analysis of the powder.

Photocatalytic activity of the samples was evaluated by degrading ca. 100 ppm benzene using a 300 W Xe lamp (CEL-HXUV300) with a UVIRCUT filter for visible-light from 400 nm to 780 nm at ambient temperature in a 1.5 L reactor. The photocatalysts were prepared by coating an aqueous suspension of as-synthesized products onto a square groove with sides of 5 cm. The weight of photocatalysts used for each experiment was kept at about 0.4 g. The photocatalysts were dried in an oven at 80 °C for about 30 min to evaporate the solvent and then cooled to room temperature before being used. After the square grooves coated with photocatalysts powders were placed into the reactor, benzene gas with a concentration of ca. 100 ppm passed through the reactor and was allowed to reach adsorption–desorption equilibrium with the catalyst prior to light irradiation. Analysis of the target gas concentration in the reactor was performed online with a GC-9560. Each set of experiments was monitored for 3 h.

3. Results and discussions

3.1. Structure and morphology

The synthesis process of Bi-based compounds at different solvothermal temperatures and times is schematically illustrated in Scheme 1, and the results are summarized in Table 1. In this Bi–W–Cl–O system, samples were prepared at 90 °C, 120 °C, 150 °C and 180 °C for 30 h respectively. According to the XRD results as shown in Fig. 1, all the identified peaks of the samples synthesized at 90 °C and 120 °C match well with the tetragonal structure of BiOCl (JCPDS card no. 85-0861), indicating that only tetragonal BiOCl was produced at these two temperatures. When temperature rises to 150 °C and 180 °C, all the diffraction peaks are ascribed to the orthorhombic structure of Bi_2WO_6 (JCPDS card no. 39-0256) and no peaks of impurities are detected, suggesting that only orthorhombic Bi_2WO_6 was obtained at these two temperatures. Based on the above results, 150 °C was selected as the reaction temperature to study the kinetic transformation of BiOCl into Bi_2WO_6. Fig. 2 shows the XRD patterns for the as-synthesized samples of 5.5 h, 5.67 h, 5.83 h and 6 h at 150 °C respectively. The structure dynamic evolution from BiOCl and BiOCl/Bi_2WO_6 composites to Bi_2WO_6 is successfully observed at 150 °C by controlling solvothermal time. For the sample of 5.5 h, all the peaks are ascribed to the tetragonal structure of BiOCl. The high diffraction intensity ratio of (110)/(001) facet indicates that the sample may exhibit ultrathin sheet-like morphology with the building units along the [001] orientation and a relatively large lateral size oriented along the [110] direction, which is in good agreement

Table 1
The products prepared at different reaction temperatures and times with urea/Bi-precursor amount ratio of 10 and pH value of 8.78.

Temperature (°C)	Time (h)	Chemical composition	Shape	Size (μm)
90	30	Tetragonal BiOCl	–	–
120	30	Tetragonal BiOCl	–	–
180	30	Orthorhombic Bi_2WO_6	–	–
150	30	Orthorhombic Bi_2WO_6	–	–
	5.5	Tetragonal BiOCl	Flower-like superstructure	1–2
	5.67	BiOCl/Bi_2WO_6	Flower-like superstructure	1–2
	5.83	BiOCl/Bi_2WO_6	Flower-like superstructure	1–2
	6	Orthorhombic Bi_2WO_6	Flower-like superstructure	1–2