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Bismuth vanadate hollow spheres: Bubble template synthesis and enhanced photocatalytic properties for photodegradation

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ABSTRACT

Hollow sphere monoclinic scheelite $BiVO_4$ (*m*-$BiVO_4$) is simply synthesized via a simple hydrothermal method by using urea as guiding surfactant. The forming process is investigated to be the incorporation of bubble guiding, oriented attachment and Ostwald ripening. The heterostructured hollow spheres are built up of truncated octahedrons which are also found to be feasible based on theoretical calculation. The preferred truncated octahedron consists of {0 4 0}, {0 1 1}, and {1 1 0} crystal planes with multiplicities of 2, 2, and 4, respectively. Besides urea, different kinds of organic additives (citric acid, Vitamin C and oleic acid) are also chosen for the synthesis of *m*-$BiVO_4$ to clarify the role of urea. The photocatalytic activities with different morphologies are evaluated on the degradation of Rhodamine B. It is found out that the *m*-$BiVO_4$ with hollow structure shows the optimalizing activity and the reaction rate constant reaches up to 0.035 min^{-1} without adding H_2O_2 as hydroxyl radicals provider. Except for activity, the as-prepared samples have high stability and durability, after four cycling runs of photodegradation of RhB, the photocatalytic ability of as-synthesized *m*-$BiVO_4$ did not show any loss. The degradation of RhB is attributed to intrinsically strong photo-oxidation ability rather than photosensitization and the synthesized samples also shows efficient photocatalytic activity for the degradation of 2-propanol. Meanwhile, the reasons for the superior activity are also carefully investigated.

1. Introduction

It is well known that heterogeneous photocatalysts, an ideal "green" technology, have been widely investigated for the sake of environmental applications [1–5]. Scientific interests in the application of photocatalysts have grown extensively, which mainly involved water splitting and degradation of organic contaminants under UV or visible-light irradiation. Over the past decades, promoting the photocatalytic activities and operating in the frequency range of visible light (or in a wider wavelength region) is the primary target in solar energy conversion [6–10]. Under this consideration, a variety of photocatalysts, such as Ag_3PO_4 [11,12], Bi_3NbO_7 [13], BiOX [14–16], Bi_2WO_6 [17,18], and composites [19–22], have been explored for the sake of overcoming shortcomings of low efficiency or narrow region absorption, since TiO_2 was reported in 1972 [23].

Recently, bismuth vanadate ($BiVO_4$) has attracted researcher' tremendous interest, because of its unique properties, such as ferroelasticity, ionic conductivity, gas sensing, and coloristic properties [24]. Moreover, it is also considered as one kind of excellent photocatalysts, due to its narrow band gap (ca. 2.4 eV) and the outstanding photocatalytic performances on both organic-contaminant degradation and oxygen generation under visible light illumination [24–29]. It is known that $BiVO_4$ mainly exists in three crystalline phases: tetragonal zircon, monoclinic scheelite, and tetragonal scheelite structure [30]. Zhang et al. investigated the photocatalytic performances of $BiVO_4$ with different crystalline phases and found that structure of monoclinic scheelite was superior for the process of photocatalysis [31]. The superior photocatalytic performances were discussed by Wang and co-workers, based on the surface photovoltage (SPV) and transient photovoltage (TPV) techniques [32]. Monoclinic scheelite $BiVO_4$ has been prepared by various methods, such as solid state reaction [33], aqueous process [34], molten salt synthesis [35], hydrothermal process [36], ultrasonic spray pyrolysis [37,38], and chemical bath deposition [39,40].

It is commonly considered that the shape of crystals plays a crucial parameter in the determination of their properties. The architectural control of nano- and micro-crystals with well-defined shapes is an attractive and challenging goal in modern materials chemistry [41]. In recent years, hydrothermal synthesis of monoclinic scheelite $BiVO_4$ is the most accepted method because of its unique superiority in terms of high crystallinity and morphology controlling. Till now, $BiVO_4$ with various morphologies, such as truncated octahedron [26], peanut-shaped [37], spindly microtubes [42], and nanosheets [27], have been successfully

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synthesized via hydrothermal process. Besides, it is reported that micro-/nanohollow structures are of great interest in many current and emerging areas of technology because the void space in hollow particles has been used to modulate refractive index, lower density, increase active area for catalysis, improve the particles' ability to withstand cyclic changes in volume, and to expand the array of imaging markers suitable for early detection of cancer [43]. Till now, only a few reports are focused on the synthesis of $BiVO_4$ with hollow structure [44,45], and to the best of our knowledge, there is no report about the simple hydrothermal synthesis of hollow $BiVO_4$ constructed by truncated octahedrons. From another point of view, during the hydrothermal process, organic additives are always adopted, such as PVP, EDTA, and SDBS. It is known that most of the organic additives are costly and hard to remove. Thus, it is an attractive challenge to develop a way of synthesizing monoclinic scheelite $BiVO_4$ with specific morphology, hollow sphere for example, via hydrothermal process by using cost-effective and easily removed organic additives.

In our work, hollow sphere monoclinic scheelite $BiVO_4$ is simply synthesized via a simple hydrothermal method by using urea as guiding surfactant. The choosing of urea is based on the following considerations. Urea is cost effective for commercial applications and water soluble for removing. Besides, urea will decompose to NH_3 which can be used as bubble template for synthesizing hollow structure. The physicochemical properties and formation mechanism of the as-prepared powders have been investigated in detail. The photocatalytic performances are evaluated by degrading rhodamine B (RhB) and 2-propanol as representative, under visible light irradiation ($\lambda > 400$ nm).

2. Experimental

2.1. Catalysts preparation

The monoclinic scheelite $BiVO_4$ powders were prepared using a simple hydrothermal method. All materials were purchased from commercial sources (analytical grade) and used without further purified. In a typical synthesis, 0.0015 mol bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), 0.0015 mol ammonium metavanadate (NH_4VO_3) and 0.1 g urea ($CO(NH_2)_2$) were dissolved in 30 mL deionized water under vigorous magnetic stirring, and then the pH of the resulting solution was adjusted to 1 with HNO_3 (65–68 wt%) solution. After stirring for 1 h, the suspension was transferred into a 40 mL Teflon-lined stainless steel autoclave to perform hydrothermal process at 180 °C for 12 h. After cooled down to room temperature, the solid product was collected by centrifugation (2000 rpm) and washed with deionized water for five times. The target monoclinic scheelite $BiVO_4$ was finally obtained by drying at 60 °C for 12 h. Besides, other samples were also prepared under identical conditions by changing pH, surfactant, hydrothermal temperature and hydrothermal time.

2.2. Characterization

The structure of the obtained monoclinic scheelite $BiVO_4$ was confirmed by X-ray diffraction (XRD) on Rigaku D/max-2000 diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). Diffraction patterns were collected from 10° to 90° at a speed of 4°/min with a scan width of 0.02°. The morphology of the products was observed by a Camscan MX2600FE field emission scanning electron microscope (FE-SEM). The operating voltage was set to 20 kV and the sample was prepared by dropping the pre-ultrasonic-dispersed (10 min) ethanol turbid liquid onto the chip of silicon. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) of the hierarchical structures were carried out on FEI Tecnai G2 S-Twin operating at 300 kV. UV–vis diffuse reflectance spectra were acquired by a spectrophotometer (TU-1900) and $BaSO_4$ was used as the reflectance standard.

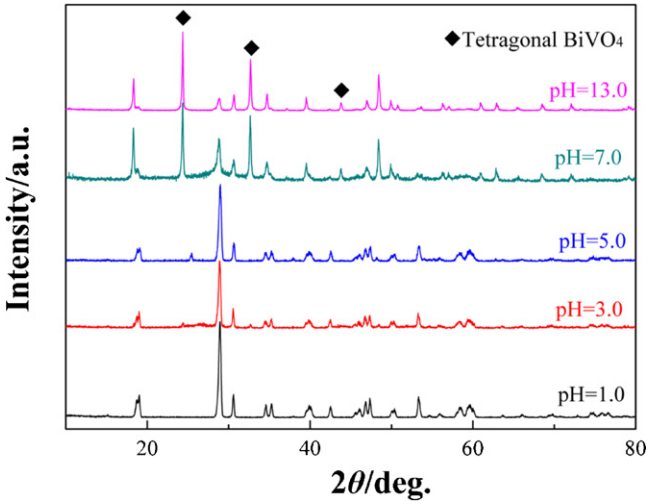

Fig. 1. XRD patterns of $BiVO_4$ synthesized under different value of pH.

2.3. Photocatalytic reactions

Rhodamine B (RhB), one of the biodegradation resistant N-containing dyes, is a popular probe molecule in the heterogeneous photocatalysis reaction. The photocatalytic activities were determined by the degradation of RhB aqueous solution under visible light irradiation ($\lambda > 400$ nm) in quartz photochemical reactor. A 300 W Xenon lamp (Trusttech PLS-SXE 300, Beijing) covered with a UV filter was used as a light source. The process of photodegradation was carried out at ambient temperature as follows: 0.0100 g of photocatalyst was added into 100 mL RhB, sonicated for 15 min and kept in dark for 1 h to reach adsorption–desorption equilibrium under magnetically stirring before irradiation. At given time intervals (10 min), 3 mL mixture was colleted out from the suspension, followed by centrifuged at 10,000 rpm for 5 min. The concentration of RhB was analyzed by measuring the absorbance at $\lambda = 553$ nm. For photodegradation of 2-propanol, 100 mg photocatalyst was transferred into a quartz cell with an aqueous solution of 2-propanol (2.6 μmol dm^{-3}, 15 mL). Prior to irradiation, the suspension was stirred for 1.5 h in dark. The sample was then irradiated with visible light with continuous stirring under O_2 atmosphere in the system. During the photoreaction, the product is analyzed by gas chromatography and mass spectrometry.

3. Results and discussion

3.1. Structure characterization

It is well known that the initial pH value of the precursor solution plays an important role in the formation of the monoclinic scheelite $BiVO_4$ microstructures. Therefore, different samples were prepared under different values of pH. The XRD patterns of the as-synthesized products illustrate that low value of pH is contributes to the formation of monoclinic scheelite $BiVO_4$ (*m*-$BiVO_4$) while high value of pH promotes the generation of tetragonal structure (*t*-BiVO4), as shown in Fig. 1. On account of the superior photocatalytic activity of *m*-$BiVO_4$, the synthesizing processes were carried out under a pH value of 1.0. Fig. 2 shows a typical XRD pattern of synthesized $BiVO_4$ by using urea as a template, which clearly indicates that the sample is made up entirely of *m*-$BiVO_4$. Based on the powder XRD data, the lattice parameters were determined as $a = 5.1896$ Å, $b = 11.7107$ Å, $c = 5.1016$ Å, and $\beta = 90.41°$, which are