



# Heterostructured bismuth vanadate multi-shell hollow spheres with high visible-light-driven photocatalytic activity



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## ABSTRACT

$\text{BiVO}_4$  as one of the promising visible-light-driven photocatalysts attracted considerable research on morphology and composition control. In this work, a modified carbonaceous spheres sacrificial template growth technique are developed to build up multi-shell hollow spheres of the heterostructured Bi–V–O. By treating the carbonaceous spheres with NaOH aqueous, the simultaneous adsorption of  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$  are achieved successfully, and through the precisely controlled calcination, the nanoparticles of  $\text{BiVO}_4$  and  $\text{Bi}_4\text{V}_2\text{O}_{11}$  are crystallized and interconnected into the Bi–V–O heterostructured multi-shell hollow spheres. These Bi–V–O hollow spheres demonstrate a high visible-light-driven photocatalytic activity towards the decomposition of Methylene blue, and the double-shell one with the highest  $\text{Bi}_4\text{V}_2\text{O}_{11}$  content shows the best photocatalytic activity. The high photocatalytic activity may due to the effective utilization of visible light induced by multiple reflections of their special multi-shell hollow spheres. The heterostructure between  $\text{BiVO}_4$  and  $\text{Bi}_4\text{V}_2\text{O}_{11}$  may also make a contribution to the enhanced photocatalytic activity.

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## 1. Introduction

Solar energy has been widely used in photocatalytic degradation of organic pollutants [1], photoelectrochemical water oxidation [2], dye sensitized solar cells [3]. In the past years, semiconductor photocatalysts have received significant attention because their broaden application including solar water splitting [4,5], photodegradation of organics [6–8],  $\text{CO}_2$  conversion [9,10]. Among numerous photocatalysts, bismuth vanadate has drawn great attention because of its suitable band gap for visible light irradiation, nontoxicity, higher stability, and environment friendliness [11–13].  $\text{BiVO}_4$  can crystallize as three phases: the monoclinic scheelite structure (ms- $\text{BiVO}_4$ ), the tetragonal scheelite structure (ts- $\text{BiVO}_4$ ), and the tetragonal zircon structure (zt- $\text{BiVO}_4$ ) [14]. It is observed that the properties of  $\text{BiVO}_4$  depend strongly on their crystalline phase and morphology [15]. Tetragonal  $\text{BiVO}_4$  with a band gap of 2.9 eV can only absorb the UV radiation, while the monoclinic ms- $\text{BiVO}_4$  with a band gap of 2.4–2.5 eV can absorb both the UV and the visible light. On the other hand, the low separation efficiency of photogenerated electrons and holes and the electrical conductivity hides the practical applications of  $\text{BiVO}_4$

[16]. Many attempts including the synthesis of heterojunction structures [17,18], doping [19] and controlling the morphologies [20] have been explored to overcome these disadvantages. Among them, morphology control attracted considerable attention, and ms- $\text{BiVO}_4$  with morphologies such as nanorods [21], thin film [22], irregular polyhedron [23], nanosheets [24] have been achieved through a variety of approaches. Recent research revealed that the special multi-shell hollow structures can help the materials to get more active site, better performance and higher effective density [25–27]. However, report on the controlled synthesis of the ms- $\text{BiVO}_4$  multi-shell hollow spheres is rather rare, due to the difficulties in the synthesis [28]. In addition, it is also proved that building up heterojunction structure or mixed crystalline phases can further improve the photocatalytic activity of the  $\text{BiVO}_4$  remarkably [29]. Apparently, to build the multi-shell hollow spheres with heterostructure or mixed crystalline phases in Bi–V–O system may be of great significance and lead to much improved photocatalytic performance.

To obtain multi-shell hollow spheres, hard template method [30–33], with uniform carbonaceous spheres as the sacrificed templates are believed as the most common and effective method. However, the conventional carbonaceous spheres hard templates approach does not work well with the systems having large ions like  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$ , due to the low adsorption capacity and difficult diffusion of large ions in the carbonaceous spheres [34], as well as

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the facility to crystallize of the  $\text{Bi}^{3+}$ -based compounds. So it is still a big challenge to use the carbonaceous spheres hard templates approach to synthesize the controlled multi-shell hollow spheres of  $\text{ms-BiVO}_4$ .

In this work, with the surface pretreated carbonaceous spheres as template, the successful absorption of  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$  were realized. Uniform Bi–V–O multi-shell hollow spheres with heterostructure ( $\text{BiVO}_4$  and  $\text{Bi}_4\text{V}_2\text{O}_{11}$ ) could be successfully obtained through controlled calcination. With this premium structure, the as-synthesized materials express excellent visible-light-driven photocatalytic activity.

## 2. Experimental section

### 2.1. Materials and preparation

#### 2.1.1. Reagents

The  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$ , NaOH and ethylene glycol were purchased from the Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical-grade reagents and used as purchased without further purification.

#### 2.1.2. The preparation of the carbonaceous microspheres templates

In a typical synthesis of carbonaceous microspheres, sucrose (130 g) was dissolved in deionized water (250 mL) to form a clear solution. The solution was then added into a 500 mL Teflon-lined autoclave and then the autoclave was heated at 200 °C for 2 h. Subsequently, when the autoclave was cooled to room temperature, the precipitates were collected and washed with deionized water and absolute ethanol for several times, then dried at 80 °C for 6 h.

#### 2.1.3. The synthesis of Bi–V–O multi-shell hollow spheres

In a water bath at 60 °C, 1.455 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was added to 30 mL of ethylene glycol. The mixture was stirred vigorously for several minutes to form a clarifying solution. Then followed by adding 0.35 g  $\text{NH}_4\text{VO}_3$ . The as-prepared carbonaceous spheres templates (0.4 g) were added and well dispersed into the above solution as hard templates. Subsequently, the mixture was adequately stirred for 6–8 h at 60 °C. At last the suspension was collected and washed alternately with deionized water and ethanol to obtain single-shell precursors. Bi–V–O single-shell hollow spheres were obtained by calcination of the single-shell precursors in air at the heating rate of  $R = 10^\circ\text{C}/\text{min}$  and the final temperature of 550 °C.

In order to increase the surface functional groups, we modified the carbonaceous spheres by immersing them in 0.1 M NaOH for 24 h. After that, the modified carbonaceous spheres were centrifuged for one time. Finally, they were dried at 80 °C for 12 h. Instead of the carbonaceous spheres, the surface pretreated carbonaceous spheres (0.4 g) were used as templates to increase the adsorption quantity of  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$ . Correspondingly precursors with higher amount of  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$  were obtained, which are further calcined at a controlled heating rates to obtain the final Bi–V–O double-shell and triple-shell hollow spheres. When the precursor was treated under the fast heating rate of  $10^\circ\text{C}/\text{min}$  and the final temperature of 550 °C, the double-shell hollow spheres were formed; while the sample was treated under the heating rate of  $2^\circ\text{C}/\text{min}$  first and then at  $10^\circ\text{C}/\text{min}$  as well as the final temperature of 550 °C, the triple-shell hollow spheres were obtained.

### 2.2. Characterization

The crystal structures of the samples were characterized by means of x-ray diffraction (XRD, X'pert PRO, PANalytical) with Cu

K $\alpha$  radiation. In order to determine the composition of the precursors and the calcination temperature of the precursors, thermogravimetric (TG) and differential scanning calorimetry (DSC) data of the precursor were recorded on a thermal analysis instrument (TG/DTA6300) with a heating rate of  $10^\circ\text{C}/\text{min}$  under the air flow. The morphologies and microstructures of the as-prepared samples were inspected by the scanning electron microscope (FE-SEM, ZEISS SUPRATM 55) and transmission electron microscopy (TEM, JEM-2100, accelerating voltage 200 kV). The UV–vis diffuse reflectance spectra were obtained on a TU-1901 spectrophotometer in the 250–800 nm wavelength range. Brunauer-Emmett-Teller (BET) surface areas of the samples were analyzed by nitrogen adsorption-desorption measurement on a Quantachrome Autosorb-1MP sorption analyzer with prior degassing under vacuum at 200 °C. A 300 W Xe lamp (CEL-HXF300) was used as a light source with a cutoff filter (Kenko L-42) was employed for the visible-light irradiation ( $\lambda > 420 \text{ nm}$ ).

### 2.3. Measurement of photocatalytic activity

Methylene blue (MB) is difficult to be degraded directly under light irradiation. In our work, MB is selected as the model pollutant to evaluate the photocatalytic activity of the Bi–V–O multi-shell hollow spheres under visible light irradiation using a 300 W Xe lamp (CEL-HXF300). A cutoff filter was placed outside the Pyrex jacket to remove the wavelengths under 420 nm completely. In each experiment, 0.1 g photocatalyst was added into 100 mL MB solution ( $10^{-5} \text{ mol L}^{-1}$ ). Before irradiation, the suspensions were magnetically stirred for half an hour in the dark to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and MB. Then, the solution was exposed to visible light irradiation with constant stirring. At given time intervals (30 min), 4 mL suspension was sampled and centrifuged to remove the remnant photocatalyst. The filtrates were analyzed by checking the alteration of intensity of the absorption-band maximum (553 nm) of MB in the UV–vis spectrum.

## 3. Results and discussion

The detailed synthesis procedures for the controlled Bi–V–O multi-shell hollow spheres are described in the experimental section. Successful synthesis of the Bi–V–O multi-shell hollow spheres are confirmed by the SEM and TEM images. The corresponding morphologies are given in Fig. 1. The phase identification of the hollow spheres was carried out by means of X-ray diffraction (XRD). The powder XRD patterns of Bi–V–O multi-shell hollow spheres are collected in Fig. S1. All the peaks of the XRD patterns of the products are in good agreement with the monoclinic scheelite  $\text{BiVO}_4$  and orthorhombic  $\text{Bi}_4\text{V}_2\text{O}_{11}$ . No impurity peaks are observed in all of the XRD patterns, indicating that all hollow spheres are heterostructure of monoclinic scheelite  $\text{BiVO}_4$  and orthorhombic  $\text{Bi}_4\text{V}_2\text{O}_{11}$ .

The Bi–V–O (Fig. 1a and b) hollow spheres with single and double-shells have uniformly spherical morphology with the average diameter of about 800 nm. The Bi–V–O with single-shell hollow structure has rough surface while the others are smooth relatively. This phenomenon can be further demonstrated by the corresponding TEM images (Fig. 1c and d). In comparison with the simple single-shell hollow spheres, double-shell hollow spheres possess more subunits which divide their inner space into several nanoscale parts. The Bi–V–O single-shell hollow spheres are obtained by controlling the low content of  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$  in the carbonaceous spheres templates and the proper calcination condition. While the concentric internal double-shell hollow spheres are achieved by increasing the  $\text{Bi}^{3+}$  and  $\text{VO}_3^-$  concentration in the surface pretreated carbonaceous spheres and using

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