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Preparation of BiVO$_4$ Hollow Spheres and its Photocatalytic Degradation of Methylene Blue

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Monoclinic BiVO$_4$ hollow nanospheres were successfully prepared via template-free method using citric acid (C$_{6}$H$_{8}$O$_{7}$) as chelating agent and characterized by X-ray diffraction patterns, transmission electron microscope, UV-Vis DRS, and TG-DTA technique. C$_{6}$H$_{8}$O$_{7}$ played an important role in the formation of hollow spheres. Morphology observations revealed that when appropriate amount of C$_{6}$H$_{8}$O$_{7}$ was introduced, the cavity with the diameter of 40 nm was obtained in BiVO$_4$ nanospheres. UV-Vis diffuse reflectance spectra indicated that the samples had absorption in both UV and visible light region. The photocatalytic activities were evaluated by the degradation of methylene blue under Xe lamp irradiation. Hollow spheres endow BiVO$_4$ samples with greatly improved photocatalytic activity. A possible formation mechanism of hollow spheres was proposed.

Key words: BiVO$_4$, Preparation, Hollow spheres, Photocatalysis

I. INTRODUCTION

Titanium dioxide is a powerful catalyst which has attracted considerable interest of environment chemist for decades due to its unique physical, chemical and optical properties [1]. However, the catalytic defects of TiO$_2$, such as the low conversion efficiency of solar energy, poor reuse, and difficult post-treatment, limited its applications. From the viewpoint of utilizing solar energy efficiently, exploitation of new photocatalytic systems with high visible-light-driven photocatalytic activity was imperative.

As one of the non-titania based semiconductor photocatalysts, bismuth vanadate (BiVO$_4$) has recently attracted considerable attention for its strong photocatalysis for water splitting and pollutant decomposing under visible light irradiation [2, 3]. There are three crystalline phases for BiVO$_4$, that is, the monoclinic scheelite-type, the tetragonal scheelite-type and tetragonal zircon-type. Among its three crystal structures, only the monoclinic scheelite BiVO$_4$ exhibited potential photocatalytic ability under visible light irradiation.

Besides the crystal structures, the photocatalytic property is also closely related to the morphology of the photocatalysts [4]. Recently, with the expectation of achieving enhanced the surface area and catalytic active center, a great deal of efforts have been focused on the controlled synthesis of BiVO$_4$ photocatalysts with specific shape such as flower-like [5], pyramid-like, strawberry-like [6], and sphere-type [7]. Inorganic materials with hollow spherical structure have been extensively studied due to their huge surface permeability, large specific area, void volume, low density and high mechanical stability. For their larger surface area and the stronger adsorption/desorption ability, hollow spherical photocatalysts would exhibit better visible-light photocatalytic reactivity and efficiency for organic pollutants decomposition [8] compared with the solid-shape samples. However, just few synthesis strategies of monoclinic scheelite BiVO$_4$ hollow spheres have been reported so far.

One general approach for preparing hollow spheres is template technology based on various organic or inorganic templates including polystyrene, carbon spheres, and so on. However, the templates require additional processing steps to remove, and the impurity of the products is usually inevitable. In contrast, the template-free preparative strategy is a more simple and effective alternative.

In this work, a series of hollow spherical BiVO$_4$ samples with monoclinic scheelite crystal structure were synthesized via template-free method using C$_{6}$H$_{8}$O$_{7}$ as chelating agent and gas bubbles generator. The effects of addition amount of C$_{6}$H$_{8}$O$_{7}$ on morphology, optical and photocatalytic behavior of BiVO$_4$ samples were discussed in details. A possible formation mechanism of the as-prepared BiVO$_4$ hollow spheres was proposed.
### II. EXPERIMENTS

#### A. Materials

Bismuth nitrate hydrate (Bi(NO$_3$)$_3$·5H$_2$O), ammonium metavanadate (NH$_4$VO$_3$), citric acid (C$_6$H$_8$O$_7$), and methylene blue (MB). All the chemicals in this work were purchased from Xi’an Chemical Reagent Company, and were of analytical grade and used without further purification.

#### B. Sample preparation

In a typical process, 0.117 g of NH$_4$VO$_3$ was dissolved in concentrated nitric acid at 70 °C, then the solution was diluted to 60 mL and was cooled to room temperature, thus green solution A was formed. 0.485 g of Bi(NO$_3$)$_3$·5H$_2$O and 0.384 g of C$_6$H$_8$O$_7$ were dissolved in nitric acid aqueous solution, adjusting the pH value to 7.5 by dropwise titration of ammonia solution under stirring, and transparent solution B was formed. Then the green mixture of solution A and B was transferred into porcelain dish and the reaction was performed in dried oven at 80 °C for 20 h, the obtained dark blue precipitate was washed with distilled water and dried. Afterwards, the obtained dried blue precipitate was annealed in muffle oven at 500 °C for 4 h under air atmosphere and light yellow BiVO$_4$ hollow nanospheres were obtained, denoted as BV-2.

In this experiment, C$_6$H$_8$O$_7$ was not only employed as chelating agent to stabilize Bi$^{3+}$, but also applied as gas bubble generator during the calcination process. The sample of BV-1 was prepared with 0.192 g C$_6$H$_8$O$_7$ and reaction condition was exactly the same as that of BV-2. The sample of BV-3 was prepared with 0.576 g C$_6$H$_8$O$_7$ and the reaction condition was also the same as that of BV-2. For the purpose of comparison, sample of BV-0 was also prepared with no addition of C$_6$H$_8$O$_7$. The reaction parameters were listed in Table I.

#### C. Characterization

The phase identification of the as-prepared powders were obtained on a Rigaku D/max-3C X-ray powder diffractometry using Cu Kα radiation (λ=1.5405 Å, 40 kV, 40 mA). The precipitate morphology and size were examined using JEM-3010 high-resolution transmission electron microscope (TEM) operating at 300 kV. The sample were dispersed in anhydrous ethanol and cast on carbon-coated copper grid. TG-DTA measurement was also made using a ZCT-B TG-DTA instrument (Beijing JXZ Digital Co., LTD). Typically, ca. 8.0 mg of sample was heated in a high purity alumina crucible from room temperature to 1273 K with heating rate of 10 K/min under air atmosphere. UV-Vis absorption spectra were recorded on Lambda 950 spectrophotometer using diffuse reflection.

### III. RESULTS AND DISCUSSION

#### A. XRD analysis

The X-ray diffraction patterns (XRD) of BiVO$_4$ prepared with different amount of C$_6$H$_8$O$_7$ were measured as shown in Fig.1. It was found the XRD patterns of all the samples presented the same profiles. The major XRD peaks at 2θ values of 18.85°, 28.85°, 30.54°, 34.38°, 35.19°, 39.91°, 42.40°, 46.00°, 46.82°, 47.25°, 50.00°, 50.26°, and 53.21° have been assigned to the (110), (011), (121), (040), (141), (130), (020), (200), (202), and (161) planes of BiVO$_4$. It was clearly suggested that all the diffraction peaks can be well indexed as monoclinic BiVO$_4$ (PDF140688). The sharp and narrow diffraction peaks indicated a high crystallinity of the m-BiVO$_4$. No other impurities such as Bi$_2$O$_3$, V$_2$O$_5$, or other organic compounds related to reactants were detected, indicating the high phase purity of the BiVO$_4$ samples.

#### B. TEM images and formation mechanism

1. TEM images analysis

The morphology of as-synthesized BiVO$_4$ samples was characterized by TEM technique, which is shown
with L, and metal-chelate composites (L added in the solution at pH=5.5. Bi ionizes according to the following Eq.(2) [10] as it is formed to stabilize BiVO₄ solutions are mixed, a yellow precipitate of amorphous is dissolved in nitric acid solution and VO₃⁻ ions are coordinate with the different citric acid amount. When 0.192 g of C₆H₈O₇ was dissolved in the system, there was some solid-shape agglomerates of BiVO₄). A hollowing effect was observed for those C₆H₈O₇ solutions from the Bi(NO₃)₃ and NH₄VO₃ solution in the absence (a) and presence ((b), (c), (d)) of C₆H₈O₇. During the calcinating process, the evolution of gas bubbles can provide the aggregation center [9] and the proposed mechanism for the formation was illustrated in Scheme 2. In our experiment, the decomposition of C₆H₈O₇ generated micro-bubbles such as CO₂, CO, and H₂O gas to provide the aggregation center, the BiVO₄ particles originating from the reaction of Bi³⁺ and VO₃⁻ assembled at the gas-liquid by the driving force such as interfacial tension, van der Waals attractive forces, and the reasonable hydrophilicity of adjacent BiVO₄ surfaces [11–13]. Finally, gas bubbles escaped from the core and gradually the hollow spheres formed.

When there was no addition of C₆H₈O₇, Bi³⁺ reacted directly with VO₃⁻ and finally formed BiVO₄ nanoparticles. The nanoparticles aggregated into spheres to minimize the systemic surface energy via reducing exposed areas [14, 15], thus resulting in the formation of densely solid-shape sphere (Scheme 1(a)). Also, the size of cavity increased in hollow microspheres according to the increase of C₆H₈O₇ concentration, as shown in Fig.2. This was presumably due to the size increase of micro-bubbles caused by the high concentration of C₆H₈O₇. However, at low C₆H₈O₇ concentration, the formation of micro-bubbles will be suppressed because of the small amount of evolved gas. Also, the tendency toward interparticle aggregation would not be high. As a result, the BiVO₄ nanoparticles do not form the self-assembled structure (Scheme 1(b)). When 0.192 g of C₆H₈O₇ was introduced during preparation, we can clearly observe the existence of some small cavities, but some solid-shape BiVO₄ agglomerates were also observed (seen in Fig.2(b)), suggesting that the C₆H₈O₇ was unable to coordinated with all the Bi³⁺ ions absolutely; some free Bi³⁺ ions reacted with VO₃⁻ ions, causing the solid-shape agglomerates of BiVO₄ nanoparticles. As 0.384 g of C₆H₈O₇ was added in the reaction system, the existence of big cavity can clearly be observed. It can be explained that BiVO₄ nuclei aggregate together around the gas bubbles interface, and finally hollow spheres formed (Scheme 1(c)). When 0.576 g of C₆H₈O₇ was added, the increase of gas pressure in the interior of hollow spheres brought the fracture of BiVO₄ hollow spheres (seen in Fig.2(d) and Scheme 1(d)).

2. The proposed formation mechanism

Scheme 1 accounts for the whole formation process of BiVO₄ samples from the Bi(NO₃)₃ and NH₄VO₃ solution in the absence (a) and presence ((b), (c), (d)) of C₆H₈O₇. During the following calculation, C₆H₈O₇ decomposed and thus BiVO₄ crystal nucleus formed (Eq.(4)).

$$\text{Bi}^{3+} + \text{VO}_3^- + \text{H}_2\text{O} \rightarrow \text{BiVO}_4 + 2\text{H}^+ \quad \text{(1)}$$

$$\text{CH}_2\text{C} \equiv \text{O}^- \underset{K_{eq}}{\xrightarrow{\text{HO}^- \text{C} \equiv \text{O}^- \text{H} \equiv \text{C} \equiv \text{O}^- \text{(HCl)}}} \text{CH}_2\text{C} \equiv \text{O}^- \text{H}^- \quad \text{(2)}$$

$$\text{Bi}^{3+} + \text{VO}_3^- \rightarrow \text{L} - \text{Bi}^{3+} \cdots \text{VO}_3^- \quad \text{(3)}$$

$$\text{L} - \text{Bi}^{3+} \cdots \text{VO}_3^- + \text{H}_2\text{O} \rightarrow \text{BiVO}_4 + \text{Gaseous byproducts} \quad \text{(4)}$$

With the addition of VO₃⁻ solution, the reaction between Bi³⁺ and VO₃⁻ is partly inhibited, and no yellow precipitate BiVO₄ is produced immediately due to the formation of an intermediate species (Eq.(3)). During the following calculation, C₆H₈O₇ decomposed and thus BiVO₄ crystal nucleus formed (Eq.(4)).
Scheme 1 Illustration of the physical and chemical processes occurring during the synthesis of the BiVO₄ samples in the absence (a) and presence of C₆H₈O₇ with different concentration: (b) low concentration, (c) appropriate concentration, and (d) high concentration.

Scheme 2 Schematic diagram of the formation process of hollow BiVO₄ nanospheres during the calcinating process.

C. TG-DTA analysis

In order to determine the appropriate temperature for thermal conversion of the precursor to BV-2 hollow sphere, we investigated the thermal behavior of the precursor of BV-2. The TG-DTA curves are shown in Fig.3. From the TG curves, it clearly indicates that there are two obvious stages of weight loss. The first weight loss (3.89%) observed from 40 °C to 200 °C, can be attributed to the evaporation of physically adsorbed water [16]. The second weight loss (33.33%) was from 200 °C to 500 °C and was accompanied by an exothermic event at 313 and 417 °C in DTA curves, probably attributable to the decomposition of chelate complex (-L···Bi···VO₃⁻ intermediate species) [17] and/or the phase transformation of the sample from orthorhombic BiVO₄ to monoclinic phase. Based on the TG-DTA results, we chose temperature of 500 °C for thermal treatment of the precursor to ensure the fully transformation to monoclinic scheelite-type BiVO₄.

D. UV-Vis DRS analysis

To evaluate the morphology on the optical property of the catalyst, the diffuse reflectance spectra of BiVO₄ samples, prepared with different concentration of C₆H₈O₇, were compared (Fig.4). The results indicated that the BV-2 showed a stronger absorption in the UV-Vis region (350−480 and 530−900 nm). The possible reasons may be that hollow sphere structure with the appropriate innerspace diameter allows multiple reflections of UV light within the interior cavity, allowing more efficient use of the light source [18]. Therefore, hollow spheres would endow BiVO₄ samples with greatly improved photocatalytic activity [19].

E. Photocatalytic activities

MB is famous for its good stability as dye materials. The photocatalytic activity of BiVO₄ samples was evaluated by measuring the degradation of the MB under visible-light irradiation. In a typical process, 100 mg BiVO₄ samples were added to 100 mL of 10 mg/L
Preparation of BiVO$_4$ Hollow Spheres

MB solution and then bubbled in the dark for 30 min, which allowed it to reach adsorption equilibrium and uniform dispersity. The solution was then exposed to visible light irradiation from a 150 W Xe lamp at room temperature. The samples were collected by centrifugation at given illumination intervals to measure the MB degradation using UV-Vis spectrophotometry. We used BV-0, BV-1, and BV-3 as reference to evaluate the photocatalytic performance of BV-2. As illustrated in Fig. 5, we plotted the change in the decolorization efficiency of MB with reaction time. Note that the decolorization efficiency was monitored by determining the absorbance around 664 nm in the UV-Vis spectra. From Fig. 5, it could be seen that the decolorization efficiency of MB dyes over BV-1, BV-2, and BV-3 were all up to 90% in 150 min, while over BV-0 was only about 76%.

To confirm the cyclic usage possibility for the as-prepared BiVO$_4$ photocatalysts, the BV-1, BV-2, and BV-3 were selected to measure their cyclic usage. After photodegradation of MB over photocatalysts for 150 min, the solution was centrifuged, decanted the above clear solution very carefully and the catalyst was used for the degradation of fresh samples of MB under the same conditions. Figure 6 shows the change in decolorization efficiency of MB with cycling operation.

It was obvious that the photocatalytic reactivity of the BV-2 photocatalyst was just slightly reduced, indicating that cyclic usage of the BV-2 photocatalyst was possible and its stability in treating polluted water was satisfactory. At the same time, it also proved that the final removal of MB from the solution was caused by the photocatalytic degradation other than the adsorption process that will lead to saturated adsorption of MB on the photocatalyst [20].

There are two possibilities for their mechanisms: photocatalytic decomposition of MB and production of the doubly reduced form of MB, leuco-MB [21]. As the addition of AgNO$_3$ into the system, the solution was not recovered to blue, indicating that the MB was not reduced to leuco-MB, which can be reversibly oxidized to MB by AgNO$_3$ [22]. Figure 7 shows the evolution of MB absorption spectra in the presence of 100 mg of BV-2 hollow spheres, from which it could be seen that $\lambda_{\text{max}}$ gradually shifts from 664 nm to 648 nm (irradiation time 90 min), and to 620–634 nm (irradiation time 120–150 min), respectively, with the decrease in absorbance during visible light irradiation.

FIG. 4 UV-Vis diffraction spectra of BiVO$_4$ samples. (a) BV-1, (b) BV-2, (c) BV-3.

FIG. 5 Decolorization efficiency of MB over BiVO$_4$ samples for different reaction time.

FIG. 6 Change in relative concentration of MB with cycling operations of photodegradation using BiVO$_4$ samples.

FIG. 7 UV-Vis absorption spectra of MB solution on hollow BiVO$_4$ nanosphere before (a) and after visible light irradiation time (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, and (f) 150 min.
This hypsochromic shift of $\lambda_{\text{max}}$ was characteristic of N-demethylation derivatives of MB, in accordance with the results in the Refs. [23, 24]. These results undoubtedly mean that the decomposition of MB on sample BV-2 under the visible light irradiation was due to the photocatalytic oxidative reactions.

IV. CONCLUSION

In summary, we here reported a facile and cheap route to prepare hollow spherical BiVO$_4$ nanoparticles via a template-free approach. On the basis of the experiment, we proposed a plausible mechanism using C$_6$H$_8$O$_7$ as chelating agent and bubble generator for the formation of the hollow structure. This hollow structure endows the spheres with greatly enhanced photocatalytic activity. This work provides a novel pathway to the synthesis of hollow spheres, as well as offering a new material platform for catalyst, microelectronic, and other applications.

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