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Construction of multi-shelled Bi_2WO_6 hollow microspheres with enhanced visible light photo-catalytic performance

Feiyu Qin[a], Pengzhen Cui[a], Lei Hu[a], Zumin Wang[a], Jun Chen[a], Xianran Xing[a], Hao Wang[b], Ranbo Yu[a,b,*]

[a] Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China
[b] Centre for Future Materials, University of Southern Queensland, Queensland 4350, Australia

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ABSTRACT

As a promising structure in enhancing the photo-catalytic performance of the materials, hollow-shell structure still faces the great challenge of constructing an effective architecture for catalytic application. Herein, multi-shelled hollow microspheres of the visible-light photo-catalyst Bi_2WO_6 with shells up to the triple (BWO-MSH), have been synthesized by using a facile and effective carbonaceous template route. Intriguingly, the photo-catalytic reaction rate constant of BWO-MSH sample is nearly 16 times higher than the Bi_2WO_6 prepared through solid-state reaction (BWO-SSR). The single-, double-shelled Bi_2WO_6 microspheres (Broken) could only be synthesized with lower quality (synthesized with many broken species), and their photo-catalytic performance was nearly the same poor as the BWO-SSR sample. Furthermore, multi-shelled hollow microsphere of Bi_2O_3/Bi_2WO_6 (BO/BWO-MSH) composite was also synthesized. The present work not only extends the scope of high-performance complex mixed metal oxides with multi-shelled microstructures, but also brings a good reference to engineer other impressive photo-catalyst.

1. Introduction

Visible-light-driven photo-catalysts have received considerable attention owing to the efficient utilization of solar energy [1–5]. Bismuth tungstate (Bi_2WO_6), as a semiconductor photocatalyst, has generated extensive interest due to the excellent photocatalytic activity, good stability, and environmental friendliness. Bi_2WO_6 crystallizes with perovskite-type $[WO_4]^{2-}$ layers sandwiched between $[Bi_2O_2]^{2+}$ layers [6], which is considered to be in favored of the efficient separation of photo-generated carriers during the photocatalytic process [7]. With preferable band composition (~2.8 eV) and the particular layered structure Bi_2WO_6 is a promising visible-light-driven catalyst material on the degradation of organic compounds and O_2 evolution from water [8,9].

A variety of researches have been focused on designing novel micro-/nanostructured materials due to the close correlation between structure, morphology, and photocatalytic property [10,11]. Among various micro-/nanostructures, the multi-shelled hollow microspheres with high specific surface area and superior mass transfer properties are of great importance [12–15]. The remarkable photocatalytic performance of multi-shelled hollow microspheres is mainly attributed to the following reasons [13,15]. Firstly, the high specific surface area allows for more adsorption of dye molecules and provides more active sites. Secondly, multi-shelled structure could boost the utilization efficiency of incident visible light by strengthening light reflection and scattering. Finally, multi-shelled materials possess shorter diffusion lengths and consequently give rise to the high transmission of mass and charge. Diverse chemical modification strategies were initialized to construct multi-shelled microspheres. Among them, carbonaceous template approach as an environmentally- friendly and facile method played an important role in controlled synthesis of multi-shelled hollow microspheres [16–19].

As a promising visible-light-driven photocatalyst, Bi_2WO_6 with diverse morphologies has been widely explored, such as nanoparticles [20], nanoplates [21], flower-like superstructure [22], nanocages [23]. Hollow microsphere of Bi_2WO_6 is scarce and need achieving better catalytic performance [24]. However, it is still a great challenge to construct the multi-shelled hollow microspheres with multiple chemical compositions through carbonaceous template route and many of the reported multi-shelled hollow microspheres are simple single-metal oxides. It is mainly because the competitive adsorption between distinct metal ions inside the carbonaceous microsphere, making it difficult to

* Corresponding author at: Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China.
E-mail address: ranboyu@ustb.edu.cn (R. Yu).

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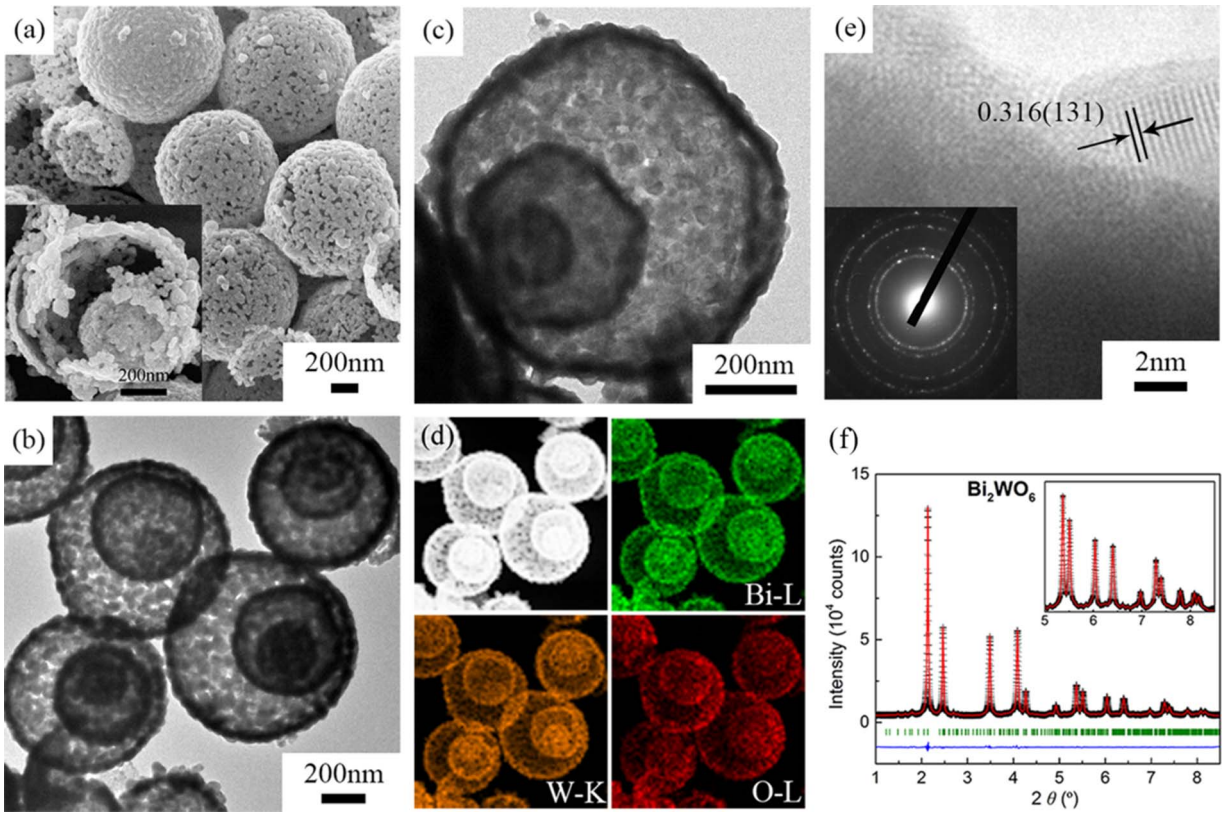

Fig. 1. (a)And (b) SEM and TEM image of BWO-MSH. (c) And (e) HRTEM images of the BWO-MSH. The inset of (e) is selected area electron diffraction. (d) HAADF-STEM element mapping. (f) SXRD pattern of the microspheres. The inset is an enlargement of high angle region.

precisely control the ion concentration and radial distribution inside the carbonaceous microspheres, and designing the desired chemical compositions of target compounds becomes relatively difficult.

Herein, we managed to synthesize the Bi_2WO_6 multi-shelled hollow microspheres with an enhanced photocatalytic performance by adjusting the adsorption process. The degradation efficiency for RhB under visible light reaches up to as high as ~95% in one hour. And its reaction rate constant achieves a boosted value of 0.0478 min^{-1}. In addition, by achieving the Bi_2O_3/Bi_2WO_6 multi-shelled hollow microspheres, even a higher photocatalytic performance is observed.

2. Experimental section

2.1. Sample preparation

The carbonaceous microsphere template was prepared under hydrothermal conditions [25]. The three shelled Bi_2WO_6 hollow structure (BWO-MSH) was taken as an example to introduce the synthesis procedure. $Bi(NO_3)_3{\cdot}5H_2O$ and $Na_2WO_4{\cdot}2H_2O$ in a molar ratio of 2:1, were mixed together in 90 mL of EG to form a clear solution [23]. Then carbonaceous microspheres (ca. 1.2 g) were added into the above solution to form a black suspension. The suspension was magnetically stirred at 60 °C for 6 h in a water bath to ensure $[WO_4]^{2-}$ and Bi^{3+} absorbed by carbonaceous microspheres. Subsequently, a rinsing process was carried out with alternate deionized water and ethanol including 3–5 cycles of centrifugation-washing-dispersion. Then the precursor of multi-shelled microspheres was obtained by oven-dried at 80 °C for 12 h. Subsequently, the precursors were heated to 400 °C in air at the rate of 15 °C/min, and kept at 400 °C for 3 h. Then the materials were kept at 450 °C for 1.5 h to totally remove carbonaceous templates. By adjusting the concentration of solution and the absorption time, the single-, double-shelled Bi_2WO_6 broken microspheres (Broken) and three shelled Bi_2O_3/Bi_2WO_6 hollow structure (BO/BWO-MSH) were obtained. For comparison, Bi_2WO_6 bulk powder was prepared through a traditional solid-state reaction (BWO-SSR) method according to a previous study [26].

2.2. Characterization

Synchrotron X-ray diffraction (SXRD) of Bi_2WO_6 has been collected at the beamline 11-ID-C of APS, Argonne National Laboratory with high-energy X-ray radiation (wavelength, 0.117418 Å). The X-ray powder diffraction (XRD) was performed on a Panalytical X'Pert Pro diffractometer system with Cu Kα radiation (λ = 1.5418 Å). Differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out on a thermal analysis instrument (DTG-60AH) to determine the calcination temperature of the obtained precursors. The morphologies and microstructures of the as-prepared samples were investigated by using scanning electron microscope (FE-SEM, ZEISS SUPRATM 55) and transmission electron microscopy (TEM, JEM-2100, accelerating voltage 200 kV). UV–vis diffuse reflectance spectrum was performed on a TU-1901 spectrophotometer using $BaSO_4$ as the reference. XPS (ESCALAB-250Xi) measurements were performed with monochromatic Al Kα x-ray source. The Brunauer-Emmett-Teller (BET) surface areas of the samples were estimated by nitrogen adsorption-desorption measurement on a Quantachrome Autosorb-1MP sorption analyzer with prior degassing under vacuum at 200 °C.

2.3. Photocatalytic reaction

Rhodamine-B (RhB) was selected as the model pollutant to evaluate the photocatalytic activity of the samples under visible light irradiation using a 300 W Xe lamp (CEL-HXF300) with a cutoff filter (λ > 420 nm). In each experiment, 0.1 g photocatalytic sample was added into 100 mL RhB solution (10^{-5} mol/L). After 5 min ultrasonic treatment, the suspensions were stirred for 60 min in dark to reach the