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Surface defect-mediated efficient electron-hole separation in hierarchical flower-like bismuth molybdate hollow spheres for enhanced visible-light-driven photocatalytic performance

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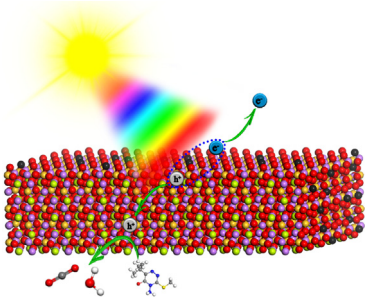
GRAPHICAL ABSTRACT

Hydrogenation hierarchical flower-like Bi_2MoO_6 hollow spheres with surface defects are fabricated via solvothermal route and subsequent surface hydrogenation, which narrowed the bandgap and exhibited excellent visible-light-driven photocatalytic performance due to the surface defects enhancing light-harvesting and spatial separation of photogenerated electron-hole pairs.



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ABSTRACT

It is desirable to develop an efficient visible-light-driven photocatalyst for practical application to degrade highly-noxious pollutants. Herein, the hydrogenation hierarchical flower-like Bi_2MoO_6 hollow spheres (H-BMO-X, where X represents the different hydrogen calcination temperatures) have been successfully fabricated by a solvothermal-surface hydrogenation process. The as-prepared nano-photocatalyst H-BMO-300 clearly exhibits a photocatalytic reaction apparent rate constant k for high-noxious pollutants by ~3-times higher than pristine Bi_2MoO_6. Moreover, the resultant H-BMO-300 sample with a narrow bandgap of ~2.70 eV possesses surface oxygen vacancy defects. Based on the scanning Kelvin probe and surface photovoltage spectroscopy, it is deduced that the photocatalytic activities are attributed to the surface oxygen vacancy of H-BMO-X favoring the electron-hole pair's separation. The enhanced photocatalytic performance can be ascribed to the synergistic effect of surface defects favoring efficient electron-hole separation and the hollow hierarchical structure benefiting the utilization of visible light, which provides more surface-active sites. This work provides a viable route to perceptibly enhance the photocatalytic activities of H-BMO-300 for environmental remediation with good mineralization properties.

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1. Introduction

The growth of human population, industrialization, and agriculture have caused much environmental and energy crisis in the last several decades [1–3]. Particularly, industrial wastewaters are frequently discharged into water bodies owing to a scarcity of effective methods to dispel these noxious pollutants [4,5]. Among these pollutants, metribuzin is a highly toxic organic pollutant that is intricate to degrade in wastewater [6–8]. To address the aforementioned issue, it has been stated that removal of environmental pollutants through photocatalysis is a very lucrative approach, and various kinds of semiconductor materials (e.g., ZnO, TiO_2, and Fe_2O_3) have been developed as photocatalysts for the photodegradation of organic pollutants [9–14]. However, practical applications of these semiconductors have greatly declined due to the insufficient absorption of solar light (3–5% for UV light) [15,16]. Therefore, it would be highly imperative to develop a high performance visible-light-driven photocatalyst, which is becoming an intensely investigated research area.

The semiconductor Bi_2MoO_6 is an important Aurivillius oxide and has been a target for the vigilant eyes of attraction for various photocatalytic applications, owing to its suitable band gap (2.6–2.8 eV) [20–22], high stability, non-toxicity, and tremendous intrinsic properties, such as dielectric nature, luminescence and catalytic properties [17–20]. It has been considered as a promising candidate in the photocatalytic degradation of toxic pollutants. Therefore, Bi_2MoO_6 photocatalysts with various morphologies, such as hierarchical flower, have been synthesized to enhance the photocatalytic activity [23–25]. Despite these desirable properties, the photoconversion efficiency of Bi_2MoO_6 is still low due to rapid recombination of photogenerated electron-hole pairs [26–28].

To address this issue, recent studies showed that the reduction of the band gap could enhance the photocatalytic performance of semiconductors by surface hydrogenation (e.g., TiO_2) [29–32], in which the surface defects played vital roles for enhancing the electron-hole separation. It provides a promising strategy for fabricating other semiconductor oxides to further improve the visible-light-driven photocatalytic performance. However, creating surface defects of Bi_2MoO_6 materials to enhance the visible-light-driven photocatalytic activity is still a great challenge.

Based on the above consideration, we synthesized visible-light-driven hierarchical flower-like Bi_2MoO_6 hollow spheres as photocatalysts for efficient degradation of metribuzin by solvothermal-surface hydrogenation. The obtained H-BMO-300 (H-BMO-X, X represents the different hydrogen calcination temperatures) possesses a relatively high surface area and large pore size of 15 $m^2\ g^{-1}$ and 17 nm, respectively, which could provide more reactions sites to facilitate the reactants to the desired oxidation places and all together create a synergistic effect on enhancing the photocatalytic activities of the nanocomposites. Moreover, the hierarchical flower-like hollow structure can increase the utilization rate of the solar light by repeatedly refracting the incident light. The H-BMO-300 with a narrow bandgap of ~2.70 eV exhibits excellent solar-driven photocatalytic degradation performance and long-term stability for complete mineralization of metribuzin. The photocatalytic reaction apparent rate constant k is ~3 times higher than that of pristine Bi_2MoO_6 under visible light irradiation ($\lambda > 400$ nm). The enhancement is attributed to the formation of surface defects favoring the separation of photogenerated electron-hole pairs and the porous hollow structure benefiting mass transfer. The reduced hierarchical flower-like Bi_2MoO_6 hollow spheres will have prevalent practical applications in environmental fields.

2. Experimental section

2.1. Chemicals

Bismuth nitrate (≥99.0%, $Bi(NO_3)_3{\cdot}5H_2O$), sodium molybdate (≥99.0%, $Na_2MoO_4{\cdot}2H_2O$), ethylene glycol (≥99.7%, EG) and ethanol (≥99.7%) were of analytical grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All chemicals were analytical grade and were not further purified. Deionized (DI) water was employed throughout experiments.

2.2. Synthesis method

The synthesis of hierarchical flower-like Bi_2MoO_6 hollow spheres was reported elsewhere by our previous study [17]. As in a typical synthesis, 1.6866 g of $Bi(NO_3)_3{\cdot}5H_2O$ and 0.4210 g of $Na_2MoO_4{\cdot}2H_2O$ were dissolved in 5 mL EG under violent magnetic stirring. After stirring for 30 min, the EG solution with $Bi(NO_3)_3{\cdot}5H_2O$ was slowly added dropwise to the $Na_2MoO_4{\cdot}2H_2O$ solution in EG. Then, under magnetic stirring for 10 min, 20 mL ethanol was slowly added and stirred for 30 min. The obtained clear solution was then transferred to a 50-mL Teflon-lined stainless-steel autoclave and heated to 160 °C for 20 h. Then, the as-synthesized samples were washed with distilled water and ethanol several times. After drying at 80 °C overnight, the resultant samples were annealed at 400 °C for 3 h with a temperature heating rate of 5 °C min^{-1} in air to remove the organic species and improve the crystallinity. Finally, the as-synthesized samples were calcined in a hydrogen flow at 300 °C for 3 h under normal pressure conditions at the rate of 100 mL min^{-1} to obtain the reduced hierarchical flower-like Bi_2MoO_6 hollow spheres, as shown in Scheme 1.

2.3. Characterization

X-ray diffraction (XRD) patterns were collected by a Bruker D8 powder X-ray diffractometer (Germany) with Cu Kα radiation (40 kV, 40 mA). Raman spectroscopic measurements were exhibited with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The transmission electron microscopy (TEM) images were obtained on a JOEL JEM-2100F operated at 200 kV. Scanning electron microscope (SEM) was used a Hitachi S-4800 instrument working at 15 kV. UV–Vis absorption spectra and diffuse reflectance spectroscopy (DRS) were conducted on a UV/vis spectrophotometer (Lambda 950 (PerkinElmer, USA)) in the range of 200–600 nm, with fine $BaSO_4$ powders as a reference. Nitrogen adsorption-desorption isotherms at 77 K were collected on an AUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. All samples were degassed under vacuum at 180 °C for at least 8 h prior to the measurement. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area. The pore-size distributions were obtained with the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of the isotherms. The X-ray photoelectron spectroscopy (XPS, Kratos, ULRA AXIS DLD) measurements were conducted on a system with monochrome Al-Kα X-ray radiation (1486.6 eV). All binding energies were calibrated by referencing to a C 1s peak at 284.6 eV. Surface photovoltage spectroscopy (SPS) measurements were carried out with a home-built apparatus equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). Scanning Kelvin Probe (SKP) measurements (SKP5050 system, Scotland) were performed under normal laboratory conditions (in an ambient atmosphere).