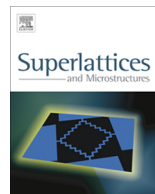




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Aqueous synthesis of hierarchical bismuth nanobundles with high catalytic activity to organic dyes



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ABSTRACT

Bundle-like bismuth (Bi) nanoarchitectures were successfully prepared on a large scale by an aqueous reducing strategy with polyethylene glycol (PEG) as directing agent at 90 °C for 55 min. The bundle-like Bi nanoarchitectures have a length of 4–5 μm and diameter of 0.5–1 μm with fairly uniform construction. Catalytic activities of the as-prepared hierarchical Bi nanobundles were investigated for degrading Rhodamine B (RhB) dye solution under visible-light irradiation. The Bi nanostructures extended excellent catalytic activity and good cycling performance toward photodegradation of RhB. Possible mechanism was proposed for Bi-assisted photocatalytic degradation of RhB under visible-light.

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1. Introduction

Photocatalysis, a “green” technique, offers a potential for complete elimination of toxic chemicals in the environment through its efficient and broad applicability. Thus various nanostructured materials have been exploited as heterogeneous photocatalysts for environment related applications, including the remediation of environmental pollutants through photocatalytic reaction [1–4]. However, the exploitation and preparation of novel and efficient catalysts is still a challenge.

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Bismuth (Bi), in bulk form, is a semimetal with a small band overgap (38 meV) [5,6], highly anisotropic fermi surface, and small effective mass. When the crystal size of Bi decreases, the induced semi-metal–semiconductor transition would be possible [7,8]. This size-induced semimetal to semiconductor transition and the related quantum confinement effects are potentially useful for optical and nanoscale devices [9–11], which have stimulated great efforts to synthesize Bi nanocrystals [12–19]. Among various synthesis methods, solution phase reduction methods provide a convenient and simple approach for the synthesis of different nanoscale materials with a very high productive yield [20–24]. Nevertheless, few studies have been directed toward photocatalytic activity of Bi particles so far.

Here we report an aqueous reducing strategy with polyethylene glycol (PEG) as directing agent to synthesize bundle-like bismuth (Bi) nanoarchitectures. We discussed the adsorption and degradation of organic pollutants with the prepared bundle-like bismuth (Bi) nanoarchitectures as catalysts. The results showed that the hierarchical Bi nanostructures exhibited high photocatalytic activity to organic pollutants with good cycling performance under visible-light irradiation.

2. Experimental section

2.1. Materials

All the reagents, including bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80 wt.%), nitric acid (HNO_3 , 98 wt.%), hydrochloric acid (HCl, 38 wt.%), polyethylene glycol 20000 (PEG 20000), polyethylene glycol 6000 (PEG 6000), Rhodamine B (RhB), and Methylene blue (MB) are analytical pure grade purchased from Sinopharm Chemical Reagents Co., Ltd and used without further purification.

2.2. Synthesis of bundle-like Bi nanostructures

In a typical experimental procedure, A mixture containing 0.03 g of PEG 6000, 10 mL of $0.25 \text{ mol L}^{-1} \text{ Bi}(\text{NO}_3)_3$ solution (with 0.009 mol of HNO_3) was stirred in a three-neck flask at 90°C for 2 min, Then, 30 mL of $13 \text{ mol L}^{-1} \text{ N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added to the above solution, and stirring continued for an additional 55 min. After the reaction completed, the resulting black precipitates were filtered and washed with distilled water and absolute ethanol for several times to remove impurities, thus bundle-like Bi nanostructures were obtained.

2.3. Characterization

The crystallization of Bi powders was determined by a Shimadzu XRD-6100 X-ray diffractometer equipped with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation in a 2θ range of $20\text{--}70^\circ$ at room temperature. The morphology and particle size of powders were characterized by field-emission scanning electron microscope (FESEM, Hitachi S-4800) and high-resolution TEM (HRTEM, JEOL JEM-2100F).

2.4. Photocatalytic experiments

The photoreactor was designed with a 100 mL beaker and a visible light source (500 W iodine tungsten lamp). The turbid suspension in the beaker included the catalyst (0.02 g of Bi) and aqueous RhB (100 mL, 10 mg L^{-1} , $\text{pH} = 3.0$), the distance from the visible light source to the suspension surface was 25 cm, the suspension was continuously stirred and the whole system was open to the air. Every a certain time interval, the turbid suspension was taken out and then centrifuged to obtain RhB solution. The concentration of the RhB in the solution was monitored by a Shimadzu UV-1800 spectrophotometer. The parameters in recycled experiments are the same as those in the first testing, excepting that the catalyst was recollected by centrifugation at $8000 \text{ rpm min}^{-1}$.

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