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Rose-like monodisperse bismuth subcarbonate hierarchical hollow microspheres: One-pot template-free fabrication and excellent visible light photocatalytic activity and photochemical stability for NO removal in indoor air

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ABSTRACT

Rose-like monodisperse hierarchical $(BiO)_2CO_3$ hollow microspheres are fabricated by a one-pot template-free method for the first time based on hydrothermal treatment of ammonia bismuth citrate and urea in water. The microstructure and band structure of the as-prepared $(BiO)_2CO_3$ superstructure are characterized in detail by X-ray diffraction, Raman spectroscopy, Fourier transform-infrared spectroscopy, transmission electron microscopy, scanning electron microscopy, N_2 adsorption–desorption isotherms, X-ray photoelectron spectroscopy and UV–vis diffuse reflectance spectroscopy. The monodisperse hierarchical $(BiO)_2CO_3$ microspheres are constructed by the self-assembly of single-crystalline nanosheets. The aggregation of nanosheets result in the formation of three dimensional hierarchical framework containing mesopores and macropores, which is favorable for efficient transport of reaction molecules and harvesting of photo-energy. The result reveals the existence of special two-band-gap structure (3.25 and 2.0 eV) for $(BiO)_2CO_3$. The band gap of 3.25 eV is intrinsic and the formation of smaller band gap of 2.0 eV can be ascribed to the in situ doped nitrogen in lattice. The performance of hierarchical $(BiO)_2CO_3$ microspheres as efficient photocatalyst are further demonstrated in the removal of NO in indoor air under both visible light and UV irradiation. It is found that the hierarchical $(BiO)_2CO_3$ microspheres not only exhibit excellent photocatalytic activity but also high photochemical stability during long term photocatalytic reaction. The special microstructure, the high charge separation efficiency due to the inductive effect, and two-band-gap structure in all contribute to the outstanding photocatalytic activities. The discovery of monodisperse hierarchical nitrogen doped $(BiO)_2CO_3$ hollow structure is significant because of its potential applications in environmental pollution control, solar energy conversion, catalysis and other related areas.

1. Introduction

Many materials in the nature, such as lotus leaf and seashell, consisting of ordinary composition, exhibit fascinating properties owing to their special structural characteristics [1,2]. Such intricate natural designs have inspired materials scientists to fabricate morphology and structure controlled materials, with expectations to obtain novel or enhanced properties [2–4].

Hierarchical hollow structured materials have been a subject of intensive research in the past decade because of their novel physicochemical properties, which differ markedly from those of bulk materials, and their potential applications as nanoscale chemical reactors, (photo)catalysts, sensing, lithium batteries, solar energy conversion, photonic building blocks and environmental applications, to name a few [5–10]. The fabrication of such structures usually relies on templating approaches, in which hard templates [11–14] (e.g., monodisperse polymer latex, carbon, silica spheres, and reducing metal nanoparticles) or soft sacrificial templates [15–19] (e.g., micelles, microemulsions, macromolecules, oil droplets, and gas bubbles) were used to direct the growth of hierarchical or hollow structure.

The template approach can be easily conducted for a specific structure. The capability of constructing complicated structure, however, is usually limited by the availability of templates. Disadvantages related to high cost and tedious synthetic procedures have also impeded scale-up of these template methods for

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applications. In comparison with these methods, which involve multistep procedures, a one-pot template-free approach for the controlled synthesis of hierarchical hollow sphere is highly attractive and desirable based on different mechanisms. Recently, a number of one-pot template-free methods for generating hollow inorganic micro- and nanostructures have been developed by using some well-known physical phenomena, for example, Ostwald-ripening [20], Kirkendall-effect [21] and oriented attachment [22].

Recently, there has been great interest in developing semiconductor photocatalysts with high activities (especially the visible light driven photocatalysts) for both energetic and environmental applications, such as photocatalytic hydrogen evolution, creation of self-cleaning surfaces, disinfection of water, degradation of organic contaminants and conversion of carbon dioxide into hydrocarbon fuels [23–32]. The key to the application of photocatalysis technology is to develop photocatalytic materials with efficient activity and high stability. Photocatalytic materials with hollow or hierarchical structure, such as TiO_2 [33,34], ZnS [35], WO_3 [36], $BiVO_4$ [37], Bi_2WO_6 [38] and Cu_2PO_4OH [39] have been fabricated by different methods, and are proved to be high-performance in environmental pollutants degradation due to their special morphological structure with respect to pore structure, light harvesting, and charge separation and so on. Development of new visible light driven photocatalytic materials may also overcome the limitations of transitional TiO_2 (reduced sensitivity to sunlight and limited visible light photocatalytic activity) [25]. Controlling the shape and morphology of new photocatalytic materials may, therefore provide new opportunities to explore their novel structural properties and photocatalytic activity. In spite of these advances, realization of controlled one-pot fabrication of novel hierarchical hollow structure by facile template-free method remains a great challenge.

The bismuth subcarbonate $(BiO)_2CO_3$ is first reported in 1984 [40]. It has an orthorhombic crystal structure with cell parameters of $a = 3.865$, $b = 3.865$, and $c = 13.675$ Å, belonging to *Imm2* space group. After the first report in 1984, there is little investigation on the fabrication and properties of $(BiO)_2CO_3$. Until very recently, synthetic $(BiO)_2CO_3$ is reported to display promising results in antibacterial and environmental applications [41–43]. Although some advances has been made, much is unknown on the controlled fabrication, morphological structure, especially the visible light photocatalytic properties of uniform hierarchical $(BiO)_2CO_3$ hollow microspheres. It will be, therefore of fundamental and technological interest to develop facile and effective methods for the fabrication of such novel structured $(BiO)_2CO_3$ with novel properties for energetic and environmental applications [28].

In this study, we developed a one-pot template-free method for the fabrication of uniform monodisperse hierarchical $(BiO)_2CO_3$ hollow microspheres for the first time based on hydrothermal reaction between ammonia bismuth citrate and urea. The as-prepared hierarchical $(BiO)_2CO_3$ microspheres were analyzed by various characterization tools to fully understand the structural properties and were used as visible light photocatalyst for indoor air NO removal. It was found that the attractive hierarchical $(BiO)_2CO_3$ microspheres were constructed by self-assembly of single-crystalline nanosheets. Interestingly, nitrogen was in situ doped into the lattice of $(BiO)_2CO_3$, which modified the band structure significantly. For the first time, the monodisperse hierarchical $(BiO)_2CO_3$ hollow microspheres were found to exhibit excellent photocatalytic activity and photochemical stability for indoor air NO removal under both visible and UV light irradiation. The attractive hierarchical $(BiO)_2CO_3$ hollow microspheres will also find wide application in other areas, such as solar energy conversion, aqueous pollution control and production of fuels by fully using solar energy.

2. Experimental

2.1. Fabrication

All chemicals used in this study were analytical grade (Sigma–Aldrich) and were used without further purification. Distilled water was used in all experiments. In a typical synthesis, appropriate amounts of ammonia bismuth citrate (1.66 g) and urea (0.72 g) were mixed with 75 ml of H_2O in a 100 ml autoclave Teflon vessel and stirred for 30 min. The resulted transparent precursor solution was then hydrothermally treated at 180 °C for 12 h. The sample obtained was filtered, washed with water and ethanol for four times and dried at 60 °C to get final $(BiO)_2CO_3$ with no further treatment. For comparison, C-doped TiO_2 were prepared by reported hydrothermal method [29] and the commercial Degussa P25 was also used as reference sample.

2.2. Characterization

The crystal phases of the sample were analyzed by X-ray diffraction with Cu Kα radiation (XRD: model D/max RA, Rigaku Co., Japan). The accelerating voltage and the applied current were 40 kV and 150 mA, respectively. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Raman: RAMANLOG 6, USA) with a 514.5 nm Ar + laser as the excitation source in a backscattering geometry. The incident laser power on the samples was less than 10 mW. X-ray photoelectron spectroscopy with Al Kα X-rays ($h\nu = 1486.6$ eV) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties and to probe the total density of the state (DOS) distribution in the valence band (VB). The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.8 eV as an internal standard. FT-IR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. A scanning electron microscope (SEM, JEOL model JSM-6490, Japan) was used to characterize the morphology of the obtained products. The morphology, structure and grain size of the samples were examined by transmission electron microscopy (TEM: JEM-2010, Japan). The UV–vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (UV–vis DRS: TU-1901, China) equipped with an integrating sphere assembly, using $BaSO_4$ as reflectance sample. The spectra were recorded at room temperature in air ranged from 250 to 800 nm. Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). All the samples were degassed at 200 °C prior to measurements.

2.3. Photocatalytic activity evaluation

The photocatalytic activity of the resulting samples was investigated by oxidation of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, which was made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). A 300 W commercial tungsten halogen lamp (General Electric) was vertically placed outside the reactor above the reactor. Four mini-fans were fixed around the lamp to avoid the temperature rise of the flow system. Adequate distance was also kept from the lamp to the reactor for the same purpose to keep the temperature at a constant level. The distance between the lamp and the sample is 30 cm. For the visible light photocatalytic activity test, UV cutoff filter (420 nm) was adopted to remove UV light in the light beam. For photocatalytic activity test under simulated solar light, the UV cutoff filter was removed. For UV light photocatalytic activity test, two 6 W UV lamps (Cole–Parmler), emitting a primary wavelength at 365 nm was used. For each photocatalytic activity test experiment, one