Applied Surface Science 319 (2014) 256–264

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Hydrothermal fabrication of N-doped $(BiO)_2CO_3$: Structural and morphological influence on the visible light photocatalytic activity

Fan Dong[a,*], Rui Wang[a], Xinwei Li[a], Wing-Kei Ho[b]

[a] Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, College of Environmental and Biological Engineering, Chongqing Technology and Business University, Chongqing 400067, China
[b] Department of Science and Environmental Studies, The Centre for Education in Environmental Sustainability, The Hong Kong Institute of Education, Hong Kong, China

ARTICLE INFO

Article history:
Received 12 June 2014
Received in revised form 9 July 2014
Accepted 11 July 2014
Available online 19 July 2014

Keyword:
Hierarchical superstructure
Nitrogen doping
Hydrothermal temperature
Visible light photocatalytic
Air purification

ABSTRACT

Various 3D N-doped $(BiO)_2CO_3$ (N-BOC) hierarchical superstructures self-assembled with 2D nanosheets were fabricated by one-step hydrothermal treatment of bismuth citrate and urea. The as-obtained samples were characterized by XRD, XPS, FT-IR, SEM, N_2 adsorption–desorption isotherms and UV–vis DRS. The hydrothermal temperature plays a crucial role in tuning the crystal and morphological structure of the samples. Adjusting the reaction temperature to 150, 180 and 210 °C, we obtained N-doped $(BiO)_2CO_3$ samples with corresponding attractive persimmon-like, flower-like and nanoflakes nano/microstructures. The photocatalytic activities of the samples were evaluated by removal of NO under visible and solar light irradiation. The results revealed that the N-doped $(BiO)_2CO_3$ hierarchical superstructures showed enhanced visible light photocatalytic activity compared to pure $(BiO)_2CO_3$ and TiO_2-based visible light photocatalysts. The outstanding photocatalytic performance of N-BOC samples can be ascribed to the doped nitrogen and the special hierarchical structure. The present work could provide new perspectives in controlling the morphological structure and photocatalytic activity of photocatalyst for better environmental pollution control.

1. Introduction

In recent years, three dimensional (3D) hierarchical structure has attracted considerable attention because of their potential applications in catalyst, sensitized solar cells, sensors, lithium-ion batteries, drugs delivery and super capacitors [1–6]. Among which, the 3D hierarchical microspheres show admirable photocatalytic activity due to their particular property including large surface areas, porous structure and enhanced photo-energy harvesting, thus being extensively applied in energy conversion and environment treatment [7,8].

Template and template-free are widely used to fabricate 3D hierarchical structured materials. The template-based approaches include hard templates and soft templates. Although the hard template directed methods have been most commonly used and found to be quite effective for the preparation, their drawbacks such as the difficulty in finding appropriate templates or the damage of the structural integrity caused by removing of the template are obvious. As for soft-templates, they are often limited by the difficulty in obtaining the uniform products. It is worthwhile to note the special gas bubble, one of the soft templates, around which the nanoparticles form and aggregate [9]. For example, ZnO microspheres [10], carbonated hydroxyapatite (CHAp) microspheres [11], poly-lactic acid microspheres [12] and $K_4Nb_6O_{17}$ [13] were all synthesized via the gas bubbles templates. Although templating methods have proved to be useful, direct fabrication without templates is still preferred in practical application due to their relatively low cost and the ease of scaling up [9].

Recently, various types of hierarchical nanomaterials fabricated by template-free methods have been reported [14]. Wang and co-works prepared 3D Nb_3O_7F hierarchical nanostructures via a facile hydrothermal method without any template [15]. Tian's group synthesized controllable hierarchical flower-like Bi_2MoO_6 hollow spheres via a template-free solvothermal method in the presence of ethylene glycol [16]. And 3D hierarchical SnO_2 architectures were self-assembled with low-dimensional nanostructured building blocks [17]. A new functional $(BiO)_2CO_3$ material with 3D hierarchical structures recently has been fabricated. For instance, Cheng and co-workers have synthesized hierarchical flower-like $(BiO)_2CO_3$ microspheres through a low-temperature solution method [18,19].

* Corresponding author. Tel.: +23 62769785 605; fax: +23 62769785 605.
E-mail address: dfctbu@126.com (F. Dong).

http://dx.doi.org/10.1016/j.apsusc.2014.07.062
0169-4332/

Cheng et al. prepared hierarchical $Bi_2O_2CO_3$ microstructures for photocatalytic degradation of organic dyes [20]. However, the pure $(BiO)_2CO_3$ has large band gap of 3.1 to 3.5 eV, making it unable to utilize visible light. Nitrogen doping has been extensively employed to narrow the band gap [21,22]. Yu et al. synthesized hierarchical graphene-$Bi_2O_2CO_3$ composites with enhanced photocatalytic performance under visible light [23]. Chen et al. constructed $(BiO)_2CO_3$/BiOX (X = Cl, Br, I) heterostructure for enhanced visible light photocatalysis [24]. Our group has recently developed a template-free method to fabricate in situ N-doped $(BiO)_2CO_3$ hierarchical microspheres by hydrothermal treatment of ammonia bismuth citrate or bismuth citrate and urea/ammonia in water [25–27]. Due to the in situ doped nitrogen substituting for oxygen in the lattice of $(BiO)_2CO_3$, the band gap of $(BiO)_2CO_3$ was significantly reduced, making N-doped $(BiO)_2CO_3$ highly visible light active [25–27]. Although some advances has been made on the synthesis of N-doped $(BiO)_2CO_3$ nanostructured materials, the synthesis of N-doped $(BiO)_2CO_3$ with new morphology is still in its infancy. Furthermore, the effects of hydrothermal temperature on the microstructures (including phase structure, pore structure, morphology, chemical composition and optical properties) and photocatalytic performance of N-doped $(BiO)_2CO_3$ have not been clearly revealed.

Very recently, we have synthesized 3D N-doped $(BiO)_2CO_3$ hierarchical superstructures self-assembled with 2D nanosheets by hydrothermal treatment of bismuth citrate and urea [25]. In the present work, we continue this research in order to elucidate the effects of hydrothermal temperature on the morphological structure and photocatalytic performance of N-doped $(BiO)_2CO_3$ superstructures. It was interesting to find that the morphology and microstructure of N-doped $(BiO)_2CO_3$ superstructures could be simply tuned by changing the hydrothermal temperature. The as-prepared N-doped $(BiO)_2CO_3$ superstructures showed enhanced visible (solar) light photocatalytic activity for removal of NO in air due to the special hierarchical structure and the introduction of N element.

2. Experimental

2.1. Materials and synthesis

All chemicals used in this study were analytical grade (Sigma-Aldrich) and were used without further purification. In a typical fabrication, appropriate amounts of bismuth citrate (1.60 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 aqueous precursor suspension was then hydrothermally treated at 120, 150, 180 and 210 °C for 48 h, respectively. The obtained solid sample was filtered, washed with water and ethanol for three times and dried at 60 °C to get final N-doped $(BiO)_2CO_3$ with no further treatment. The samples were labeled as N-BOC-120, N-BOC-150, N-BOC-180 and N-BOC-210, respectively.

2.2. Characterization

The crystal phases of the sample were analyzed by X-ray diffraction with Cu $K\alpha$ radiation (XRD: model D/max RA, Rigaku Co., Japan). FT-IR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. X-ray photoelectron spectroscopy with Al $K\alpha$ 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 was corrected using the C1s level at 284.8 eV as an internal standard. A scanning electron microscope (SEM, JEOL model JSM-6490, Japan) was used to characterize the morphology of the obtained products. The morphology and structure 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 100% $BaSO_4$ as reflectance sample. Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA). All the samples were degassed at 150 °C prior to measurements.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity was investigated by removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, 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. Four mini-fans were used to cool the flow system. 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. Photocatalyst (0.15 g) was coated onto a dish with a diameter of 12.0 cm. The coated dish was then pretreated at 70 °C to remove water in the suspension. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 450 ppb by the air stream supplied by a zero air generator (Thermo Environmental Inc., model 111). The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 3.3 L/min by a mass flow controller. After the adsorption–desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., model 42c), which monitors NO, NO_2, and NO_x (NO_x represents NO + NO_2) with a sampling rate of 0.7 L/min. The removal ratio (η) of NO was calculated as η (%) = $(1 - C/C_0) \times 100\%$, where C and C_0 are concentrations of NO in the outlet steam and the feeding stream, respectively.

3. Result and discussion

3.1. Phase structure

The phase structure of the samples under different hydrothermal temperatures was investigated by XRD as shown in Fig. 1. Only one broad diffraction peak can be observed in the XRD pattern of N-BOC-120, which indicates that the sample is nearly amorphous due to the low hydrothermal temperature. When the temperature exceeds 150 °C, the diffraction peaks of the N-BOC-150, N-BOC-180 and N-BOC-210 samples can be indexed to the standard card of $(BiO)_2CO_3$ (JCPDS-ICDD card No. 41-1488), and no other peaks can be detected, illustrating that the three samples are highly pure in phase. The peaks of the four samples increase in intensity while the width at half-height decrease as the temperature increases, indicating the enhancement of crystallinity. In accordance with the crystal structure of $(BiO)_2CO_3$, the $(Bi_2O_2)^{2+}$ layers and CO_3^{2-} layers are mutually perpendicular and inter-grown with the plane of the CO_3^{2-} group. The internal layered structure would guide the crystal growth to form 2D nanosheet morphology along certain axis. Compared with the standard pattern, the intensified (1 1 0) diffraction peak means the as-prepared samples have a preferential oriented