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In-situ topotactic synthesis and photocatalytic activity of plate-like BiOCl/2D networks Bi_2S_3 heterostructures

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ABSTRACT

We herein demonstrate the uniform porous hierarchical plate-like BiOCl/2D networks Bi_2S_3 heterostructures realized by a facile two-step hydrothermal technique. The synthesis involved an anion exchange process by reacting pre-synthesized BiOCl irregular octagonal nanoplates with $Na_2S_2O_3{\cdot}5H_2O$ in an aqueous solution. The experiment results revealed that the 3D plate-like heterostructures were composed of internal BiOCl and outside networks interwoven by 1D Bi_2S_3 nanorods. Interestingly, the heterostructures had almost the same thickness and the bigger length compared to the precursor BiOCl. We proposed the possible formation mechanism of the composites which involved selective ion-exchange reaction, the following Ostwald ripening process and epitaxial growth. And the crystal lattice matching between the a- or b-axis of tetragonal BiOCl ($a = b = 3.89$ Å) and the a-axis of orthorhombic Bi_2S_3 ($a = 3.981$ Å) could be responsible for the in-situ topotactic transformation. Due to the formation of hetero-nanostructures, the unique spatial architecture features and the existence of oxygen vacancies, the $BiOCl/Bi_2S_3$ composites exhibited significantly extended photo-responsive range and improved photocatalytic activity for reduction of Cr^{VI} under visible-light irradiation. Moreover, the possible mechanism of photocatalysis process was investigated. Our work is expected to inspire further attempts for hierarchical and unconventional hetero-nanostructures with unique spatial architecture, which is very promising for photocatalysis and other applications.

1. Introduction

Many novel applications of nanomaterials in solar cells [1], photonic and optoelectronic devices [2], photocatalysis [3], and bionanotechnology [4] are driving the exploration and development of the techniques to design and synthesize their chemical compositions, structures, and morphologies[5–7]. Three-dimensional (3D) nanomaterials, which usually possess distinctive spatial architecture features, have been attracting great attention [8–10]. Up to now, there have been increasing attempts and successes in the preparation of 3D nanostructures. Firstly, 3D nanostructures were based on zero-dimensional (0D) nanoparticles, such as the Te plates composed of 0D Te nanoparticles obtained by two-step method [11]. Secondly, 3D nanomaterials were synthesized using the one-dimensional (1D) nanorods or nanowires. N-Si/n-TiO_2 core/shell nanowire arrays were synthesized from 0D TiO_2 by growth on their surfaces of 1D Si electroless etched nanowire arrays [12]. Hyperbranched nanowires were prepared by gold nanoclusters deposition on Si nanowires [13]. Homo- and hetero-branched nanowires were obtained by the secondary growth of 1D nanowires [14]. The third kind of 3D nanostructures were based on the 2D precursors. The following growth of nanowires on the 2D nanoplates can be realized to obtain complex 3D nanostructures [15]. Fourthly, 3D nanomaterials were gained by treating 3D precursors with ion-exchange or the Kirkendall effect methods. S^{2-} ions are introduced into pre-synthesized 3D $BiVO_4$ discoid-like particles to form 3D hollow mesoporous heterostructures by a facile ion-exchange method [16].

Hetero-nanostructures, which always possess staggered array of band edges at the interface [17,18] and mesoporous structures or hollow interiors [16,19,20], are usually considered to be of great potential for various applications due to their enhanced or new physicochemical properties. It is worth noting that there are some 3D heterostructures taking advantages of both 1D and 2D compositions, geometries. 1D nanorods grew selectively on the pre-synthesized 2D nanoplates to form hierarchical 1D/2D heterostructures [15,21,22]. However, the rational design and synthesis of hierarchical 3D heterostructures with distinctive architecture and performances remain a great challenge. The obstacles come from combining the existence of interfaces, different growth modes and the incompatibility, which

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usually results in uniformity and poor structural stability [16].

Among Bi-based semiconductor materials, BiOCl, characterized by [Bi_2O_2] slabs interleaved by double layers of Cl atoms, is promising for many applications in pigments, photocatalysis, catalysts, as well as storage materials due to the unique layered structure and excellent optical and electrical properties [23,24]. However, BiOCl has an indirect wide band gap (E_g = 3.2-3.6 eV) and limited absorbance of UV light, which prevent its further applications. To overcome these obstacles, some effective strategies were studied, such as controlling exposed crystal facets, varying morphology and size, ion or metal doping, as well as creating heterostructures. Zhang et al. found that BiOCl nanosheets with exposed {001} and {010} facets showed different activities for pollutant degradation [25]. Our lab reported the porous BiOCl hexagonal prisms for the first time [26]. Xiong et al. synthesized Ag/Pd/BiOCl which showed improved photocatalytic performance by synergistically utilizing Schottky-junction and plasmonic effect [27]. BiOCl-based heterostructures, such as Co_3O_4/BiOCl [28], In_2O_3/BiOCl [29], TiO_2/BiOCl [30], BiOCl/ZnO [31], exhibited enhanced performance compared to their individual ones. Among these methods, creating heterostructures is more flexible and interesting.

As a metal sulfide with a layer structure, Bi_2S_3, with a direct narrow band gap of 1.3-1.7 eV, is of great potential for applications, such as lithium ion batteries [32], electrochemical hydrogen Storage [33], visible-wavelength photodetectors [34] and so on. Though Bi_2S_3 has good visible light response, it is hindered for applications due to the rapid photogenerated electron–hole recombination [35]. Doping and creating heterostructures are the effective methods to achieve electron–hole pair effective separation. Our lab synthesized Sn doped Bi_2S_3 microspheres which showed improved photocatalytic activity for RhB degradation [36]. The Bi_2S_3–ZnO heterostructure nanosheets exhibited higher activity than pure ZnO and Bi_2S_3 [35]. There are some works in the preparation of Bi_2S_3/BiOCl [37–41] with enhanced photocatalytic performance through in-situ etching, one-pot approach at room temperature, biomolecule-assisted solvothermal method and ion-exchange method. Although synthesizing heterostructured materials is a big challenge, it still receives increasing attention. The formation of heterostructure between two semiconductors may endow the material with excellent performance due to the extended photoresponse range and improved separation efficiency of e–h pairs.

Herein, we report the uniform, porous and hierarchical BiOCl/2D networks Bi_2S_3 heterostructures synthesized by a facile two-step hydrothermal method. The strategy involved a facile anion-exchange process by treating uniform BiOCl irregular octagonal nanoplates with $Na_2S_2O_3{\cdot}5H_2O$ in an aqueous solution to perform a hydrothermal process. We tuned the content of Bi_2S_3 phase in the hybrids by controlling the concentration of $Na_2S_2O_3{\cdot}5H_2O$ in the reaction system. The possible formation mechanism of the composites was investigated by characterizing the samples obtained after the time-dependent reactions. The crystal lattice matching between the a- or b-axis of tetragonal BiOCl (a = b = 3.89 Å) and the a-axis of orthorhombic Bi_2S_3 (a = 3.981 Å) could be responsible for the topotactic transformation from BiOCl nanoplates to BiOCl/Bi_2S_3. Benefiting from the formation of heterostructures, the unique spatial architecture and the oxygen vacancies, the BiOCl/Bi_2S_3 heterostructures exhibited significantly enhanced optical properties and photocatalytic activity for reduction of Cr^{VI} under visible-light illumination. This work provides insight into the formation mechanism of BiOCl/Bi_2S_3, and is expected to inspire further attempts for well-designed and unconventional hetero-nanostructures with shape-dependent enhanced performances.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate [$Bi(NO_3)_3{\cdot}5H_2O$], sodium chloride [NaCl], sodium thiosulfate pentahydrate [$Na_2S_2O_3{\cdot}5H_2O$], nitric acid [HNO_3], potassium dichromate [$K_2Cr_2O_7$] were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Chitosan was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). All of the reagents were analytical grade and used as received without any further purification.

2.2. Preparation of BiOCl irregular octagonal nanoplates

BiOCl irregular polygonal nanoplates were prepared in advanced. In a typical synthetic process, 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was put into a 50 mL beaker which contained the mixed solution of 19 mL deionized water and 1 mL nitric acid. The mixture was stirred and sonicated until $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved absolutely and labeled as solution A. Simultaneously, 5 mmol NaCl was dissolved into 5 mL deionized water, followed by addition of 40 mL 10 g L^{-1} aqueous solution of Chitosan, resulting in a transparent solution B. Subsequently, solution A was slowly added to solution B in drops with continuous stirring and sonication. Then, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was subsequently placed in an oven at 180 °C for 6 h. When cooling down to ambient temperature naturally, the obtained white precipitates were collected by filtered and washed with deionized water and ethanol for several times to thoroughly remove residual ions, and finally dried at 60 °C in air for 12 h for further use.

2.3. Preparation of uniform porous hierarchical BiOCl/2D networks Bi_2S_3 heterostructures

BiOCl/Bi_2S_3 was synthesized though a hydrothermal method. The pre-synthesized BiOCl (2 mmol) was dispersed in 20 mL deionized water and magnetically stirred for 20 min. Afterwards, 20 mL sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) aqueous solution was added into the suspension, followed by magnetically stirring for 20 min. The mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave to perform the hydrothermal process at 180 °C for 6 h. After cooling down to ambient temperature naturally, the resulting precipitates were collected by filtered and washed with deionized water and ethanol for several times to remove the residual impurities, and finally dried at 60 °C in air for 12 h for further characterization. To investigate the effect of $Na_2S_2O_3{\cdot}5H_2O$ concentration on the formation of BiOCl/Bi_2S_3 hetero-nanostructures, $Na_2S_2O_3{\cdot}5H_2O$ solutions with different concentrations (0.025, 2, 4 and 6 mmol) were used in the anion exchange process, while keeping other conditions unchanged. The samples were designated as H-1, H-2, H-3 and H-4, respectively. To observe the growth process of BiOCl/Bi_2S_3 composites, we carried out the time-dependent reactions. The 4 mmol $Na_2S_2O_3{\cdot}5H_2O$ solutions was used to perform the anion exchange process for 20 min, 40 min, 1 h, 2 h, 4 h, 6 h, 12 h, 24 h and 48 h under otherwise identical conditions.

2.4. Characterization

The powder X-ray diffraction (XRD) (Bruker D8 Advance; Cu Kα = 1.5404 Å) was employed to study the crystalline structure of the prepared samples. The 2θ range was from 10° to 80° with a scanning rate of 0.05°/s. The microstructure and size of the samples were investigated by a SU8010 field-emission scanning electron microscope (FESEM, Hitachi, Japan) at a decelerating voltage 2 KV. Energy dispersive spectrum (EDS) was connected to the SEM. Transmission electron microscope (TEM) and high resolution *trans*-mission electron microscopy (HRTEM) were obtained on a Tecnai G20 (FEI Co., Holland) microscope operated at an accelerating voltage of 200 kV, the sample powder was dispersed into ethanol by ultrasonic treatment and dropped a very dilute suspension onto a copper grid. X-ray photoelectron spectroscopy (XPS) was recorded on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using monochromatic Al Kα radiation as the excitation source under vacuum at 2×10^{-6} Pa. All the binding