

Urchin-like boron nitride hierarchical structure assembled by nanotubes-nanosheets for effective removal of heavy metal ions



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ARTICLE INFO

Keywords:

Hierarchical structure
Boron nitride nanotubes
Boron nitride nanosheets
Water treatment

ABSTRACT

Water pollution has become a serious global issue owing to the large amounts of contaminants generated from industrial and agricultural development. Recently, various boron nitride-based micro/nano-materials have exhibited efficient sorption capacity for contaminants from water. Herein, novel urchin-like boron nitride hierarchical structure assembled by free-growing boron nitride nanotubes and crapy boron nitride nanosheets is firstly fabricated via a sample two-step approach, including the synthesis of analogous "core-shell" structured boron-containing precursor and thermal catalytic chemical vapor deposition. A combined growth mechanism of vapor-liquid-solid and vapor-solid is proposed to control the formation of BN hierarchical structure. The unique structure exhibits superior removal capacity of 115.07 mg g⁻¹ and 92.85 mg g⁻¹ for Pb²⁺ and Cu²⁺ in water solution, respectively. The excellent adsorption performance of the product mainly derives from the vast lattice imperfections, the high-density edge active sites, the expanded interplanar spacing, as well as the unique structural characteristics. They are beneficial for structural stability and enough space for accommodating the adsorbed heavy metal ions. These results indicate that the urchin-like boron nitride hierarchical structure is a promising adsorption material for water treatment.

1. Introduction

Nowadays, water pollution is one of the most severe worldwide issues for human beings because of the large amounts of pollutants generated from industrial and agricultural development. The contaminants of the aqueous environment by toxic heavy metal ions give rise to enormous damage for the environment and health of human beings [1,2]. It is urgently to take advantages of new materials and techniques for effective removal of aqueous pollutants. Adsorption technology has been recognized as an efficient and attractive strategy for water purification [3,4]. However, the conventional polymeric and inorganic adsorbents have slow adsorption rate or limited adsorption capacity [5,6]. Therefore, it is a significant research project to develop advanced adsorbing materials with fast adsorption rate and high adsorption capacity for eliminating the aqueous contaminants.

Hexagonal boron nitride (*h*-BN) is a layered material analogous to graphite in which planar networks of BN hexagons are regularly stacked [7]. BN nanomaterials, such as boron nitride nanotubes (BNNTs) and boron nitride nanosheets (BNNs), possess excellent mechanical properties, high thermal conductivity and chemical stability, and high temperature oxidation properties owing to their similar intralayer

strong σ bonds and interlayer weak *Van der Waals* forces [8]. In recent years, carbon-based nanomaterials are utilized to removal of heavy metal pollutants, including carbon nanotubes [9–11], graphene and its derivatives [11,12], and graphene oxide-based materials [13–15]. Meanwhile, BN-based micro/nano-materials (including functionalized BNNTs [16], nanosheet-structured BN spheres [17], BN hollow spheres [18], porous BN whisker [19], BN foam-like porous monoliths [20], and activated BN [21–23], etc.) have been demonstrated with high efficiency for removal of heavy metal ions due to their high specific surface area and large pore volume, high chemical stability, functional groups and the "lop-sided" densities characteristic of polar B-N bonds. However, the application of BN-based materials for water treatment is lack of deep research, although the structure is similar between BN and graphite [24].

Recently, hierarchical structures exhibit enhanced adsorbent properties due to their large amounts of active adsorption sites from the nanoscale building blocks, enhanced mass transfer and decreased blocking of channels compared with their bulk counterparts [25–27]. To the best of our knowledge, the application of BN hierarchical structure for pollutants removal from water have not yet been reported.

Herein, we develop a facile route to synthesize novel urchin-like BN

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hierarchical structure assembled by free-growing BNNTs and crapy BNNSs via a sample two-step approach, including the synthesis of analogous "core-shell" structured boron-containing precursor and thermal catalytic chemical vapor deposition. Moreover, the formation mechanisms of BN hierarchical structure is explored. Finally, the adsorption kinetics and adsorption isotherms of as-prepared product are investigated using heavy metal ions (Pb^{2+} and Cu^{2+}) as the paradigms. This work indicate that the novel-structural BN-based nanomaterial is a promising adsorption material for water treatment.

2. Experimental

2.1. Synthesis of BN hierarchical structure

- (1) Synthesis of boron-containing precursor: in a typical experiment, 0.1 mol boron powders, 0.01 mol $\text{Ni}(\text{NO}_3)_2$ and 0.025 g polyvinylpyrrolidone (PVP, K30) were added into 25 mL deionized water through stirring for 30 min, 0.1 mol $\text{CO}(\text{NH}_2)_2$ was added into above solution, then the mixtures were put into polytetrafluoroethylene (PTFE) high-pressure reactor at 80 °C for 12 h. Finally, the product was filtered and dried at 60 °C for 12 h under vacuum to obtain boron-containing precursor with analogous "core-shell" structure.
- (2) Fabrication of BN hierarchical structure: the boron-containing precursor was placed into the alumina crucible of a horizontal tube furnace with a high purity corundum tube. The tube furnace was firstly heated to 330 °C with a heating rate of 10 °C min^{-1} for 2 h in air, then the chamber was continuously ventilation with high-purity argon (500 sccm, 99.99% purity) flow for 30 min to eliminate the residual air, and gradually heated up to 1400 °C (with heating rate 5 °C min^{-1}) for 3 h in ammonia gas (99.9% purity) flow with a flow rate of 100 sccm. Finally, the chamber was cooled to room temperature under continuous high-purity argon flow. After the synthesis, the obtained primary product was dispersed in acid solution and stirred for 3 h, and then filtered and washed with deionized water and absolute ethyl alcohol for several times. The final purified product was dried at 60 °C for 12 h under vacuum.

2.2. Materials characterization

The composition, structure and morphologies of the obtained samples were characterized and analyzed via thermogravimetric analysis and differential scanning calorimetry (TG-DSC, Netzsch, STA449F3), X-ray diffraction (XRD, Bruker, D8 Advance Cu $K\alpha$), Fourier transform infrared spectroscopy (FT-IR, Nicolet6700), Raman microscopy (Raman, Renishaw, InVia), Field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus) coupled with energy dispersive X-ray spectroscopy (EDS, X-Max 50), High-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F) coupled with selected area electron diffraction techniques (SAED) and Atomic force microscopy (AFM, Veeco Nanoscope).

2.3. Heavy metal ion adsorption experiments

Heavy metal ion solutions (Pb^{2+} and Cu^{2+}) with different concentrations were prepared by dissolving appropriate amounts of $\text{Pb}(\text{NO}_3)_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into deionized water, respectively. In a typical adsorption experiment, 10 mg of the BN hierarchical structure were added into 10 mL Pb^{2+} and Cu^{2+} aqueous solution with an initial concentration of 50 mg L^{-1} under stirring with different time for adsorption at 25 °C, respectively. Then the solutions were centrifuged at 8000 rpm for 5 min to separate the sediment from the solutions. The concentration of residue heavy metal ions in supernate was determined by inductively coupled plasma-optical emission spectra (ICP-OES, Prodigy 7).

The adsorption isotherms were obtained by varying the initial heavy

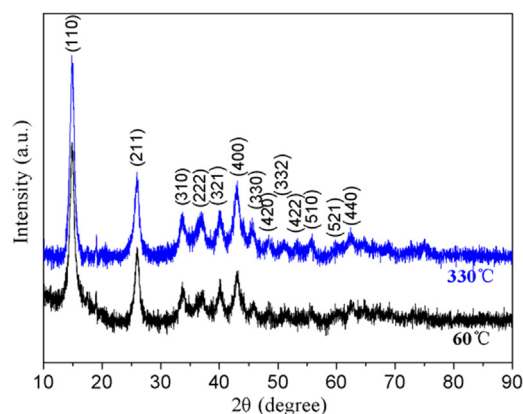


Fig. 1. XRD patterns of the boron-containing precursor obtained at 60 °C and the pretreated precursor at 330 °C for 2 h in air atmosphere.

metal ions concentrations. Equilibrium removal capacity of the sample is calculated by the following equation:

$$Q_e = \frac{(C_o - C_e)V}{m}$$

where Q_e (mg g^{-1}) is the equilibrium removal capacity of the adsorbent, C_o (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium solute concentrations of the heavy metal ions, V (L) is the total volume of the solution, and m (mg) is the mass of the BN hierarchical structure for each trial.

3. Results and discussion

3.1. Phase composition and microstructures of boron-containing precursor

Fig. 1 shows the XRD patterns of the boron-containing precursor obtained at 60 °C and the pretreated precursor at 330 °C. The diffraction peaks of boron-containing precursor obtained at 60 °C is assigned to the $\text{Ni}(\text{HCO}_3)_2$ (JCPDS card No. 00-015-0782). The diffraction peaks of boron are not observed due to the mainly amorphous structure of boron powders. The main composition has no significant change when the precursor is treated at 330 °C for 2 h in air atmosphere.

The microstructures of initial boron powders, boron-containing precursor obtained at 60 °C, and pretreated precursor at 330 °C are characterized by FESEM and TEM, as shown in Fig. 2. Compared with the smooth surface of raw boron powders (Fig. 2a), there are many $\text{Ni}(\text{HCO}_3)_2$ nanoparticles (according to XRD analysis in Fig. 1) on the surface of boron powders in the boron-containing precursor obtained at 60 °C (Fig. 2b). From the higher magnification image (Fig. 2c), the diameter of the $\text{Ni}(\text{HCO}_3)_2$ nanoparticles is confined to 10–20 nm and they dispersed on the surface of boron powders homogeneously. The microstructures of boron-containing precursor obtained at 60 °C are further investigated by TEM, as shown in Fig. 2d and Fig. 2e. The $\text{Ni}(\text{HCO}_3)_2$ nanoparticles encapsulate on the surface of boron powders to form the analogous "core-shell" structure (Fig. 2d), which is consistent with the FESEM results. The HRTEM image of $\text{Ni}(\text{HCO}_3)_2$ areas (Fig. 2e) shows that the parallel lattice fringes with interplanar spacing of 0.59 nm and 0.34 nm are corresponding to (110) and (211) planes of cubic $\text{Ni}(\text{HCO}_3)_2$, respectively. The corresponding SAED pattern of $\text{Ni}(\text{HCO}_3)_2$ areas (Fig. 2e inset) shows the families of (222), (400), (332), (440), (622), (651), (800), (840), (844) and (101) crystal planes of cubic $\text{Ni}(\text{HCO}_3)_2$, respectively. The uniform distribution of $\text{Ni}(\text{HCO}_3)_2$ nanoparticles are mainly attributed to the dispersed effect of polyvinylpyrrolidone, which can prohibit the agglomeration and growth of $\text{Ni}(\text{HCO}_3)_2$ nanoparticles. It is shown that the morphology and particle sizes of $\text{Ni}(\text{HCO}_3)_2$ nanoparticles are almost no change when the boron-containing precursor was pretreated at 330 °C for 2 h in air atmosphere

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