Research Article

Synthesize and Characterization of Hollow Boron-Nitride Nanocages

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The boron-nitride (BN) nanocages are synthesized by nitrogenation of amorphous boron nanoparticles at 1073 K under nitrogen and ammonia atmosphere. The BN nanocages exhibit a well-crystallized feature with nearly pentagonal or spherical shape, depending on their size. High-resolution transmission electron microscopy studies reveal that they are hollow nanocages. The growth mechanism of the BN nanocages is proposed.

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1. Introduction

Much attention has been focused on boron-nitride (BN) nanotubes and other fullerene-like nanostructures since the discovery of carbon nanotubes. BN nanotubes have been synthesized by an arc-discharge method using boride-based rods such as HfB_2 and ZrB_2 [1, 2]. The formation of *hexagonal*-BN nanocapsules encapsulating metal/oxides, including cobalt oxides [3], iron oxides, gold, and germanium [4], Zr compounds [5], silver/oxides [6], iron, and cobalt nanoparticles [7], has been reported. BN nanocages are synthesized in large amounts by nitriding Fe-B nanoparticles under mild conditions, which shows rather promising solid-state lubricating properties [8]. A synthesis mechanism is also proposed. The effects of catalytic metals for synthesis of BN fullerene nanomaterials have also been investigated [9].

Graphite-like BN nanomaterials have layer structure similar to graphite. Nanocages belong to an important category of fullerene-like structures, to which particular attention should be addressed. This is because substances of hollow cages may show novel physical and chemical properties. For instance, nanocages may serve as nanocontainers for gas storage [10–12]. Insulating BN nanocages may prevent

encapsulated particles from oxidization and contamination [13]. In our recent work, we encapsulated the boron nanoparticles with boron nitrides [14]. In the present work, we prepare BN nanocages, by means of arc-discharging in a mixture of diborane and nitrogen, followed by a subsequent annealing under a mixture of nitrogen (N_2) and ammonia (NH_3) atmospheres at 1073 K. The structures of as-prepared nanoparticles and as-annealed BN nanocages are investigated by means of X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM).

2. Experimental Procedures

A mixture of amorphous boron nanoparticles and Ni (B) nanocapsules sheathed with boron oxide was prepared by arc-discharge in a mixture of diborane (B_2H_6) and nitrogen (N_2) atmosphere. The anode was bulk Ni of 99.9% purity, while a flexible tungsten needle of 3 mm in diameter served as the cathode. The chamber was evacuated to 0.003 Pa before the introduction of gases. A mixture of B_2H_6 (purity 99.7%, 2000 Pa) and N_2 (purity 99.7%, 16000 Pa) was introduced into the chamber. The gas mixture serves as a reactant gas

and a source of hydrogen plasma. A voltage in the range of 20 to 30 V was applied between the cathode and the anode for evaporation. The deposits on the water-cooled wall of the chamber were collected.

To synthesize BN nanocages, the nanoparticles collected from the wall were first laid down on an aluminium oxide crucible lying in an aluminium oxide tube of the furnace, isolated from air by flowing pure NH_3 and N_2 , and then heated to 1073 K for 4 hours. Finally, the sample was cooled down to room temperature under pure N_2 .

The samples for TEM observation were prepared in two steps. First, the deposit was dispersed in ethanol in an ultrasound bath and then a drop of the suspension was transferred onto a carbon-coated TEM mesh grid and the ethanol was allowed to evaporate. The samples were examined by a JEOL 2000EX HRTEM operating at 200 kV. XRD spectra were recorded at room temperature in a Rigaku D/max-2500pc diffractometer with $\text{Cu K}\alpha$ radiation and a graphite monochromator.

3. Results and Discussion

Diffraction peaks in the XRD spectrum of the as-prepared nanoparticles (shown as Figure 1(a)) can be indexed as Ni and B_2O_3 phases. We cannot find XRD peaks for boron nanoparticles. The reasons may be that (1) Boron is in amorphous state, and (2) boron nanoparticles are surrounded by B_2O_3 shells, and it was too small to be detected by XRD. Figure 1(b) shows the XRD spectrum of the nanoparticles, after annealed under NH_3 and N_2 and then heated to 1073 K for 4 hours. Besides those for Ni, the XRD peaks that appear at about $2\theta = 26.5^\circ$ could be indexed as BN phase.

The typical morphology of the as-prepared nanoparticles is represented in a TEM micrograph (Figure 2). There are two kinds of nanoparticles in Figure 2, that is, boron nanoparticles and Ni (B) nanocapsules. Boron nanoparticles are in irregular shape and it is difficult to identify their size exactly. The typical size of the Ni (B) nanocapsules is in range of 20 ~ 200 nm and the discernible contrast in the TEM micrograph clearly shows that these Ni (B) nanocapsules are composed of a core and a shell. In our previous work [15], the phases in the shell of Fe (B) nanocapsules were confirmed by HRTEM to be amorphous boron oxides. It is believed that it is true also for the phases in the shell of the present Ni (B) nanocapsules.

After annealing the as-prepared nanoparticles under NH_3 and N_2 at 1073 K for 4 hours, we succeeded in synthesizing hollow BN nanocages. A general view of the morphology is represented in Figure 3(a). It was clearly shown that big BN nanocages are in a nearly pentagonal shape, accompanied with some smaller nanocages in nearly spherical shape. The size of the big nanocages in the nearly pentagonal shape is about 200 nm, while the diameter of the nearly spherical nanocages is about 12–20 nanometers. The formation of multilayered hollow BN nanocages by nitriding boron nanoparticles has been confirmed by enlarged A and B parts in Figures 3(b) and 3(c). Lattice fringes, originating from c planes of *h*-BN parallel to the incident electron beam,

FIGURE 1: XRD spectrum of B nanoparticles and Ni (B) nanocapsules (a) as-prepared and (b) annealed under nitrogen and ammonia atmosphere.

FIGURE 2: TEM images of B nanoparticles and Ni (B) nanocapsules.

are observed around the nanocages. The spacing of about 0.34 nm for equally separated BN layers is consistent with the interplanar distance of 0.334 nm in bulk hexagonal BN. The large BN nanocages have sharp inner angular, some defects as indicated by arrows, and the cages have some distortions. The contrast of the enlarged image reveals that they are really hollow nanocages (see Figures 3(b) and 3(c)).

The selected-area electron diffraction patterns from the big nanocages correspond to the (002) planes (with a spacing of 0.334 nm) of hexagonal BN bulk (see inset of Figure 3(b)).

FIGURE 3: (a) Low magnification of BN nanocages and (b) HRTEM images of the BN nanocages in a nearly pentagonal shape with the corresponding selected-area electron diffraction pattern (inset (b)). HRTEM images of the BN nanocages in (c) a spherical shape and (d) a nearly pentagonal shape. Insets (d) are Fourier transform images.

The three sets of patterns correspond to the three sides of the nanocages, as proved by Fourier transform. Fourier transform reveals that these patterns come from sides A, B and C (Figure 3(d)).

Encapsulation of cobalt nanoparticles in BN nanocapsules was obtained from Co and boron powders in H_2/NH_3 atmosphere under heating to 1073 K [13]. BN encapsulated Fe_2B nanoparticles were synthesized by annealing the mechanochemically treated Fe-BN mixtures at 1133 K [16]. Oku et al. prepared huge BN nanocages by acid treatment of BN encapsulated Fe nanocapsules [17]. BN nanocages were also synthesized by arc discharge method using Ga/B powders [9]. It is our understanding that in this work the BN nanocages grew from the boron nanoparticles, not the Ni (B) nanocapsules. Usually, the traditional vapor-liquid-solid (VLS) can be used as the formation mechanism of the BN nanocages. But the VLS mechanism cannot be employed to the formation mechanism in this work, because the reaction temperature of about 1073 K is too low to evaporate boron. We ascribe the formation of the hollow BN nanocages to a solid reaction, as what have been illustrated in our previous work [14]: boron atoms at the surface of a boron nanoparticle first react with N_2 gas to form a local BN layer, and then the layer grows along the surface of the

boron nanoparticle. Compared with our previous work [14], we obtain the completely hollow BN nanocages at lower temperature. It is due to the existence of NH_3 , because NH_3 is found to be much more effective than N_2 in enhancing the sorption of nitrogen [18]. This gives a promising prospect for manufacturing different types of BN nanoparts easily.

4. Conclusion

Hexagonal boron-nitride (BN) nanocages were prepared by nitriding the amorphous boron nanoparticles at 1073 K under nitrogen and ammonia atmosphere. The big BN nanocages exhibit a well-crystallized feature with nearly pentagonal shape, while some small nanocages form with nearly spherical shape. HRTEM studies reveal that they are hollow nanocages.

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