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Large-scale fabrication of boron nitride nanohorn

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Boron nitride nanohorns (BNNHs) are synthesized in large scale. Their morphology and structure were investigated by scanning electron microscopy and transmission electron microscopy. The hollow conical structure and particular aggregation behavior are revealed. Cathodoluminescence measurement is performed and ultraviolet light emission is observed, which indicates the potential applications of BNNHs in optical devices. © 2005 American Institute of Physics. [DOI: 10.1063/1.2009056]

Since the electronic properties of boron nitride nanotube (BNNT) have been predicted to be independent of various morphological and/or geometrical factors,¹ Boron nitride (BN) nanostructures continuously attract significant interest. In fact, BN nanomaterials have excellent mechanical properties,² a high resistance to oxidation,³ and chemical stability, which makes them highly valuable in electronic devices as far as their usage at elevated temperatures or in hazardous environments is concerned. Following the successful synthesis of BNNTs,4,5 the search for related BN nanostructures has been initiated.⁶⁻⁸ A cone-shaped structure is of special interest since the deviations from a flat graphitic surface are accompanied by the appearance of topological defects located at its apex.^{9,10} Recently, BN conical nanotubes have been found in a material containing large quantities of BNNTs.¹¹ Their structures were explained based on the model of orderly stacked 240° disclinations (a disclination angle is defined as the angle of the sector removed from a flat sheet to form the cone), which is the smallest cone geometry ensuring the presence of B-N bonds only.¹² The conical nanotubes have a solid core and are made of stacked BN nanocones or formed by a continuous BN sheet wrapped up in a helical fashion. However, this novel nanostructure was only a byproduct of the BNNT synthesis and its yield was marginally low, which make it is impossible to investigate the properties of this nanostrucuture.

It is noteworthy that the nanohorns have been discovered in graphitic carbon.¹³ Keeping in mind the unique structural similarities between C and layered BN, it is natural to expect the existence of such nanostructure in BN. However, to date, reports about such structure are overlooked in the literature. Here, we report large-scale synthesis of an intrigue BN nanostructure: BN nanohorns (BNNHs). The BNNHs exhibit specific aggregation behavior and possess a hollow conical structure. Their morphology and structure were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The synthesis in large scale makes it possible to measure the properties of this kind of nanostructure. Cathodoluminescence (CL) measurement is performed and ultraviolet light emission is observed, which indicates the potential applications of BNNHs in optical devices.

An induction furnace was used to synthesize BNNHs. In a typical run, a mixture of MgO and boron powder was heated in a BN crucible to 1700 °C. The heating yields a Mg vapor and B_2O_2 ,⁵ which are transported by an Ar gas and meet with ammonia. During heating, a white-colored smoke was observed coming out of a crucible and adhering to a quartz tube. After synthesis over 2 h, approximately 30 mg of a white-colored product were collected from the inner surface of a quartz tube.

Figure 1(a) presents the SEM image of our product. It can be seen that the product contains numerous hollow conical structures, resembling horns. The diameters of their bottom parts are typically 100-200 nm; the length varies from 500 nm to 1 μ m. An encapsulated particle can be observed in the bottom part of each BNNH, which is proven to be MgO by energy dispersive spectroscopy during TEM. The BNNHs were sonicated in alcohol for 30 min before being mounted onto a clean silicon wafer and a carbon-film-coated copper grid for detailed SEM and TEM investigations. After dispersion, the specific horn aggregation was revealed by SEM, as shown in Fig. 1(b). The tips of BNNHs prefer to stick together; this assembles the BNNHs into a flowerlike nanostructure. During TEM, the aggregation behavior was displayed more clearly, as shown in Fig. 1(c). The flowerlike structure is fairly tough and stable under various operations. For example, more than 80% of BNNHs are still assembling into the flowerlike morphology even after 30 min of sonication. This indicates the strong interactions and the formation of chemical bonds between the adjacent BNNH tips. The detailed structure of the two particular interacting BNNH tips was investigated by high-resolution TEM (HRTEM). The result is shown in Fig. 1(d). Two tips have independent BN graphiticlike layers. The structure may be sketched as a schematic shown in inset B (different from that shown in inset A). The observations suggest that the chemical bonding between tips forms after the formation of tips.

Different types of tips are shown in Fig. 2. Figure 2(a) is a BNNH with the tubular tip, the diameter of a five-walled BN tube is approximately 7 nm. Figure 2(b) is a BNNH with the triangular tip. Some transverse layers are found in the tip part of BNNHs, while the body of BNNH has a hollow struc-

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FIG. 1. (a) SEM image of as-grown BNNHs. (b) SEM image of flowerlike structures of BNNHs, the inset is an isolated "flower" formed by two BNNHs. (c) TEM image of BNNHs, the inset shows the aggregation of two BNNHs. (d) HRTEM image of the two interacting tips of BNNHs.

ture, as shown in Fig. 3. The wall thickness of the nanohorns is fairly uniform, always being approximately 20 nm, in spite of the marked difference in the BNNH sizes. The structure of a BNNH is not as perfect as a BN cone.¹¹ Varieties of disclinations appear in each BNNH. This is supposed to be induced by a nonlinear increase of the catalyst size during the growth. Inset A of Fig. 3 is a selected area electron diffraction pattern (SAED) obtained from the small tip area. A single disclination is indicated by the two BN₀₀₂ reflections separated by an angle, which is caused by the scattering from the two opposite sides of the horn's wall parallel to an incident electron beam. The BN₀₀₂ reflections become arcs when a larger tip area is selected, as shown in inset B, which indicates that several disclinations coexist within a single tip. Most disclination angles appear in the BNNH is in the range of 20°-40°.

The growth process of the BNNHs determines their resultant morphology and microstructure characteristics. The formation of BNNH can be explained in the frame of a vapor-liquid-solid mechanism.¹⁴ It is believed that Mg is a catalyst for the growth of BNNH. The growth is hampered very soon after the synthesis starts, because Mg is quickly

FIG. 2. (a) Tubular tip and (b) triangular tip of a BNNH.

oxidized to a solid MgO (the melting point of MgO is approximately 2800 °C, while the temperature in the growth area is less than 1700 °C) and then loses its catalytic activity. This results in the short lengths of BNNH. As the ambient temperature decreases dramatically, when the BNNHs escape from a crucible with a vapor flow, a Mg drop enlarges due to the aggregation and the dimensions of a BNNH's bottom increase accordingly. The simultaneous growth of a nanostructure and a catalytic particle leads to the formation of a horn-shaped structure. The tips of BNNHs are prone to numerous defects and dangling bonds.¹² They are apt to bond with each other to finally form a flowerlike structure.

CL measurements are performed using a field emission SEM. The spectra obtained from two different sites of the sample are shown in Fig. 4. Both of the spectra are collected from several BNNHs, which are dominated by peak at 410 and 436 nm, which corresponds to 3.0 eV and 2.8 eV, respectively. The electronic structure of BNNH has been investigated in some theoretical works.^{15,16} The highest occupiedlowest unoccupied molecular orbital gap of B₃₁N₃₁ nanohorn was given to be 0.8 eV by molecular orbital calculation,¹⁵ while a more reasonable band gap at around 3.0 eV is given by density function theory calculation.¹⁶ Since BNNTs have a constant band gap independent of their geometrical properties, the variable CL peak position for different BNNHs is thought to be induced by variable impurities, defects, or B and N vacancies in each BNNH. The CL peaks of BNNTs are centered around 3.3 eV,^{17,18} which is attributed to defects, or B or/and N vacancies. So, a similar band structure is expected for BNNHs and BNNTs.

In summary, BNNHs have been synthesized in large scale. The yield during a single experimental run may reach several tens of milligrams. The tips of BNNHs prefer to stick together to organize BNNHs as a flowerlike structure. A typical BNNH has a conical hollow structure and several bridging layers are found in its tip parts. Ultraviolet light emission is observed when BNNHs are excited by electrons, which indicated BNNHs may have applications in optical devices.

FIG. 3. TEM image of a single BNNH. The insets A and B are SAED patterns taken from a small area and a large area of the BNNH tip, respectively.

Also, it is believed that BNNHs can be used as a field emission source, if they can be adequately dispersed to form a film. In fact, both the horn tip areas and structural defects within BNNHs can work as effective electron sources. In addition, after tip-end catalyst particles are removed, the bottom of a BNNH can be open to accept foreign atoms. This

FIG. 4. CL spectra of BNNHs obtained from different sites of the sample. Both of them are collected from several BNNHs. The spectra are shifted vertically.

gives the possibility for the prospective usage of BNNHs as hydrogen (or lithium) storage medium.

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