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Effective growth of boron nitride nanotubes

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Abstract

An effective route of growing boron nitride nanotubes was developed. By reacting boron, silica and iron oxide catalysts supported on alumina, gas-phase reactants and liquid-phase catalyst could be generated in-situ. When ammonia was then introduced, boron nitride nanotubes could be formed by the reaction of boron oxide and ammonia inside the liquid-phase catalysts. The synthesized boron nitride nanotubes are highly-crystallized and multi-walled structures with 10–30 nm in diameter. The growth process was explained based on vapor–liquid–solid wire-like growth mechanism. © 2002 Published by Elsevier Science B.V.

1. Introduction

Original theoretical studies predict that pure boron nitride (BN) nanotubes are energetically stable in geometry and, in electronic properties, are semiconductors with a uniform large bandgap regardless of the radius and chirality, or the number of walls of the tubes [1]. The characteristic contrasts markedly with the heterogeneity of carbon nanotubes [2], for which electronic properties range from metallic to semiconducting depending on the diameter and chirality. BN nanotubes have been fabricated by different techniques, such as arc-discharge, laser ablation, carbon nanotubes template-confinement and some specifically de-

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signed methods [3–9]. Unfortunately, these methods have not been effective for synthesizing bulk BN nanotubes; for example, when considering the insulating nature of boron nitride for arc-discharge technique, low vapor pressure for laser ablation and carbon contamination for templateconfined methods. Very recently, a hazardous procedure of producing high-yield BN nanotubes via chemical vapor deposition of the precursor borazine on nickel boride catalysts has been reported [10]. So far there is no reliable method to produce bulk quantities of BN nanotubes and therefore, the exploration on its synthesis is still a challenging subject.

Crystal growth of one-dimensional structure requires a pathway to continuously provide gas- or liquid-phase reactants in a specified site, in which an anisotropic driving force exists to assure an oriented growth [11,12]. When gas reactants and

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liquid impurity (catalyst) are used, the vapor–liquid–solid (VLS) growth mechanism is responsible for the synthesis of wire-like structure. The mechanism was first proposed by Wagner and Ellis in 1960s for synthesizing Si whisker [13]. Morales and Lieber synthesized Si and Ge nanowires by combining laser ablation and a vapor–liquid–solid method [14]. This technique can produce nanoscale liquid catalysts, which finally determine the diameter of the final nanowires. Now it is commonly accepted that these factors, the formation and activity of the ultra-fine liquid catalyst, the absorption of the reacted gas, and the nucleation and crystallization growth inside liquid catalyst, play a crucial role in synthesizing nanowires.

Recently, for growing nanowire-like structure, we developed a simple and reliable technique named as in-situ silica-assisted catalytic growth method within the framework of VLS mechanism. The method involved the in-situ formations of reacting gases and catalysts being in liquid phase, and turned out to be an effective procedure for synthesizing some oxide nanowires and gallium nitride nanowires [15,16]. We believe that it could also be used to synthesize BN nanotubes by rationally choosing reaction routes. Indeed, here BN nanotubes are successfully produced on a large scale, by heating the mixture of boron, silica and iron oxide catalyst supported on Al_2O_3 under ammonia gas.

2. Experiments

The catalyst was prepared by impregnating, then stirring and drying the appropriate amount ferric nitrate and fumed alumina with methanol solution. The size of Fe₂O₃ catalysts are about 10 to 20 nm. Amorphous boron and silica powers with molar ratio of 1:1 were thoroughly mixed and homogenized with the pre-synthesized Fe₂O₃ catalyst. About 500 mg of the mixture was placed in a quartz tube mounted in a tube furnace. An argon flow passed through the quartz tube as the furnace was heated to reach 1080 °C, and then was shut off and pure ammonia gas was introduced at a flow rate of 80 standard cubic centimeters per minute and lasted for 1 h. After cooled to room temperature in argon atmosphere, a gray product can be obtained. The product was washed with diluted hydrofluoric acid (1M) and then filtered for several times to remove the residual silica. About 100 mg of the product after purification could be obtained. However, this purification procedure could not fully remove the impurities remnant in the final product. The remnant composition was identified as the mixture of silica, alumina and BN by X-ray diffraction analysis.

The product was checked by scanning electron microscopy (SEM, JEM-6301F) and transmission electron microscopy (TEM, JEOL-2010F) with energy dispersive spectrometry system (EDS) and electron energy loss spectrometer (EELS).

3. Results and discussion

SEM examinations indicate that a one-dimensional structure has been synthesized, although some silica, alumina and BN impurities with the grain morphology coexist in the sample. However, one-dimensional BN is dominant and its volume percentage was estimated to be higher than 80%.

TEM image of the product shows that the onedimensional structure exhibits the straight nanotube-like morphology with 10 to 30 nm in diameter and several micrometers in length (Fig. 1a). A high-resolution TEM image from individual nanotube further shows that the nanotubes are highly crystallized in a multi-walled structure with the layer spacing of 0.34 nm (Fig. 1a, inset). The interlayer space is consistent with the interplanar distance of 0.333 nm in bulk graphite-like BN. EELS quantitative analysis allows us to determine the chemical compositions of the synthesized nanotubes and shows that they only contain B and N with B:N ratio of 1.05 ± 0.10 , as shown in Fig. 1b. EDS measurement for the part of BN nanotube with pure tube-like structure indicates that no contamination from silica, iron oxide and alumina was observed (Fig. 1c).

Beside BN nanotubes with hollow structure, some BN nano-bamboos could also be occasionally observed from the TEM images. A typical morphology of the bamboo structures was shown in Fig. 2, which also exhibit a crystallized structure



Fig. 1. (a) TEM image of the BN nanotubes synthesized by insitu silica-assisted catalytic growth method, and a high-resolution TEM image from individual nanotube shown in the inset. (b) Typical EELS determining the chemical compositions of the synthesized nanotubes only containing B and N with B:N ratio of 1.05. (c) EDS spectrum of BN nanotube with pure hollowlike structure.

with 40 to 60 nm in diameter. These bamboos usually grow directly from the solid grains that are comprised of boron, silicon and iron oxides, as identified by EDS analysis. The morphology is similar to the BN filaments synthesized by nitriding borides [17].

In addition, TEM images show that BN nanotubes have a closed circle tip at one end of the nanotubes and terminate at another end in a nanoparticle. Although having the nearly same outer and inner diameters at most parts of an individual nanotube, the synthesized BN nanotubes usually exhibit discontinuous or variable diameters near their closed tips and the nanoparticles. A gradually decreasing tendency of the tube diameter near the closed tips could be observed, as shown in Fig. 3. The existence of such unstable growth indicates that the growth of BN nanotubes might go through a non-equilibrium process, especially at the beginning and ending of nanotubes growth.

Usually, two different morphologies of nanoparticles can be found from TEM images on the tips of most nanotubes. One of the nanoparticle exhibits the elongated fillings inside the nanotube channels, as labeled in arrows in Fig. 1a, and the circular particles encapsulated at the tip ends shown in Fig. 4a. EDS analysis shows that they contain only Fe and Si, and no Al content was detected. Fig. 4b shows another nanoparticle with irregular shape, which closely attaches on the supported alumina and becomes a starting point of



Fig. 2. TEM image of the BN nano-bamboo.



Fig. 3. TEM image showing the gradually decreasing diameter of BN nanotubes near the closed tips (arrows).



Fig. 4. (a) TEM image of the nanoparticles closely attached on the supported alumina. (b) Another type of nanoparticles wrapped into the BN nanotubes.

the BN nanotube growth. EDS analysis indicates that the irregular pillar is the Al_2O_3 used to support the catalyst, whereas the nanoparticle contains Fe and Si. In addition, our EDS observations for these nanoparticles show that and the molar rates of Si and Fe are variable. These characteristics of nanoparticles indicate that these BN nanotubes were produced by a VLS growth mechanism.

We will ascribe the in-situ silica-assisted catalytic growth method to a VLS growth mechanism to explain the large-scale growth of BN nanotubes. First, our method takes into account of the distribution of the reacting vapors concentration. Due to the involved redox reaction between boron and oxides (SiO_2, Fe_2O_3) , the in-situ generation of boron oxide gas $(B_2O_2 \text{ or } B_2O_3)$ could be expected. The method to produce the reactant gas guarantees enough concentration of boron oxide atmosphere in the reaction area. Therefore, when ammonia was introduced, the continuous BN crystal growth could be achieved. Second, we consider the catalytic activities of the Fe₂O₃ catalyst. The high-temperature interaction of the Fe₂O₃ catalyst and its support Al₂O₃ will reduce iron catalytic effect and therefore, a low reaction temperature is needed. However, VLS growth requires a liquid-phase iron and consequently a high reaction temperature. In our experiment, with the addition of SiO_2 , the temperature can effectively be mediated to reach a specific range, in which a liquid-state catalyst exists and catalytic activity preserves. Under reducing atmosphere (boron and ammonia), silica is reduced to silicon and then it alloys with iron to form a low melting point FeSi_x phase [18]. The observations of the nanoparticles with variable ratio of iron and silicon indicate that the composition of the liquid nanoparticles should be $\text{FeSi}_2 + \text{Fe}$ or $\text{FeSi}_2 + \text{Si}$. Moreover, the melting point of nanoscale iron is lower than the corresponding bulk solid [19], therefore, we believe that at our experimental temperature the catalyst should be in liquid state.

Due to the existence of high Si content in raw reactants, Si might occur in the final product as an impurity. Indeed, except silica of incompletely reacted, we also observed another Si structure from the TEM image and with EDS analysis. It is amorphous Si nanowires with the variable diameters and lengths up to several microns (Fig. 5). Usually the Si nanowires have a slightly larger diameter than BN nanotubes and shows a curved morphology. We also noticed the recent reports on the synthesis of the Si nanowires by oxide-assisted method; therein Si nanowires can be obtained by the direct sublimation of SiO gas at about 1200 °C [20]. Therefore, we believe that SiO also appears near the reaction area due to the reaction of silica with boron or ammonia.

We performed further experiments in order to confirm the above assumptions on the BN nanotubes growth. When ammonia is reacted with a



Fig. 5. Amorphous Si nanowires existing in the BN nanotubes (arrows).

mixture of boron and iron powder with the size of about 1 µm at the temperatures from 1000 to 1400 °C, no BN nanotubes were produced. However, if we introduced enough iron oxide rather than the used iron powder, BN nanotubes and filaments with a low yield and wide diameter distribution can be observed from the TEM examinations. The synthesized temperature must be higher than 1300 °C. The experiments of some direct chemical reactions of boron with Fe₂O₃ supported on Al₂O₃ have been also carried out and no BN nanotubes were found when a low amount of the catalyst was used, although BN nanotubes with low yield can be obtained at the temperature higher than 1300 °C when the excess catalyst was used. Therefore we believe that the in-situ formation of oxide atmosphere containing boron is the key to synthesize BN nanotubes. Indeed, when heating the mixture of boron, silica and the catalyst only under argon atmosphere, thermogravimetric analysis indicates that the formation of gas-phase products begins at 1050 °C and ends after 1130 °C.

The above described method suggests that two conditions, in-situ formation of reacting gas and VLS catalyst being in liquid state, are essential for BN nanotubes growth on a large scale. Nanometric Fe_2O_3 catalysts supported on alumina are responsible for the diameters of the products of BN nanotubes.

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