High-yield Boron Nitride Bamboo Nanotubes

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High-yield bamboo-like boron nitride nanotubes (BBNNTs) were synthesized using a ball-milling and annealing method. Amorphous boron powder was first ball milled at room temperature in a planetary ball mill for 50 hrs in ammonia atmosphere, and then the resultant was heated in a tube furnace in nitrogen gas flow at 1100°C to grow nanotubes. The milling process introduced nanosized iron particles into the boron powder, which played a critical, catalytic role in the growth of BBNNTs as revealed by TEM observation. The associated growth model is proposed in this paper.

1. Introduction

Boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are isostructural. Different sizes and electronegativities between boron and nitrogen endow BNNTs with many distinctive properties, such as semiconductive property [1], better oxidization resistance [2] and piezoelectric property [3]. All these promising properties lead to a great potential for BNNTs to be used as a fundamental component to construct various functional devices. For instance, the BBNNTs are proposed to have an important hydrogen storage capability. Evidently, it is crucial to explore high yield BNNTs for further property and application studies.

The longest single wall carbon nanotube has been reported to reach 4-cm in length [4]. Comparing with CNTs, the BNNTs are more difficult to be fabricated in a high yield and a long length, because multi-elements and a higher annealing temperature are required. So far, probably only two synthesis methods could provide high-yield and pure BNNTs, which are ball-milling and annealing process [5] and induction heating method [6]. Especially, the first method can produce a big batch commercial BNNTs sample. Here we report the synthesis of high-yield, pure BBNNTs by the ball-milling and annealing process. The associated growth model is proposed and discussed as well.

2. Synthesis of BBNNTs

The ball-milling and annealing process was used to produce BBNNTs in this work. The starting material was amorphous boron (95%, Aldrich), which was treated by milling in a planetary mill (Pulverisette 5) for 50 hrs in ammonia atmosphere. In this process, the boron powder was contaminated by iron and chromium particles from milling balls and container. They could actually act as catalyst and benefit the growth of BNNTs. The precursor obtained was loaded into an alumina crucible and placed into a tube furnace. The annealing temperature was determined by thermogravimetric analyser (TGA, Shimadzu 50). The most accelerated point of nitriding reaction of boron is at 1100°C. This temperature was thus chosen as the annealing temperature. Annealing process was carried out under N_2 gas flow at 1100°C for 10 hrs.

The structure and morphology of BNNTs were characterized using X-ray powder diffraction (XRD, Philips 3020), field emission scanning electron microscope (FESEM, Hitachi 4500), and transmission electron microscope (TEM, Philips CM300).

3. Results and Discussion

Fig. 1a represents a low magnification FESEM image of as-synthesized BNNTs, showing clearly the formation of high yield BNNTs. The BNNTs have a bamboo-like shape and a narrow diameter range as shown in Fig. 1b. Again, it is more apparent to show the BBNNTs have a variable diameter along the tube. Since the ratio of length to diameter of BNNTs is too large, it is impossible to display the whole image using one photo. Fig. 2 gives the TEM images of these BBNNTs. The iron particle is identified by selected area electron diffraction pattern (see insert diffraction pattern in Fig. 2). The upper insert image shows the clear bamboo structure of the BNNTs at the nodes connect part, which will be explained in the growth mechanism below.

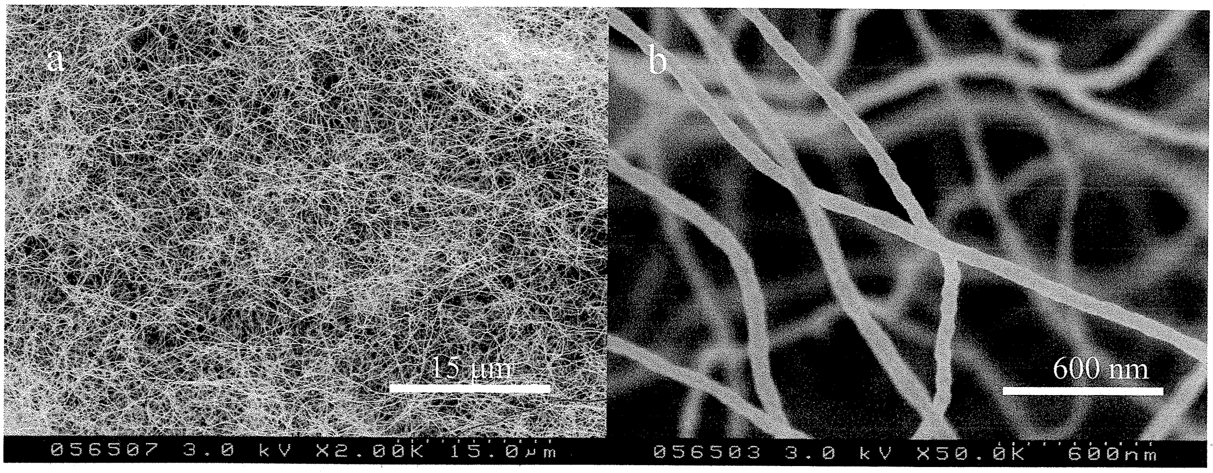

Figure 1 FESEM images of the BNNTs obtained. (a) the low-magnification image showing a high density and purity of BNNTs; (b) the high-magnification image showing the uniform diameter of the tubes and the typical bamboo shape.

The BN phase was determined by XRD and a broad BN (002) peak is a distinctive feature of BNNTs.

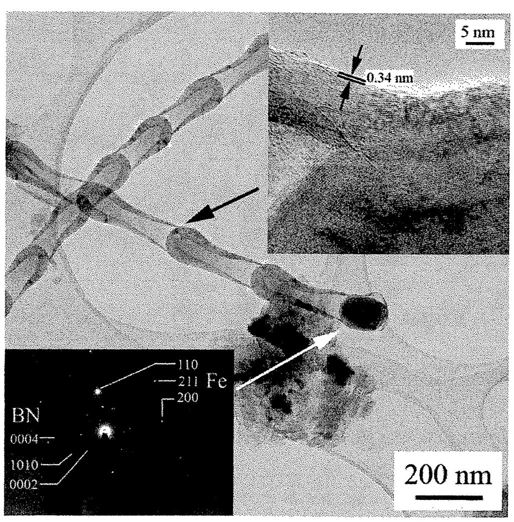

Figure 2 TEM images of BBNNTs

Based on SEM and TEM observations, a BBNNTs growth model is proposed. Vapor-liquid-solid (VLS) model generally is suitable for the growth of BNNTs at high temperature at which boron vapor is generated. It is a "top-based" growth model where the iron catalyst can be found in the top of tubes. In the current case, the synthesis temperature is relatively low, and boron vapor pressure is too low to provide enough boron to grow BNNTs via a pure VLS model. In fact, boron may be absorbed by the iron through solid state diffusion and as a result, the iron particles are encapsulated in the root of nanotubes, corresponding to a "base-growth" mechanism. This suggests that two growth mechanisms might co-exist in BNNTs obtained by this process.

Figure 3 is a schematic drawing of the

growth process of the BNNTs. Iron nanoparticles are first dispersed homogeneously in amorphous boron during the ball-milling process. They become quasi-spherical catalyst particles during annealing owing to melting of iron. And then boron atoms diffuse into iron particles whilst the N_2 is decomposed to the N atoms on the surface of the catalyst particle and also diffuse in to the catalysts (see Fig. 3a). When the B and N reach to a certain amount, the BN is produced. When the BN species are supersaturated, they precipitate layer by layer to form of BN shells as described in Fig. 3b. The BN layers grow up from the interface between the catalyst and BN shells, the outer layer at two ends become stressful, afterwards, the outer layers break one by one at the ends. The curvature of the inner layers increases and sucks the catalyst particle into the nanotube by the capillary action of the nanotube (see Fig.3c). The particle sucked to the tube (see Fig. 3d) results in the transportation of boron and nitrogen source because the contact area with the boron powder and nitrogen deceases in this reaction, which leads to an increase of the surface tension of the catalyst particle, and the sucked part pulls back by the surface tension. When the catalyst particle is fully pulled back to the quasi-spherical shape, one node of the bamboo is formed (see Fig. 3e). And finally, the bamboo-like tube can grow up through repeating the above process (see Fig. 3f and 3g). Insert in Fig.3 shows a real tube tip as described in this model.

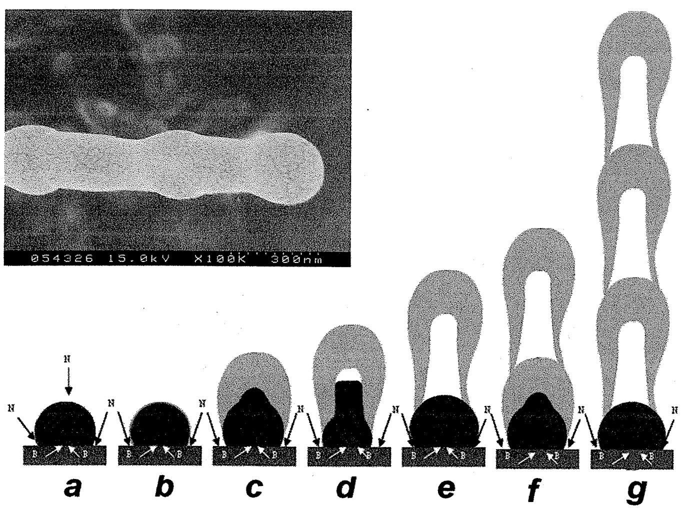

Figure 3 Growth model of high yield bamboo-like BNNTs. Insert is a real nanotube tip.

Conclusions

High-yield pure BBNNTs were successfully synthesized using a ball-milling and annealing method. The growth model in this case comprises both VLS and solid diffusion. The obtained pure BBNNTs with a high quality and high yield provide a great possibility to further explore their genuine physical properties and practical applications, which are under taken.

References

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