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Original article

Synthesis of boron nitride nanotube films with a nanoparticle catalyst

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ABSTRACT

Boron nitride nanotube (BNNT) films were synthesized by combining ball milling and thermal chemical vapor deposition (CVD) using nano-Fe_3O_4 as a catalyst. The as-produced BNNTs have a bamboo-like structure and have a diameter in the range of 50∼200 nm with an average length of more than 40 μm. Moreover, BNNT nanojunction structures were synthesized. The structure and morphology of the BNNTs were characterized by XRD, SEM, TEM and HRTEM. The possible growth mechanism of BNNTs and BNNT nanojunction structures were proposed. Though the BNNT films were observed, out of our expectation, BNNTs with thin tube wall and small average diameter have not been achieved, and this could be mainly ascribed to the aggregation of the nanoparticle catalyst, resulting in greater catalyst particles during the process of BNNT growth. This result will provide a promising approach to obtain the desired shape of BNNTs and produce branched junctions of BNNTs.

1. Introduction

Since Rubio theoretically predicated the existence of the stable boron nitride nanotubes (BNNTs) in 1994 [1], BNNTs have attracted extensive attention because of their superior mechanical properties, excellent thermal stability and chemical stability, which make them a promising candidate in a wide range of applications [2–4]. Several methods have been used to produce BNNTs, such as laser ablation [5,6], substitution reactions [7,8], chemical vapor deposition (CVD) [9–12] and ball milling [13,14]. Moreover, the mixtures of iron oxide and other metal oxides, such as the mixture of MgO and FeO, the mixture of MgO and Fe_2O_3, have been used as catalysts under NH_3 atmosphere in recent research.

In this article, taking account of remarkable catalytic activity of nanoparticle catalysts, we investigated the growth of BNNT films using nano-Fe_3O_4 as a catalyst based on ball milling and thermal chemical vapor deposition under N_2 with 15% H_2 atmosphere, which is much safer than NH_3 atmosphere.

2. Experimental

A crystalline boron powder (B, 99%) as a raw material, was milled for 18 h at a rotating speed of 200 rpm in a horizontal-type high energy ball mill under N_2 atmosphere to enhance the reaction activity of the precursor. The balls with a diameter of 6 mm were used to smash and grind B powder. The weight ratio of hardness stainless steel ball to boron powder was 30:1. Then the milled B powder and nano-Fe_3O_4 (diameter: ∼20 nm) were dispersed into an ethanol solution to form B ink after 20 min ultrasonication. The mass ratio of the catalyst to B powder was 0.25:1. Then the ink was poured into an alumina sintering boat, and several stainless steel substrates were placed on the top of the alumina sintering boat. Moreover, the ink was also smeared on the upper surface of the stainless steels with a brush. The alumina boat covered with stainless steels was placed in a cylindrical crucible, and then was pushed into a tube furnace and annealed at 1150 °C for 1 h under N_2 with 15% H_2. After the furnace was cooled to room temperature naturally, white BNNT films can be found on both sides of the stainless steels.

The morphology and chemical composition of the as-synthesized BNNT films without purification were studied using X-ray diffraction (XRD, PANalytical Empyrean), scanning electron microscopy (SEM, Tescan VEGA 3 SBH) and energy dispersive X-ray spectroscopy (EDS, ThermoNORAN) attached to the SEM. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) investigations were performed using a JEOL JEM-2010 instrument.

3. Results and discussion

Fig. 1a presents the image of the as-synthesized BNNT film, showing a snow-white looking. The whole stainless steel substrate

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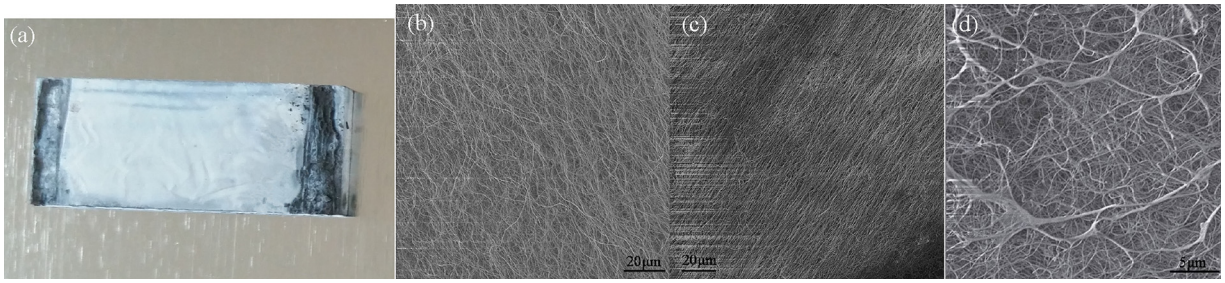

Fig. 1. Image of the as-synthesized BNNT film: (a) and the SEM images; (b) unordered films; (c) ordered films; (d) nanojunction structures.

with an area of 2 × 1 cm^2 is covered by BNNT film, confirming the synthesis of a mass of BNNTs. Fig. 2b–d present the SEM images of the as-synthesized BNNT films without purification. High-density and high-quality BNNT films were fulfilled without obvious impurity phases or particles. The as-produced BNNTs have a diameter in the range of 50~200 nm with an average length of more than 40 μm. Besides the morphology that BNNTs grew in random orientations as shown in Fig. 1b, BNNTs also were well-aligned in some regions (Fig. 1c), which could be a result of the direction of brushing ink and the gas flow [15,16]. In addition to the BNNTs in bulk quantities being obtained, two-dimensional BNNT nanojunction structures with various shapes, such as ringlike, Y type and treelike, were found as shown by the arrows in Fig. 1d. Moreover, almost all the nanojunction structures were observed on the surface of BNNT films. The generated nanojunctions made of nanotubes may have potential applications in nano devices, such as nano systems and nano circuits [17–19].

An EDS spectrum taken from the samples is shown in Fig. 2a. It clearly demonstrates that the dominant elements in the films are B (50.62%) and N (45.01%) with an atom ratio of approximating to 1:1, which shows the synthesis of BNNTs. O was found in the EDS profile, which is common in the synthesis of nano materials using CVD. The O may come from the oxidation of milled B powder.

Detailed microstructure characterizations of the BNNTs are illustrated in TEM images (Fig. 2b–f).TEM images reveal there are two types of bamboo BNNTs, which are similar to that of the BNNTs reported previously [20–22]. Both types of BNNTs possess multi-walled and spindle-like structures, in which all the spindles stretch along the same direction. The TEM image (Fig. 2c) of the first type BNNTs with short distance bamboo structures show that the BNNT owns a bended morphology, additionally, the bamboo at the bending point (indicated by arrow) is slightly longer compared to the other bamboos. The internal diameter of bamboo-like structures continuously and steeply varies from point to point, very similar to a spindle, while the outer diameter of BNNTs remains the same. They possess a larger diameter and thicker wall than the second type BNNTs shown in Fig. 2d. The second type BNNTs with long distance bamboo structures exhibit long spindle and the length of individual spindle is about 500 nm. The internal diameter of BNNTs remains almost the same, and only varies on the local sharp terminals. Owing to the accepted correlation between the catalyst size and nanotube diameter and the fact that reducing the catalyst size is found to decrease the final nanotube diameter [21,23,24], we argued that the difference of above mentioned two types of BNNTs is due to different aggregation degree of catalyst particles and agglomeration produces greater particles, increasing the nanotube diameter. Fig. 2e describes the high-resolution TEM (HRTEM) image of the tube wall segment of BNNT in Fig. 2d. The wall with a thickness of 20 nm is built up of layer-by-layer stacked BN graphite-like layers. The wall of BNNT

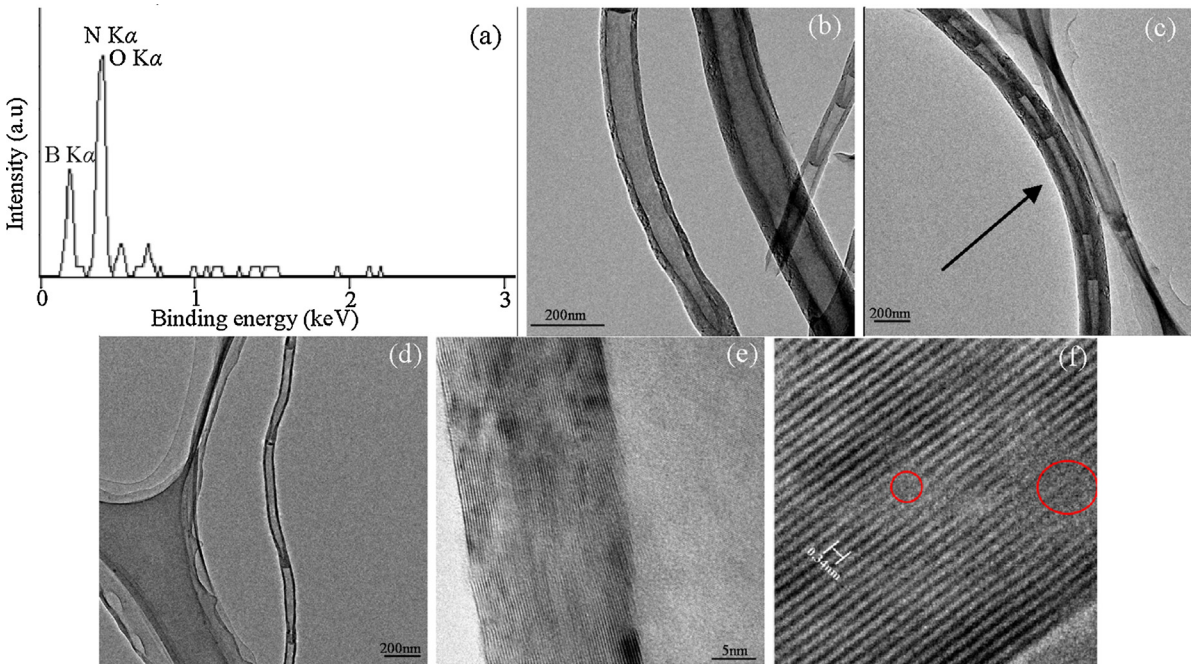

Fig. 2. EDS spectrum and TEM micrographs of as-synthesized BNNTs: (a) EDS spectrum; (b) TEM image of BNNTs; (c) TEM image of short bamboo structure; (d) TEM image of long bamboo structure; (e) and (f) HRTEM images.