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Insight into carbon nanotubes-template reaction at high temperature

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Abstract

Different types of carbon nanotubes (CNTs), including multi-walled CNTs, single-walled CNTs bundles, isolated single- or double-walled CNTs and nano-bamboo structured CNTs, were used as the templates to synthesize SiC and BN one-dimensional nanostructures within the framework of high-temperature CNTs-template reaction. We found that the structures of SiC and BN products weakly depend on the topology of the used CNTs. BN can completely maintain the starting topology of CNTs, while the hollow CNTs collapsed to SiC nanowires with solid interiors. The involved reaction mechanisms were discussed based on TEM observations for the products synthesized from the different reaction sources.

1. Introduction

Since carbon nanotubes (CNTs) were synthesized in bulk quantity, it has been suggested to decorate or convert CNTs into other one-dimensional nanomaterials. Various high-temperature CNTs-template reaction methods were thus proposed and used to synthesize one-dimensional tube- and wire-like materials containing or not the starting carbon element [1–14]. The initial impetus to the investigation of the reaction originates from a simple idea that CNTs might confine the chemical reaction in a local space around nanotubes [1,4]. From this sense, geometrical stability of the CNTs at high temperature should be a prerequisite to maintain one-dimensional structure of final product. The common route, via a chemical reaction between vapor (oxide or halide vapors) and solid (CNTs), has thus been widely used based on the shape-memory synthesis mechanism that the products would keep the shape of the starting nanotubes after reaction [7]. However, the mechanism can work well only to explain the one-dimensional topology of the final product. Although there's been some improvement, such as the proposal of two-step epitaxial growth model [3] and melting point effect [14], in the explanation of diameter and shape changes, the underlying mechanism of the morphology modification of CNTs during high-temperature chemical reactions remains a challenge.

A remarkable uncertainty appears to know which morphology the final product will exhibit after the high temperature CNTs reaction. Previous researches obtained solid SiC nanowires by reacting CNTs and SiO_x vapors [1,3,7], while hollow BN nanotubes are the final product when CNTs reacted with BO_x vapors in the presence of nitrogen [5,11,12]. The different morphology modifications to CNTs imply that there are other growth mechanisms during the CNTs-template reaction, in addition to shape-memory growth process.

In this work, we compared the morphology modifications of SiC nanowires and BN nanotubes synthesized by the high-temperature CNTs-template reactions, when

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different types of CNTs-templates were used. The growth details and possible mechanism were discussed.

2. Experimental

Four types of CNTs with different morphologies were used in this study, as shown in Fig. 1a–d: (a) Multi-walled CNTs having the uniform diameter distribution of 15 ± 5 nm were synthesized at 780 °C by catalytic decomposition of ethylene and hydrogen in a CVD system, $Fe_{1.5}Mo_{0.5}O_3$ nanoparticles supported on nano-scale Al_2O_3 were adopted as the CVD catalysts. High-resolution TEM examinations exhibit that the curved CNTs possess a great amount of defects in the tube walls [15]. (b) The purified high-pressure CO conversion (HiPCO) single-walled CNTs bundles with ~1 nm diameter between the imperfect walls were purchased from Carbon Nanotech. The bundle thickness ranges from several nm to 20 nm. No isolated single-walled CNTs can be found from the samples. (c) The isolated single- or double-walled CNTs of several nm in diameter were synthesized by methane decomposition in the presence of bimetallic Fe–Mo catalysts at 800 °C [16]. TEM investigations indicate that the product contains a great amount of the impurities such as metal catalysts and amorphous carbon particles. (d) Nano-bamboo-structured CNTs, having the diameter of 10–60 nm, were synthesized by catalytic pyrolysis of methane and ammonia at 800 °C [17].

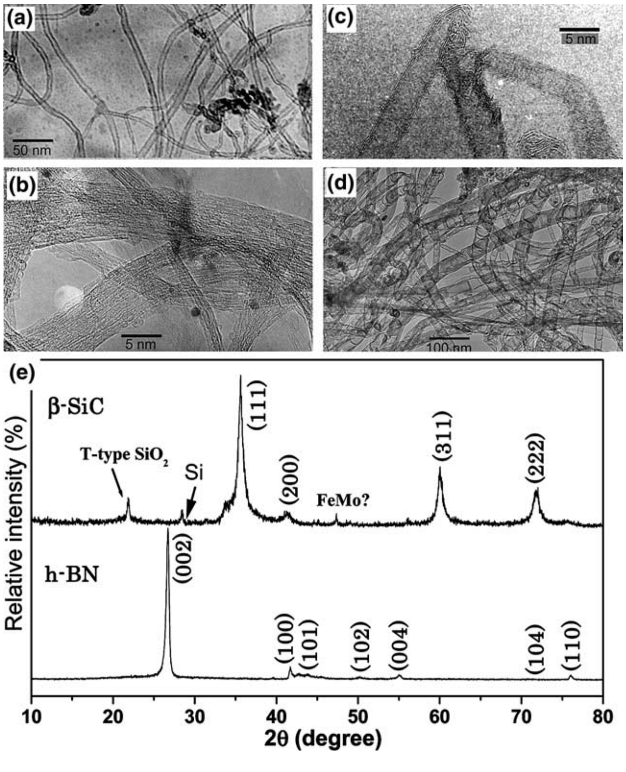

Fig. 1. TEM images of the starting carbon nanotubes used in this study: (a) multi-walled CNTs of 10–20 nm in diameter, showing a great amount of defects in the tube walls; (b) HiPCO single-walled CNTs bundles; (c) isolated double CNTs; (d) multi-walled tubular carbon nanofibers of 10–40 nm in diameter and doped with N content of ~5 at.%; (e) XRD patterns for the products through CNTs-template reaction, (top) cubic SiC synthesized by the reaction of nano-bamboo structured CNTs with SiO vapor; (bottom) hexagonal BN produced by the conversion of single-walled CNTs under N_2. The peak positions of SiC and BN are marked by their indices, respectively.

The following chemical reactions have been proposed for the conversion of CNTs via vapor–solid reactions, leading to the formation of SiC and BN crystals [1,3,7,4,11,18]:

$$SiO_2(s) + Si(s) \rightarrow 2SiO(g) \tag{1}$$

$$SiO(g) + C(s,\ CNTs) \rightarrow SiC(s) + CO(g) \tag{2}$$

$$B_2O_3(s,l) \rightarrow BO_x(g) \tag{3}$$

$$2BO_x(g) + 2xC(s,\ CNTs) + N_2(g) \rightarrow 2BN(s) + 2xCO(g) \tag{4}$$

The apparatus for CNTs-template reactions was same as that reported previously [4,5]. The vapor precursors (the mixture of SiO_2 and Si in molar ratio 1:1 or B_2O_3) were placed into a BN boat, and CNTs were kept clear of the precursors along the downstream direction of transport (Ar for SiC) or reaction (N_2 for BN) gas. The synthesis temperature was raised to 1450 °C within 15 min and reacted for 1 h.

Upon completing the reactions the collected products from the area that the starting CNTs located were identified by means of X-ray diffraction (XRD, D/max-rB, Cu Kα radiation) and transmission electron microscopy (TEM, JEM-2010F), equipped with a micro-analysis system of energy dispersive spectrometry (EDS) and an electron energy loss spectroscopy (EELS).

3. Results and discussion

XRD measurements for all the products indicate that, regardless of the morphologies, all the starting CNTs were converted into SiC or BN. No noticeable impurity peaks could be observed from the BN pattern; however, the crystalline SiO_2 and Si (and Fe/Mo-contained impurities when the used CNTs were synthesized by catalytic growth route) were obviously detected in all SiC products. Fig. 1e shows the typical XRD patterns mentioned above.

TEM examinations were used to further investigate the relationship between the morphologies of the final products and of the starting CNTs. The investigations clearly exhibited the considerably different morphology modifications with respect to BN and SiC one-dimensional materials after the CNTs-template reaction.

3.1. The reactions of multi-walled CNTs

Shown in Fig. 2a, are the collected TEM images of SiC crystals synthesized via the reaction of the SiO vapor with the multi-walled CNTs. The synthesized SiC crystals display the expected one-dimensional nanowires that are curved and twisted around each other, similar as the starting CNTs. However, the starting hollow structures of CNTs completely collapsed to the coarse solid nanowires with the diameter distribution ranging from ∼20 to ∼40 nm. The increasing diameter with respect to the start CNTs has been explained according to an epitaxial post-growth on the surface of as-grown SiC nanowires, and the involved chemical reaction results from the reaction between SiO and CO gas byproduct as follow [3,7]:

$$SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g) \qquad (5)$$

High-resolution TEM images exhibit that the SiC nanowires are composed of the nanocrystals with the different crystalline orientations. No determinable axial growth direction for single SiC nanowire can be obtained. This indicates that the formation of SiC nanowires starts from some defects points, especially from the end of CNTs because there are the highest densities of defects. Occasionally the observed heterostructues made of a SiC nanowire and an un-reacted CNT, marked by arrows in Fig. 3a, further confirm the multi-points growth model of CNTs-template chemical reactions.

However, considerably different with the SiC nanowires, BN crystals display a nanotube-like morphology with the diameters from several nm to ∼50 nm, as shown in Fig. 2b. Although the BN nanotubes have the similar hollow structure as the starting CNTs, the curved wall of the starting CNTs were converted into a well-arranged shell after the reaction and therefore, the BN nanotubes exhibit a straight outer surface. Considering the oxygen occurrence from the high-temperature evaporation of B_2O_3, the diameter of the starting CNTs-template might be reduced due to the surface chemical peeling as follow:

$$O_2 + 2C(s,\ CNTs) \rightarrow 2CO(g) \qquad (6)$$

Therefore, some BN nanotubes with the diameter smaller than that of the starting CNTs could be found from the product. The increasing diameter of BN nanotubes might also be explained based on the epitaxial growth on the surface of as-formed BN nanotubes, like SiC case

$$B_2O_3(g) + 3CO(g) + N_2 \rightarrow 2BN(s) + 3CO_2(g) \qquad (7)$$

Another characteristic of the BN nanotubes produced in the experiment is the flat-structured tip end, obviously different to the semi-sphere ending of the CNTs. This suggests a self-assembly process during the growth of BN nanotubes because the flat-tip closure at the end of the BN nanotubes is energetically preferable [19].

3.2. The reactions of single-walled CNTs bundles

The tube-like morphology of the single-walled CNTs bundles still collapsed into nanowires composed of nanocrystals when reacting CNTs with SiO vapor at high temperature (Fig. 3a). Slightly unlike the SiC

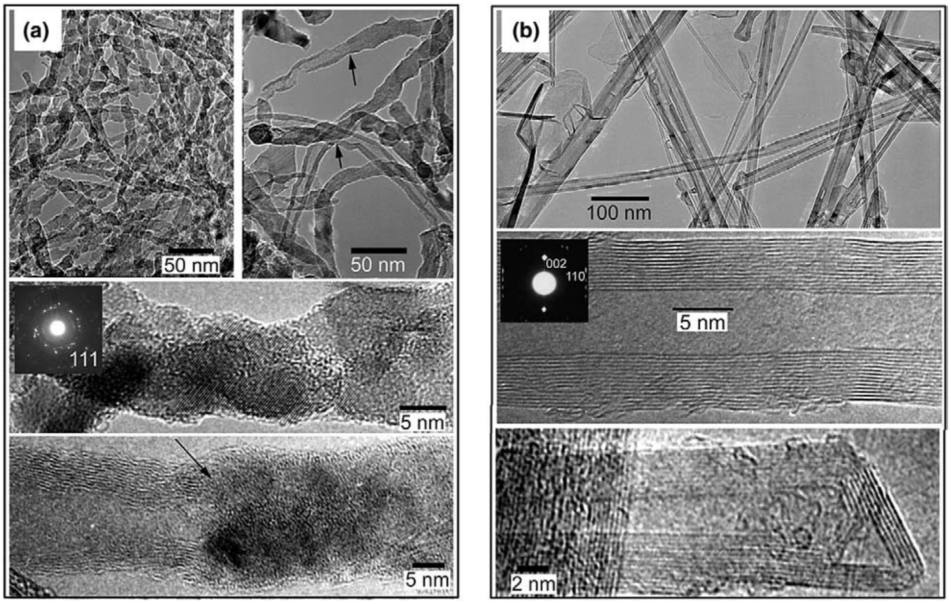

Fig. 2. Comparative TEM images of SiC nanowires (a) and BN nanotubes (b), both synthesized via the reactions of multi-walled CNTs at the same temperature.

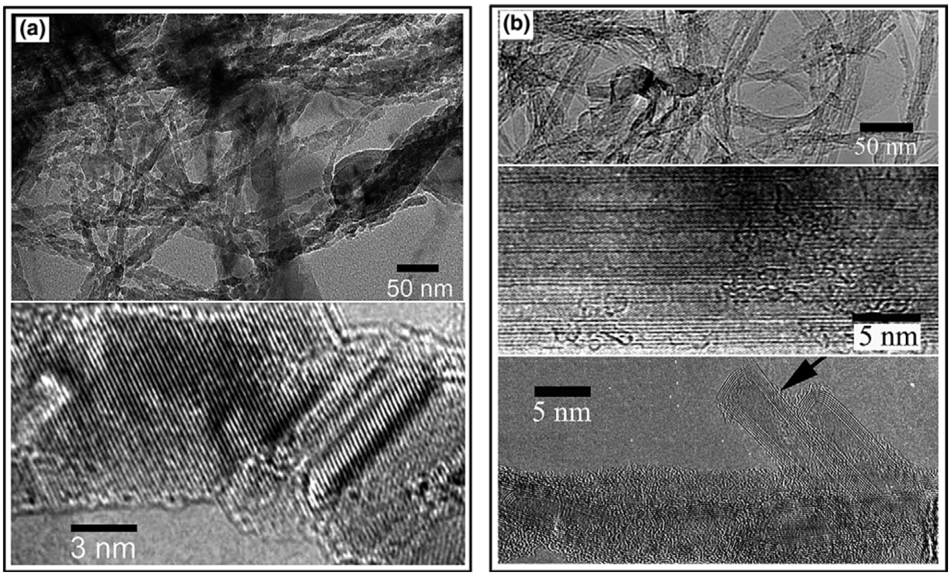

Fig. 3. Comparative investigation of TEM images of SiC nanowires and BN nanotubes synthesized by the high-temperature reactions of single-walled CNTs bundles.

nanowires from multi-walled CNTs, the nanowires discussed here exhibit a normal axial growth along $\langle 1\ 1\ 1\rangle$ direction though the nanowires contain a great amount of stacking faults, as shown in the high-resolution TEM image.

Shown in Fig. 3b, are the collected TEM images of BN products synthesized through the single-walled CNTs bundles reaction. The products still exhibit the nanotubes-like morphology with the diameters similar to the thickness of CNTs bundles. This diameter-changing tendency of BN nanotubes is in agreement with that of SiC nanowires synthesized using the same C source, and can still be explained based on post-epitaxial growth mechanism mentioned above.

Noticeable structure modification is the considerably straight BN wall shell, compared to the used CNTs. Even so, although the starting topology of some starting single-walled CNTs kept unchanged, the BN nanotubes with a few of wall shells were most commonly observed. As shown in the high-resolution TEM image, 3–7 layers of BN nanotubes with the inner diameters of ~5 nm obviously grow from the same single-walled CNTs bundle. The observed multi-walled morphology and the marked flat-tip ending (labeled by arrow in Fig. 3b) indicate a self-assembly process during the high-temperature reaction, which single-wall CNTs are converted into multi-walled BN nanotubes.

3.3. The reactions of isolated double-walled CNTs

Fig. 4 shows the typical TEM images of SiC nanowires and BN nanotubes synthesized by the reactions between the isolated single- or double-walled CNTs and the SiO and BO_x vapors, respectively. Because the starting reactant dominantly contains amorphous carbon particles, the main products after the reactions are SiC or BN particles (Fig. 4a). Like the topology of SiC nanowires mentioned above, one-dimension SiC still are solid wires. The diameters of SiC nanowires are relatively uniform ~10 nm (Fig. 4b), which is larger than that of the starting CNTs. The BN nanotubes still

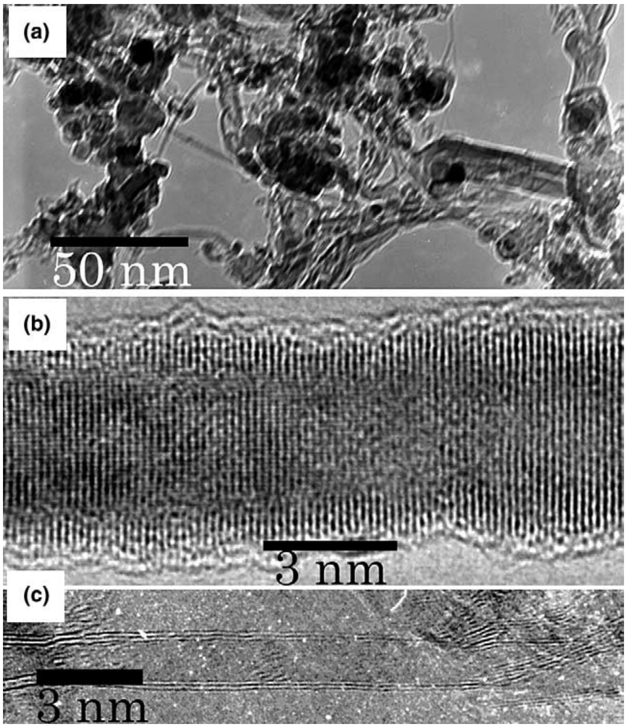

Fig. 4. SiC nanowires (a,b) and BN nanotubes (c) synthesized by the double-walled CNTs reaction with SiO and BO_x vapors, respectively.

exhibit a tube-like topology. No obvious diameter change can be observed from the synthesized nanotubes, as shown in Fig. 4c.

3.4. The reactions of nano-bamboo structured CNTs

When nano-bamboo structured CNTs reacted with SiO vapors, we found an interesting morphology modification of SiC nanowires. Shown in Fig. 5a are the collected TEM images of the synthesized SiC nanowires, indicating an evident diameter-dependent effect. The starting CNTs with the diameter smaller than ~30 nm were converted to the SiC nanowires with rough surface, a similar morphology modification discussed above. However, we frequently observed some SiC nano-bamboos structures with the diameter larger than ~30 nm. High-resolution TEM examinations indicate that the bamboo-structured SiC consists of the micro-crystals with the different crystalline orientations. It is the first time for us to observe the hollow morphology in good preservation of the starting CNTs.

However, the synthesized BN nanotubes well preserve the starting bamboo structure. TEM images shown in Fig. 5b, established that the nanostructures are straight nanotubes with internal wall closures or internal cap structures. Two types of the internal endings were observed by high resolution TEM. The commonly observed internal endings have the topology that the inner diameter of nanotubes gradually decreases until an internally closed segment occurs. Such closure morphology has been reported by BN nanotubes synthesized by chemical reaction methods [20], wherein the diameters of BN nanotubes are usually large. Another internal closure exhibits a coaxial growth appearance, that is, the inner nanotube grows inside the outer nanotubes to form the internal closure. EELS measurements for these internal closure areas usually exhibits a considerable amount of C remnants (C/BN molar ratio: 10–50%). Although the measured values of C concentration are dispersive, the coaxial closures usually have the lower C residence.

3.5. Discussion on high-temperature CNTs-template reaction

The present comparative study on the SiC nanowires and BN nanotubes synthesized within the framework of high-temperature CNTs-template reactions clearly indicate that the intrinsic energy favorable growth of the final product plays a crucial role in determining the hollow nanotubes and solid nanowires. Although SiC hollow bamboos can be synthesized from the bamboo-structured CNTs with large diameters, it is considerably difficult to obtain hollow SiC nanotubes by the reaction of CNTs with SiO vapors. In contrary to SiC, the BN crystals synthesized via the similar routes usually have the hollow one-dimensional structure, independent on the CNTs diameter. This happen because the sp^2 hybridized CNTs and sp^3 hybridized SiC possess completely

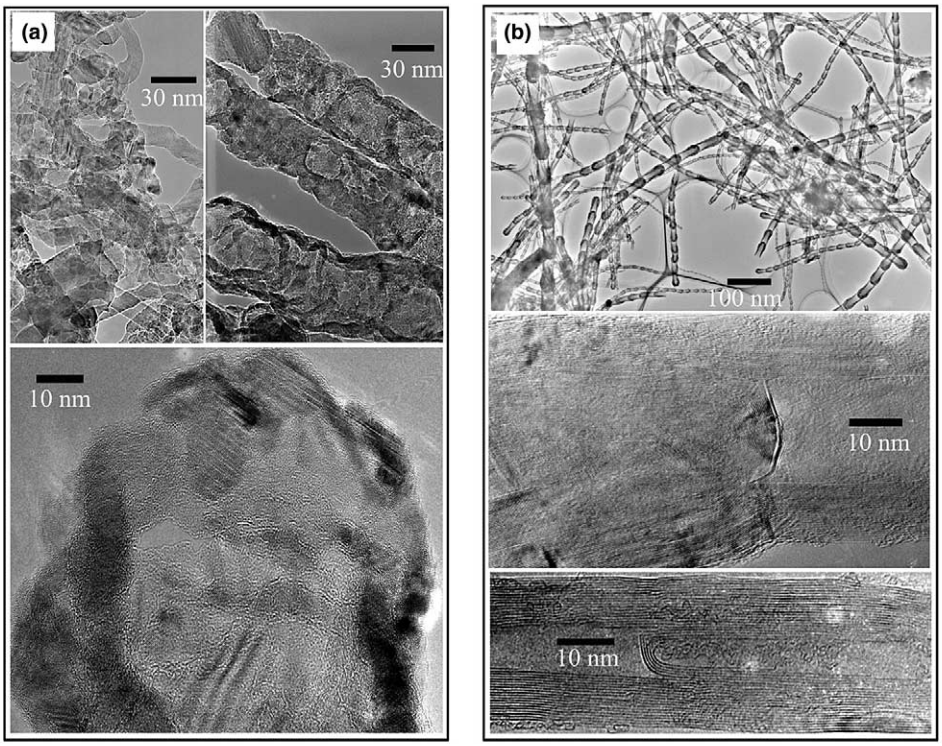

Fig. 5. Comparative TEM investigations for SiC nanowires and BN nanotubes synthesized by the reaction between CN_x nano-bamboos and SiO and BO_x vapors, respectively.

different bonding characteristics, while BN is the bonding similarity of graphite. Starting from a defect point, the sp^2 real nature of layered materials is prone to make linear or planar growth while SiC prefers three-dimensional growth. SiC nanotubes is considerably unstable in hollow structure. Our experimental results are in agreement with the recent ab initio calculations for silicon-rich CNTs [21].

Although the intrinsic energy-modulated growth proposal can explain the different morphologies of solid SiC nanowires and hollow BN nanotubes, the formation of the micro-crystals structured SiC nano-bamboos with larger diameters implies that SiC nanotubes with larger diameters can be synthesized, although the theoretical calculations and experiment investigations are still lack. Very obviously, now shape memory process does take effect in the formation of SiC nanotubes.

4. Summary

In this study, we have studied the syntheses and morphologies of one-dimension structured BN and SiC by the high-temperature CNTs-template reactions. We found that the structure of SiC and BN products weakly depends on the topology of the used CNTs, although the diameter, curvature and crystallization of SiC and BN slightly change with those of the starting CNTs. BN can completely maintain the starting topology of CNTs, while the hollow CNTs collapsed to SiC nanowires with solid interiors when reacted with SiO vapors.

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