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Straight boron carbide nanorods prepared from carbon nanotubes

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Boron carbide nanorods were prepared on a large scale directly from the reaction of carbon nanotubes with boron powder at 1150 °C. The bent carbon nanotubes transform into straight nanorods during the reaction. The atomic ratio of B to C in the nanorods is very close to 4 : 1, corresponding to the compound B_4C. Carbon nanotubes act here as templates at the beginning of the formation and as a carbon source for the growth of the boron carbide nanorods.

I. Introduction

Since the discovery of carbon nanotubes[1] (CNTs), many researchers have paid great attention to the synthesis and properties of similar one-dimension materials, such as BN nanotubes[2–5] and B–C–N nanotubes.[6] These nanotubes or nanowires are of unique structure and electronic properties.[7–9] For instance, Wei *et al.*[10] investigated electrical transport in boron-doped carbon nanotubes and found that boron-doped carbon nanotubes have lower resistivity than pure CNTs. Boron carbide is an important material with excellent mechanical and electrical properties, particularly it is very hard.[11,12] Many researchers have focused their work on the synthesis of carbide nanowires and boron-doped CNTs using different methods. Dai *et al.*[13] prepared carbide nanorods from CNTs by reacting them with volatile metal or non-metal complexes above 1200 °C. Satishkumar *et al.*[14] synthesized B-doped carbon nanotubes of $C_{35}B$ by pyrolysis of acetylene–diborane mixtures. Han *et al.*[15] prepared boron-doped carbon nanotubes through the partial substitution of the carbon atoms on CNTs with B_2O_3. Although B_4C and $B_{13}C_2$ nanorods can be found in such samples, most of these products are B-doped nanotubes. Both Satishkumar's and Han's doping ratio of boron are lower than 10% (at.%). Zhang *et al.*[16] prepared boron carbide nanowires by using plasma-enhanced chemical vapor deposition methods. These nanowires are of various morphologies and have rough walls. Han *et al.*[15] and Ma *et al.*[17] also found boron carbide encapsulated in BN nanotubes during their synthesis of BN nanotubes.

Due to the existence of topological pentagonal and heptagonal defects in the networks of rolling graphenes,[18] CNTs often occur in bent shapes or are entangled, which might decrease their mechanical and electrical properties. The entangled CNTs are very difficult to disperse, resulting in their having limited use in composites. To get straight nanotubes or nanorods is still a challenge for scientists working in the field of one-dimensional material. In this paper, we prepare boron carbide nanorods on a large scale by using CNTs and boron powder as raw materials. During the reaction with boron, the bent CNTs synthesized using the chemical vapor deposition method transform into very straight boron carbide nanorods.

II. Experimental

The experiments were carried out in a horizontal tubular furnace with an inner diameter of 60 mm. The CNTs used in the experiments were prepared by chemical vapor deposition (CVD) methods[19] using Ni as catalyst supported by diatomite. The as-grown carbon nanotubes were immersed in mild HF acid for 24 hours to remove the diatomite and most of the metal catalyst particles cohering on the CNTs. Boron powder (>99.5%) and CNT powder were homogeneously mixed in a B to C ratio of 4 : 1 (atomic ratio). The mixture of powders was then placed in a ceramic boat and mounted in the middle of the furnace tube. The furnace was then heated to the designated temperature (1150 °C, for example) under the protection of flowing argon.

The obtained gray powder-like products were examined and evaluated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) equipped with electron energy-loss spectroscopy (EELS). Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were also used to characterize the samples.

III. Results and discussion

A typical SEM image of the obtained gray powder is displayed in Fig. 1, which shows a large proportion of very straight nanorods in the sample. Although some individual bent carbon nanotubes can still be found during the SEM observation, the sample is mainly composed of straight nanorods. Some little balls at the end of the nanorods can be frequently seen during the SEM observation, as the arrows show.

Fig. 2a and b are two typical TEM images of the as-prepared CNTs and the final boron-containing products after 2 hours

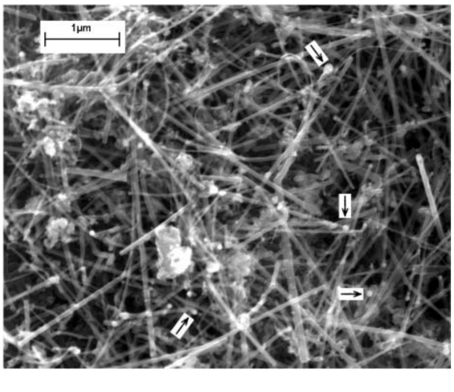

Fig. 1 A typical SEM image of the sample.

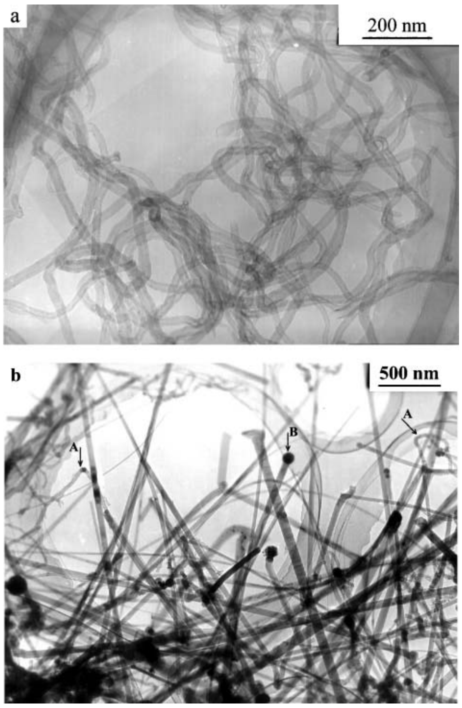

Fig. 2 TEM images of the as-prepared CNTs and the boron carbide nanorods prepared by using boron powder as boron sources. (a) The original carbon nanotubes are seriously bent. (b) Abundant straight boron carbide nanorods in the sample. Arrow A shows the tubular structures of the boron-doped CNTs, arrow B shows a large catalyst ball with a diameter of 90 nm.

reaction at 1150 °C, respectively. The as-prepared CNTs as shown in Fig. 2a are bent and tangled together. The diameters of the CNTs are about 30 nm and the lengths are up to several micrometers. Catalytic particles encapsulated within the CNTs can be occasionally observed during the TEM examination due to their survival after the acid treatment.

Abundant boron carbide nanorods can be seen in Fig. 2b. The morphologies of the nanorods, which are quite different from those of the starting CNTs and those of other B-doped CNTs and B_4C nanowires,[16,20,21] are surprisingly straight. The carbide nanorods have relatively smooth surfaces, which are quite different from the results given in ref. 14. The diameters of the nanorods are distributed between 20 nm and 60 nm, which are slightly larger than those of the as-grown CNTs, while the lengths of the nanorods are about a few micrometers, corresponding to those of the as-grown CNTs.

Some small black balls, indicated by arrow B in Fig. 2b, can often be seen at the end of the boron carbide nanorods during the TEM observation. The black balls were proved to be nickel-containing particles by energy dispersive X-ray spectroscopy (EDS) equipped with HRTEM. These particles may come from the metal catalyst encapsulated in the CNTs, in which the catalyst metal was not entirely removed by HF acid. We suppose that these remaining nickel particles act as catalysts for the growth of the boron carbide nanorods.

Besides boron carbide nanorods, some tubular structures, marked by arrows A, can also be seen occasionally during the TEM observation. The outer diameters of these nanotubes are similar to those of the as-grown CNTs, while the inner diameters are smaller. They are so-called B-doped carbon nanotubes.[15] The atomic ratio of B to C in the B-doped nanotubes is smaller than 0.1 : 1 according to EELS measurements. The B-doped nanotubes can be observed more often when the reaction temperature is lower than 1100 °C, even though the reaction time extends to 5 hours. However, when the reaction temperature exceeds 1100 °C, more than 90% of the products are boron carbide nanorods, indicating that the reaction temperature is a critical parameter for the formation of nanorods.

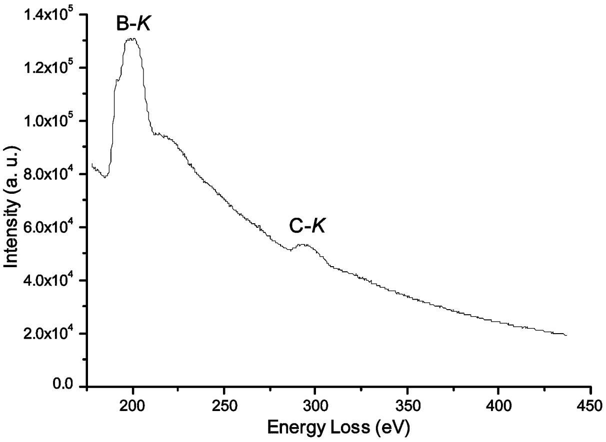

Fig. 3 A typical EELS spectrum of an individual boron carbide nanorod.

The atomic ratio of B to C in the nanorods can be measured through EELS. A typical EELS spectrum measured from an individual nanorod is shown in Fig. 3. There are two distinct absorption features in the EELS spectrum, which are characterized by B-*K* and C-*K* edges, respectively. The atomic ratio of B to C in the nanorods is very close to 4 : 1 calculated from EELS spectra, indicating that the nanorods are probably B_4C crystals rather than $B_{13}C_2$. We changed the atomic ratio of B to C from 4 : 1 to 1 : 1 in the raw materials while keeping the reaction temperature at 1150 °C, however the B to C ratio in the nanorods in the products is maintained at about 4 : 1.

Fig. 4a shows a typical HRTEM image of a boron carbide nanorod with a black particle at its tip. The diameter of the catalyst particle, measured to be 90 nm, is larger than that of the nanorods. There is a transition region connecting the catalyst particle to the nanorod. More details of the junction part are shown in Fig. 4b.

We divided the nanorod with a catalyst particle attached into three regions: a highly crystallized structure region (**I**), a transition region (**II**) and a catalyst particle region (**III**), as shown in Fig. 4b. At the crystallized part, the boron carbide nanorod crystallizes well and possesses a single crystal feature from a selective area diffraction pattern. The distance between the two horizontal lines is 0.449 nm. At the transition part, boron carbide is not arranged in the form of a single crystal but shows some clusters of boron carbide. Because of the ball-like shape generated by the surface tension the nanosized nickel-containing particle might be in a liquid state when the temperature is higher than 1100 °C.

A Raman spectrum excited by the 514.5 nm argon laser is given in Fig. 5. The background of the spectrum was corrected to remove any fluorescence features by empirical fitting procedures. There are several strong Raman peaks at 196, 705, 1059, 1349, and 1577 cm^{-1}, and also two shoulders at 780 and 925 cm^{-1}. The Raman spectrum is dominated primarily by B_4C modes based on the study of McIlroy *et al.*[21] The Raman peaks were broadened compared with bulk boron carbide[21,22] due to finite size effects.[23] The A_{1g} modes at 705 and 1059 cm^{-1} are attributed to the icosahedral breathing modes of the boron carbide nanorods. Because there are B-doped CNTs in the sample (see Fig. 2b), the Raman peaks at 1349 and 1577 cm^{-1} may derive from both carbon nanotubes and boron carbide nanorods.

We analyzed the gray powder using X-ray photoelectron spectroscopy to identify the boron in the product. Fig. 6 is a typical boron B(1 s) XPS spectrum of the gray powder. It shows a main peak at 186.5 eV, which indicates that the nanorods in the sample are B_4C. A small peak at 192.2 eV can

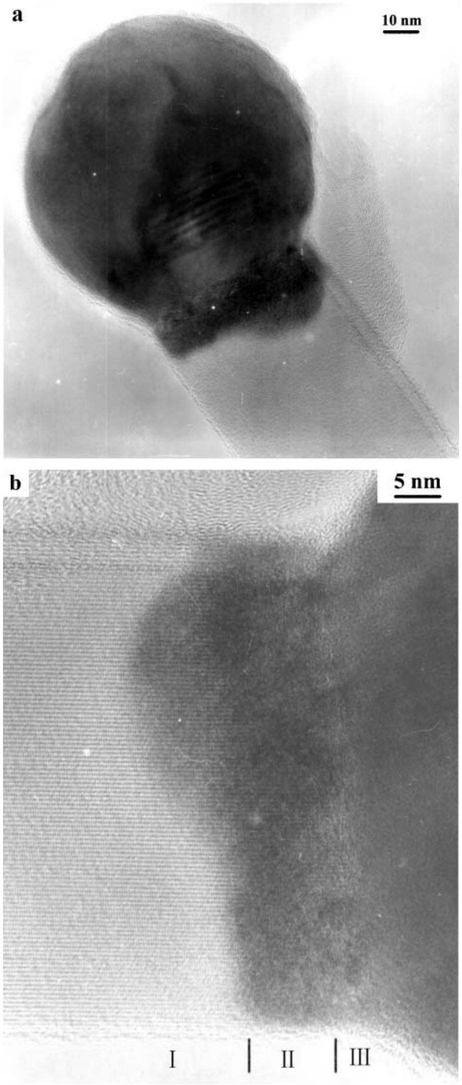

Fig. 4 HRTEM images of a boron carbide nanorod. (a) Boron carbide with a nickel-containing particle at the end. (b) The junction of the catalyst particle and boron carbide nanorod. **I** Part of the crystallized structure of boron carbide. **II** The junction between the boron carbide and the catalyst particle. **III** Part of the catalyst particle.

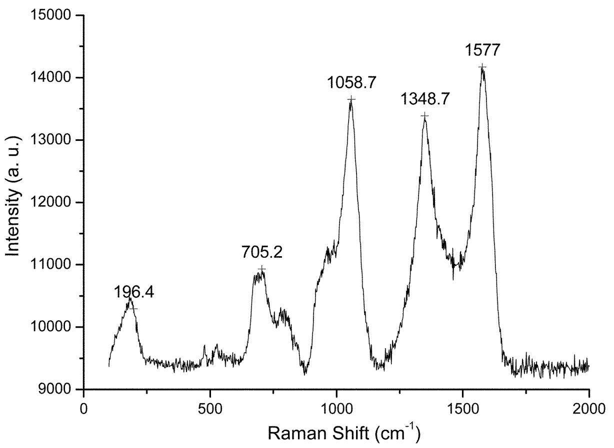

Fig. 5 Background corrected Raman spectrum of the boron carbide nanorods powder excited with a 514 nm wavelength laser line.

also be seen in Fig. 6, which corresponds to the small amount of B_2O_3 in the sample.

It is well known that boron atoms are very active at temperatures above 1000 °C. They react with carbon atoms and form a compound B_4C ($B_{12}C_3$) according to the reaction:

$$4B + C \rightarrow B_4C$$

CNTs act as templates at the beginning of the formation of boron carbide nanorods. The boron atoms might be adsorbed and react with the carbon atoms from the bent parts or the caps of nanotubes as they are rich in active dangling bonds. When a chain of C_3 combines with twelve boron atoms, it presents more dangling bonds to the CNTs and this will accelerate the combination of boron and carbon. As the carbon atoms at the bent parts react with boron atoms, the boron atoms will enter into the defective areas of the CNTs eliminating the free energy. This, of course, will reduce the number of CNT defects and form a straight nanorod. The carbon nanotubes also provide more carbon atoms for the growth of nanorods.

The growth of boron carbide nanorods is not only in the axial direction, but also in the radial direction (the diameters increase slightly compared to nanotubes). Because the B_4C crystals are not in a layered structure, it is impossible to form a tubular B_4C structure. The B–B bond length in B_4C is 0.1789 nm, which is larger than that of the C–C bonds, 0.1435 nm, so the volume of B_4C is about five times as large as that of the as-prepared CNTs, corresponding to the changes in diameter between boron carbide and CNTs and changing from nanotubes to nanorods.

To further investigate the role of boron powder in the formation of straight B_4C nanorods, we compared the results prepared from boron powder with those prepared from boron oxide both in our and others experiments.[15,21] Fig. 7 shows a typical TEM image of the product prepared using B_2O_3 as boron source at 1150 °C for 2 hours. The boron carbide nanorods bend dramatically in Fig. 7. A similar morphology

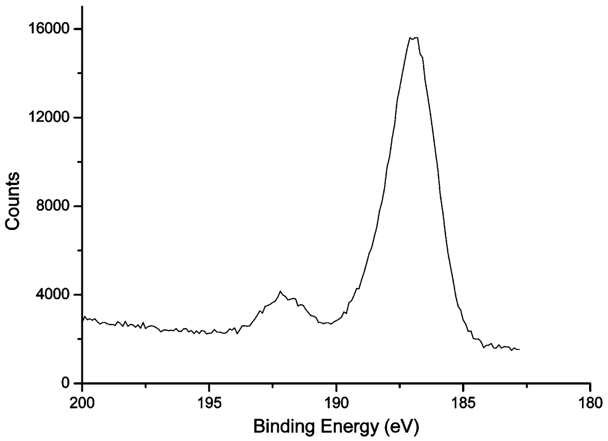

Fig. 6 XPS spectrum of boron B(1 s) of the boron carbide nanorods powder.

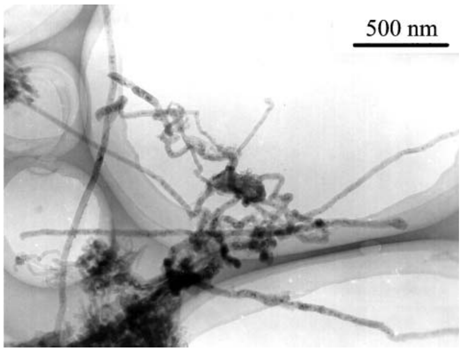

Fig. 7 A typical TEM image of B_4C nanowires prepared using B_2O_3 powder as boron source at 1150 °C for 2 hours.

for boron-doped CNTs can be seen in ref. 15. The bent boron carbide nanorods may result from the oxidising effect of B_2O_3. When B_2O_3 reacts with CNTs and forms boron carbide nanorods, the oxygen atoms react with carbon atoms and form CO as well, resulting in plenty of defects in the nanorods (or B-doped nanotubes) that will change the growth direction of the nanorods.

IV. Conclusions

Straight boron carbide nanorods have been prepared successfully on a large scale through direct reaction between CNTs and boron powder. The boron carbide nanorods straighten the CNTs and are easily dispersed. These straight B_4C nanorods may greatly improve the mechanical properties of composite materials and could be used in high temperature electronic devices.

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