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Citation	Huo, K. F., Hu, Z., Chen, F., Fu, J. J., Chen, Y., Liu, B. H., et al. (2002). Synthesis of boron nitride nanowires. Applied Physics Letters, 80(19), 3611-3613.
Date	2002
URL	http://hdl.handle.net/10220/6895
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Synthesis of boron nitride nanowires

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(Received 17 December 2001; accepted for publication 18 March 2002)

A chemical method has been developed for synthesizing boron nitride nanowires through the reaction of a mixture gas of nitrogen (N_2) and ammonia (NH_3) over nanoscale α -FeB particles at 1100 °C. Boron content in the product comes from the α -FeB catalyst itself. Transmission electron microscopic image indicates an abundant quantity of BN nanowires with diameter about 20 nm and length up to several tens of microns. The product has also been characterized by high-resolution electron microscopy and electron energy loss spectrometer. The perfectly straight lattice fringes with an interlayer spacing of about 0.333 nm corresponding to d_{0002} spacing of h -BN indicate that the BN nanowires are well crystallized. Also, a growth mechanism has been speculated. © 2002 American Institute of Physics. [DOI: 10.1063/1.1479213]

The study on the synthesis and properties of one-dimensional nanostructures such as nanotubes (NTs) and nanowires (NWs) has increased steadily since the discovery of carbon nanotubes (CNTs).¹ Boron nitride (BN) is an important wide-gap semiconductor with high melting point, high mechanical strength, hardness, corrosion resistance, oxidation resistance, and outstanding thermal and electrical properties.² These properties imply that one-dimensional BN nanostructures will have potential applications in nanosized electronic and photonic devices. Much effort has been devoted to the synthesis of one-dimensional BN nanostructures since the initial report in 1995.³ Many experimental methods, such as arc discharge,^{3–6} laser ablation,^{7–9} CNTs substitution,^{10–13} and chemical vapor deposition,^{14–17} have been developed to synthesize BN–NTs. However, the BN–NWs have not been reported so far. In this letter, we report an efficient method for the preparation of BN–NWs through the reaction of a mixture of NH_3 and N_2 over α -FeB nanoparticles. The results indicate that this route has the advantages of easy operation, low cost and uniformity of the product.

In our previous study, it is found that amorphous FeB and crystalline α -FeB nanoparticles could be produced by solid-state chemical reaction.¹⁸ These nanoparticles have been employed as catalyst to grow BN–NWs in this study. In brief, Fe–B nanoparticles were prepared by ball-milling water-free $FeCl_3$ and $NaBH_4$ (1:3.3 in mole ratio) for 8 h, followed by the annealing in Ar at 500 °C for 3 h. FeB nanoparticles were pressed to a solid tablet settled in the central zone inside an alumina tube. A commercially available mixture gas of NH_3 and N_2 (10 mol % NH_3) was used as precursor for the N atom source. The gas flowing rate was 100 sccm. After the chamber was evacuated several times, an

argon gas flow was introduced to about atmospheric pressure and the alumina tube was heated until to 1100 °C. Then the argon was replaced by the mixture reaction gas and processed for 2 h. After the chemical reaction, the reactor was cooled to room temperature in an argon environment. A gray sponge-like product was found.

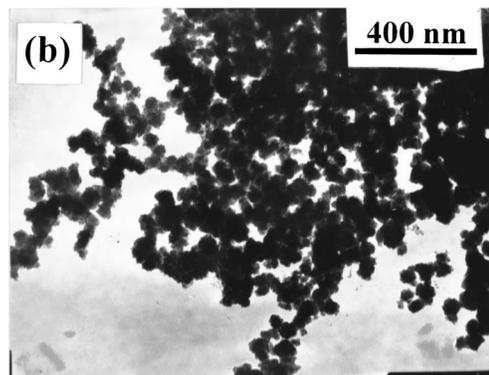
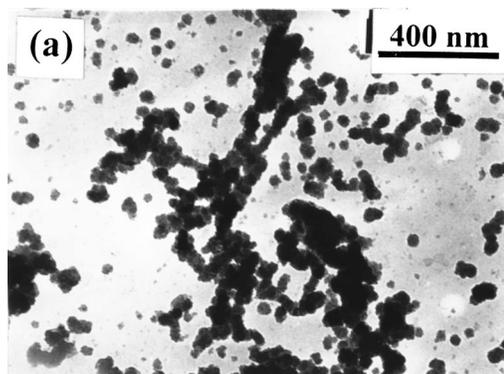


FIG. 1. TEM image of the FeB particles. (a) Amorphous FeB particles. (b) α -FeB particles by annealing corresponding amorphous FeB particles in (a) at 1100 °C for 2 h in Ar.

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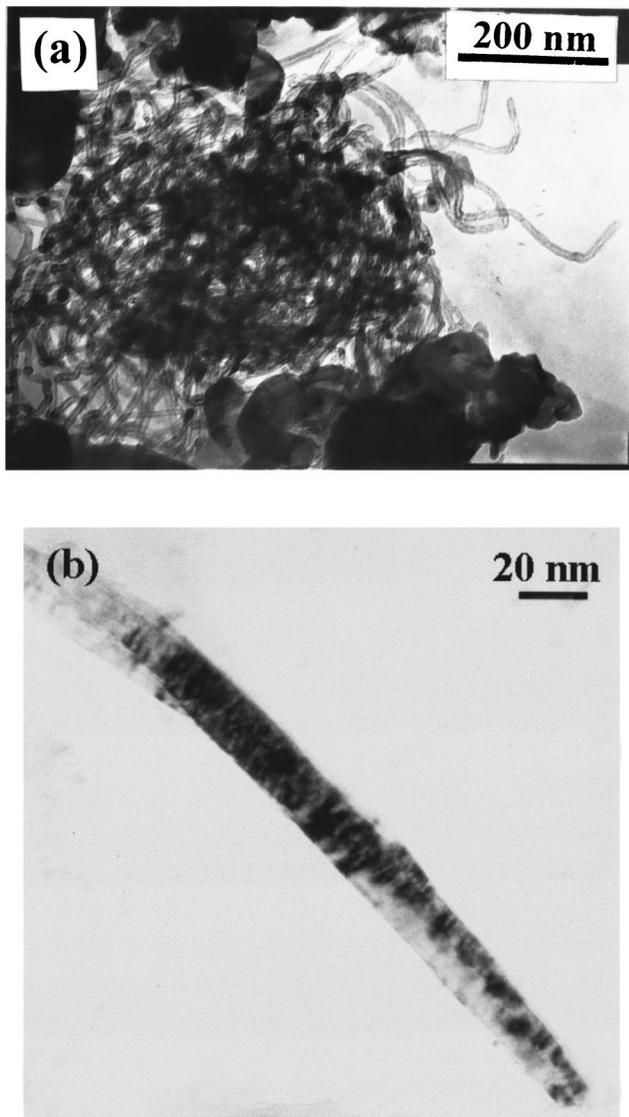


FIG. 2. TEM image of BN-NWs. (a) An abundant quantity of BN-NWs. (b) A typical nanowire in (a) with diameters about 20 nm.

The as-prepared product was characterized by transmission electron microscopy (TEM at 100 keV JEOL-JEM-2010). High-resolution transmission electron microscopic (HRTEM) study was carried out in a JEM-3010 microscopy operated at 300 keV, attached with parallel detection Gatan-666 electron energy loss spectrometer (EELS).

Figure 1(a) shows the TEM image of the amorphous FeB particles. The image revealed FeB particles are monodispersion with the size about 20 nm. Figure 1(b) is the image of the α -FeB particles by annealing the amorphous FeB particles at 1100 °C for 2 h in argon, which indicated that the α -FeB particles were good to sintering resistance and still remained monodispersion with the sizes in the range of 20–40 nm.

The TEM image of BN-NWs is shown in Fig. 2, which indicates that there is an abundant quantity of BN-NWs with diameters about 20 nm and length up to several tens of microns.

Under HRTEM examination, a typical well-developed BN-NWs [Fig. 2(b)] is shown in Fig. 3(a). HRTEM image shows the BN nanowire has good graphite-like layers with

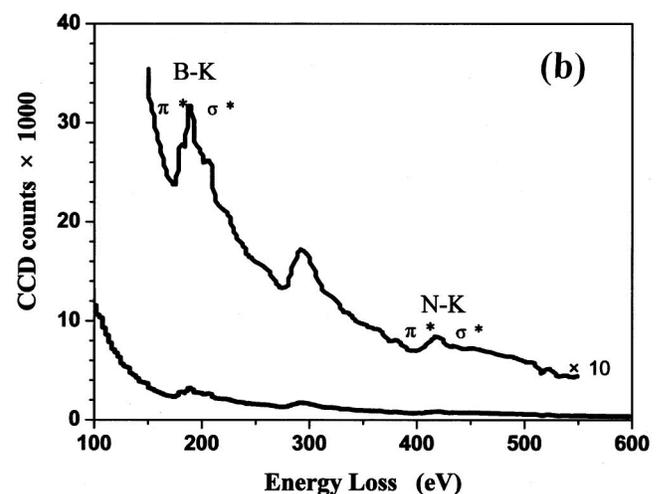
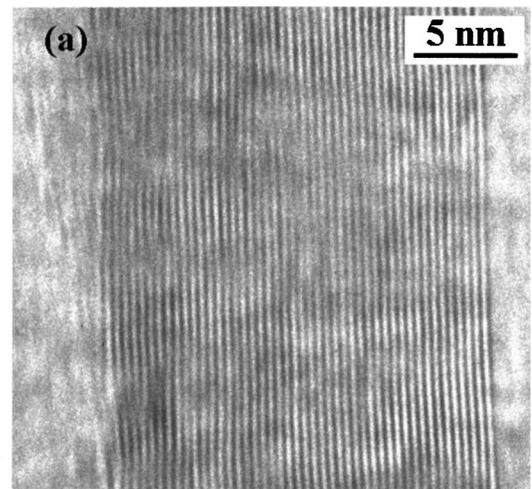


FIG. 3. HRTEM image of the typical BN-NW and its EEL spectrum. (a) The well-developed BN-NW [Fig. 2(b)] with diameter about 20 nm and interlayer spacing of about 0.333 nm. (b) EELS K -shell core-edge spectrum corresponding to the nanowire in (a). The distinct K -shell ionization edges at 188 and 401 eV demonstrate that the nanowire distinct absorption peaks of B and N. The upper curve is ten times of the lower one.

interlayer spacing of ~ 0.333 nm, corresponding to the d_{0002} spacing of h -BN.² EELS analysis reveals that the product is pure BN. A representative EEL spectrum corresponding to the nanowire in Fig. 3(a) is shown in Fig. 3(b). It demonstrates distinct absorption peaks of B and N characteristic K -shell ionization edges at 188 and 401 eV, respectively. The carbon absorption peaks at 284 eV is caused by carbon film of copper grid. Each K -shell core-edge fine structure consists of a sharp π^* peak and a well resolved σ^* band characteristic of sp^2 hybridization.

It is reasonable to speculate that BN-NWs started to grow from the surface of α -FeB grains, especially from bumps at the surface. The growth mechanism could be analogy to the vapor-liquid-solid mechanism for the growth of various nanowires or nanotubes from surrounding vapor.^{19–22}

The main difference is that, in our case, the components in the final BN product come not only from vapor, i.e., N from NH_3/N_2 , but also from the “catalyst” itself, i.e., B from Fe-B. Strictly speaking, Fe-B is not the catalyst rather than the reactant since it is changed after chemical reaction. Accordingly, it is expected that, at high temperature around

1100 °C, Fe–B catalyst should be in molten droplet state and N_2/NH_3 decomposes on the surface of Fe–B particles resulting in surface nitrogen. Then the liquid Fe–B droplet accepts the nitrogen atoms to form BN species by combination with the boron atom inside the droplet. Upon the BN concentration is supersaturated, it is precipitated to grow the BN nanowire single crystal gradually, rather than the polycrystal of short aspect ratio, due to the continuity of the crystal growth process. Here, the Fe–B particles not only act as the medium for transport from the vapor to the crystals, which is the case in common vapor-liquid-solid growth of nanowires or nanotubes, but also supply partial component for the final product. This feature provides the possibility in exploring some nanostructures when the vapor source is highly toxic or unavailable while the solid catalyst containing partial target component could be easily prepared as the case in this letter. The high boron content in our α -FeB particles probably favors the wire morphology rather than the hollow tubular figuration. We are currently attempting to prepare Fe–B nanoparticles with different boron content to study the growth of BN nanostructures.

According to the preceding discussion, the growing extent of BN–NWs would be determined by the releasable boron amount in α -FeB particles through diffusion under reaction condition, especially the reaction temperature. This is the reason that BN–NWs could not be synthesized below 900 °C at the same other conditions described earlier and the yield of BN–NWs could not increase further over 2 h in our experiment observation.

In conclusion, a chemical reaction has been developed for synthesizing well-crystallized BN–NWs through the reaction of a mixture gas of nitrogen and ammonia over nanoscale α -FeB particles. Different from other catalyst synthesis, the boron content in the product comes from the α -FeB particles in this approach. This method may be helpful for preparing other systems or aligned arrays on substrates for potential device applications. By following the evolution of the Fe–B particles during preparation, the growing mechanism would be clarified.

The financial supports from Natural Science Foundation of China (NSFC) and Chinese Education Ministry are greatly acknowledged.

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