Supporting Information

Growth of boron nitride nanotubes from magnesium diboride catalysts

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Experimental section

Synthesis of BNNTs. An alumina combustion boat containing 50 mg of powdered MgB_2 was covered with several silicon wafers and placed into a tube furnace. Next, another alumina boat containing B_2O_3, or H_3BO_3, or a B/CaO mixture (i.e., boron source), was also placed into the tube furnace at a distance of 8 cm from MgB_2 catalyst for B_2O_3 and H_3BO_3, or 3 cm for the B/CaO mixture (Fig. S2). Subsequently, the tube furnace temperature was maintained at 1573 K for 2 h in 200 standard cubic centimeters per minute (sccm) NH_3. After that, the system was cooled down to room temperature, and the silicon wafers were found to be covered with white BNNTs. To prove the fact that BNNTs could not be obtained without the appearance of MgB_2 or B_2O_3 (i.e., boron source), the experiments shown in Fig. S2 were conducted in the absence of MgB_2 or B_2O_3.

Reactions of 2B-MgO/Ar and Mg_3N_2-B_2O_3/Ar. The B/MgO (mole ratio 2:1) and Mg_3N_2/B_2O_3 (mole ratio 1:1) mixtures were annealed in Ar, respectively. The volume flow for these tests was 200 sccm. The temperature was hold at 1573 K and the reaction time was 2 h.

Mg_3N_2 and MgO NPs catalyzing the growth of BNNTs. To verify the catalytic abilities of Mg_3N_2 and MgO nanoparticles (MgO NPs, with average particle size about 20 nm), they were served as catalysts to synthesize BNNTs. These tests were also conducted at 1573 K for 2 h.

Characterizations. The morphologies of the obtained BNNTs were characterized using a scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, Tecnai G2 F20 S-Twin), and the corresponding chemical compositions were confirmed by Raman spectroscopy (HORIBA Jobin Yvon), Fourier transform infrared spectroscopy (FTIR), and energy-dispersive X-ray spectroscopy (EDX). The products obtained from 2B-MgO/Ar, MgB_2/NH_3, and Mg_3N_2-B_2O_3/Ar were characterized by X-ray powder diffraction (XRD, D8 Advance, Bruker AXS). The resultants of using MgO NPs and Mg_3N_2 catalysts were characterized by SEM and Raman spectrum. To investigate the luminescent properties, a cathodoluminescence (CL) spectrum of the BNNTs was measured at a thermal fieldemission scanning electron microscope (Quanta 400 FEG) with an accelerating voltage of 20 kV at room temperature. The contact angle (CA) of water was tested using a contact angle meter (OCA15EC, Germany).

Computational Methods. Ab initio molecular dynamics (AIMD) simulation was carried out using the “Vienna ab initio simulation package” (VASP 5.3.5)[1-4]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerh (PBE) functional was chosen to describe the exchange-correlation interaction[5,6]. A plane-wave basis set with a cut off energy of 600 eV was employed within the framework of the projector augmented wave (PAW) method to describe the electron-ion interaction[7,8]. A 7 Å MgB_2 nanosphere was placed in a 50 Å periodic cubic box at 1600 K. With the large simulation cell, only the gamma point was used.

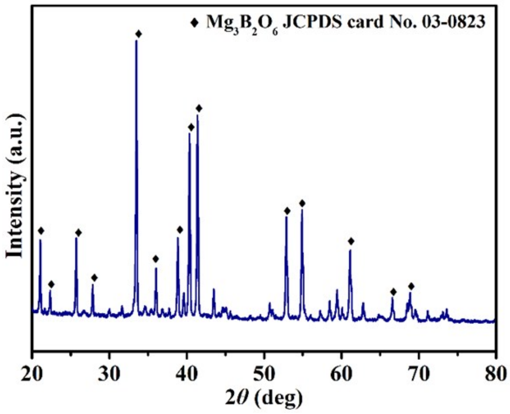

Fig. S1 XRD spectrum of the resultant obtained from the 2B-MgO/Ar reaction.

The 2B-MgO/Ar reaction proved that a lot of $Mg_3B_2O_6$ is formed when annealing the B/MgO mixture (mole ratio 2:1) at 1573 K, which may be derived from the reaction between MgO and B_2O_3. Various borates are composed of MgO and B_2O_3 with different mole ratios. In addition to B_2O_2, B_2O_3 may also be produced by the reaction of boron and MgO during the heating process. These reactions are described as follows.

$$2B(s) + 2MgO(s) \rightarrow 2Mg(g) + B_2O_2(g) \tag{1}$$

$$2B(s) + 3MgO(s) \rightarrow 3Mg(g) + B_2O_3(g) \tag{2}$$

$$3MgO(s) + B_2O_3(g) \rightarrow Mg_3B_2O_6(s) \tag{3}$$

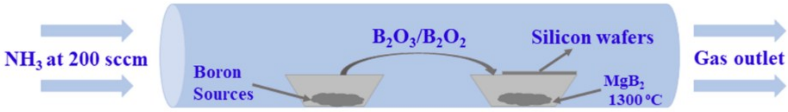

Fig. S2 Experimental setup used for BNNTs formation.

The B_2O_3 has a glass transition temperature of 598 to 723 K. Placing it 8 cm before the MgB_2 catalyst can produce enough B_2O_3 vapor for the growth of BNNTs. However, boron and CaO could not react at low temperature. Thus, we placed the B/CaO mixture 3 cm before the MgB_2 catalyst, which also has a temperature of 1573 K. Similar to the B/MgO reactions, both B_2O_3 and B_2O_2 gases may be produced by the B/CaO mixture, and the chemical reactions can be described as follows.

$$2B(s) + 2CaO(s) \rightarrow 2Ca(l) + B_2O_2(g) \tag{4}$$

$$2B(s) + 3CaO(s) \rightarrow 3Ca(l) + B_2O_3(g) \tag{5}$$

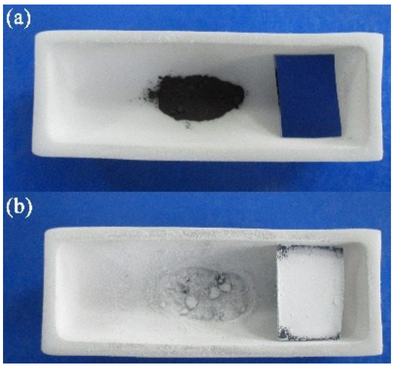

Fig. S3 Optical images of MgB_2 catalyst and silicon substrate contained in an alumina boat (a) before and (b) after the reactions. For the convenience of taking photos, the silicon substrate was moved from the above to the right of the MgB_2 catalyst and rotated 180 degrees.

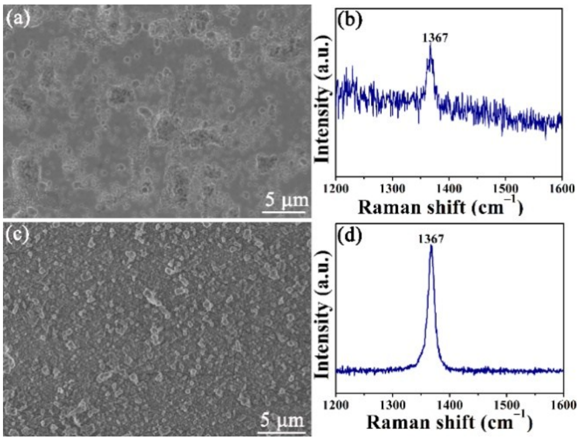

Fig. S4 (a, c) SEM images and (b, d) Raman spectra of the products obtained from (a, b) B_2O_3 and (c, d) MgB_2 separately reacted with NH_3.

Although the MgB_2 catalyst contains boron atoms, it could not produce BNNTs when solely reacted with NH_3. This indicated that MgB_2 might only be effective as a catalyst for the growth of BNNTs, and additional boron sources (e.g., B_2O_3, H_3BO_3, and B/CaO) are required.

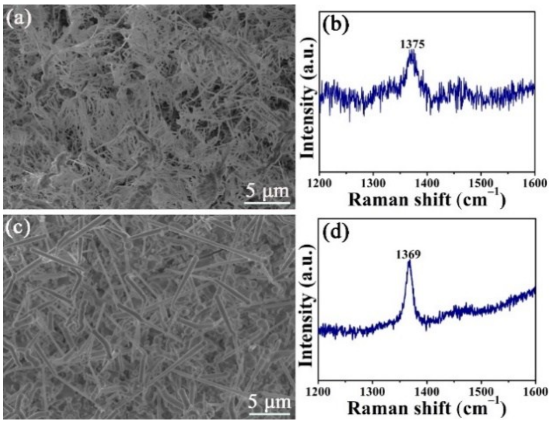

Fig. S5 (a, c) SEM images and (b, d) Raman spectra of the products obtained from (a, b) Mg_3N_2 and (c, d) MgO NPs catalysts.

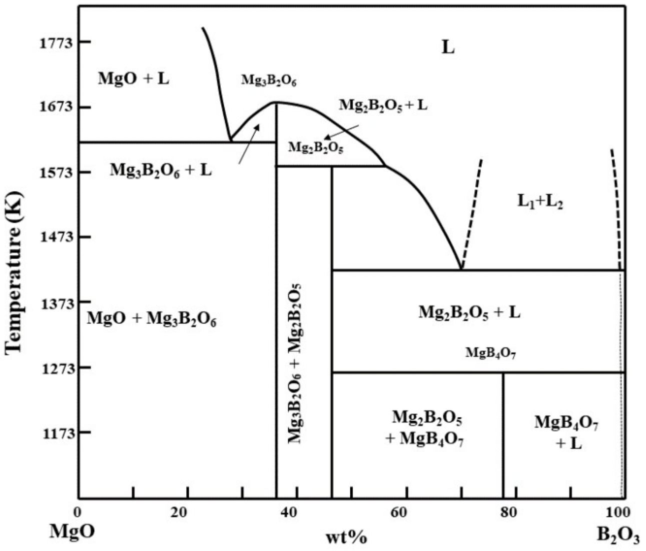

Fig. S6 Binary phase diagram of MgO-B_2O_3.[9]

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