# **Supporting Information**

### Magnesium Induced Preparation of Boron Nitride Nanotubes and Application in

## Thermal Interface Materials

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## **1. Experimental Section**

#### **1.1 Materials**

The High purity gases (99.999%, Ar, NH<sub>3</sub>) were purchased from the Linde Gas (China) Co.Ltd. The B<sub>2</sub>O<sub>3</sub>, Mg powders, boric acids (H<sub>3</sub>BO<sub>3</sub>), Mg(OH)<sub>2</sub>, hydrochloric acid (HCl) and magnesium oxide (MgO) were all supplied by Sinopharm Chemical Reagents Company. Polyvinyl alcohol (PVA, Mw=67,000), ethanol, and isopropyl alcohol (IPA) were purchased from Aladdin Reagent Co. Ltd. Deionized water was used for all the experiments. All chemicals were analytical grade and were used as received, without further treatment.

## **1.2 Preparation of Magnesium Borate (Mg<sub>x</sub>B<sub>y</sub>O<sub>z</sub>):**

The mixtures of H<sub>3</sub>BO<sub>3</sub> and Mg(OH)<sub>2</sub> according to molar ratios of 1:4, 1:1, and 2:3 were dissolved in 50 ml deionized water, then heated and stirred to form a milky suspension, respectively. Then, the suspensions were heated to 100 °C until the water completely volatilized and the white powders were obtained, respectively named MgB<sub>4</sub>O<sub>7</sub>, Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>. Lastly, three kinds of powder (MgB<sub>4</sub>O<sub>7</sub>, Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, and Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>) were heated to 950 °C, 1000 °C, and 1100 °C, respectively, and kept for 2 h in an air atmosphere to increase the crystallinity of the synthesized magnesium borate.

#### **1.3 Preparation of BNNTs**

The BNNTs were synthesized in a horizontal electrical resistance heated furnace (Hefei Kejing Materials Technology Co., LTD, GSL-1700X) with a temperature zone of about 60 cm, consisting of an alumina tube 150 cm in length and 60 mm in

diameter (as shown in Figure 1a). In each experiment, initially Mg powder (258 mg) was loaded in the alumina plate as the catalyst precursor. The  $B_2O_3$  (500 mg) powder was positioned in an alumina crucible as the boron precursor, 10 cm away from the loaded Mg alumina plate avoiding premature reaction of magnesium and boron source (Figure 1a). A SiO<sub>2</sub>/Si substrate was placed 4-10 mm above the  $B_2O_3$  powder, in the center of the horizontal alumina tube heating zone. After a five-minute Ar purge, the precursors were heated to 800 °C in an Ar flow of 200 standard cubic centimeters per minute (sccm), for 30 minutes. Then Ar was then replaced by 200 sccm NH<sub>3</sub>, and the temperature was ramped up to 1350 °C at a temperature ramping rate of 10 °C/min. The alumina tube was kept at 1350 °C for 90 minutes. After the reaction finished, the NH<sub>3</sub> was shut down and cooled in 200 sccm Ar to room temperature. The synthesis parameters of BNNTs with the combinations of Mg metal with different boron precursors (H<sub>3</sub>BO<sub>3</sub>, Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>) followed the same procedures as above.

#### **1.4 Preparation of PVA/BNNTs**

The obtained BNNTs were purified by 5 mol HCl by magnetic stirring for 2h, then the purified BNNTs were collected by air pump filtration and dried in a vacuum oven at 60 °C overnight. The purified BNNTs (100 mg) were dispersed in an isopropyl alcohol solution (50 mL) and sonicated for 2 h. Then, a PVA aqueous solution (5 wt %) was obtained by 5 g PVA dissolved in 95 g deionized water at 90 °C, and stirred for 3 h using a magnetic stirrer (800 rpm/min). The BNNT solution and PVA solution were blended at a specific weight ratio to form a PVA/BNNT (5 wt%) suspension, and sonicated for 1h. Then, the 5 mL PVA/BNNT solution was poured into a glass dish ( $\Phi$ = 60 mm), displaced at room temperature for 12 h, and dried in an oven at 80 °C for 2 h. Finally, the PVA/BNNTs composite films were peeled off from the glass dishes by immersion in ethanol. The preparation process of the pure PVA film was similar with the process of PVA/BNNTs composite, only without the addition of BNNTs.

#### **1.5 Characterization**

SEM images were obtained on a field-emission SEM (Hitachi S4800, Japan). The chemical compositions of the BNNTs were characterized using an X-ray energy dispersive spectrometer attached to a thermal field emission SEM (Quanta 400 FEG). TEM was performed on a Tecnai G2 F20S-TWIN with an operating voltage of 200 kV. Raman spectroscopy was collected over the spectral range of 1000 cm<sup>-1</sup> to 2000 cm<sup>-1</sup> using a LabRam ARAMIS Raman confocal microscope (Horiba HR800 Raman system) equipped with a 532-nm laser. The TGA test was performed on a Netzsch TG209 F1 under air conditions, with a ramping rate of 10°C/min. The X-ray diffraction information of the BNNTs was obtained by Powder X-ray diffraction (XRD, D8 Advance) using Cu Ka radiation (45 Kv and 40 mA). XRD data was collected at room temperature, using Cu-Ka ( $\lambda$ =1.5418 Å) X-rays. Additional acquisition parameters are: 20 range, 10~90°; scan rate, and 0.02° s<sup>-1</sup>. Diffraction patterns were referenced against the JCPDS database for sample identification. The chemical nature of prepared BNNTs were characterized by Fourier Transform Infrared Spectroscopy (FTIR, Thermo Scientific Instruments, model NicoletiN10), and the spectroscopy of BNNTs was received at room temperature with a wave number range of 400-4000 cm<sup>-1</sup>. Cathode luminescence (CL) spectroscopy is a useful technique for the characterization of the luminescence properties of nanostructures, due to its high spatial resolution and structural information obtained by using secondary electron imaging. Therefore, CL spectroscopy of the BNNTs was carried out with a thermal field-emission electron microscope, at room temperature (Quanta 400 FEG).



## 2. Growth BNNTs Demonstrated by Without Mg

Figure S1. (a) SEM and (b) Raman spectra for products synthesized by  $B_2O_3$  reaction with NH<sub>3</sub> covered on the Si substrate.