

Chemical Vapor Deposition of Boron Nitride Nanosheets on Metallic Substrates via Decaborane/Ammonia Thermolysis

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Supporting Information

Materials. Polycrystalline nickel foil (25 μm) and polycrystalline copper foils (25 μm) were purchased from Alfa-Aesar. Decaborane was freshly sublimed before use. Ultra high purity grade nitrogen, hydrogen and ammonia gases were purchased from Airgas. Poly(methylmethacrylate) (PMMA) solution was obtained from Microchem Corporation.

Experimental Procedures. The experimental set up used for the CVD deposition of BNNS is shown in **Figure S1**. All manipulations were carried out using standard high vacuum or inert-atmosphere techniques as described by Shriver and Drezdson.¹ All CVD experiments were carried out at atmospheric pressure. All gas flow rates were controlled by mass flow controllers (MFC) calibrated in standard cm^3/min or sccm and with suitable flow ranges.

In a typical experiment, the growth zone of a Lindberg 1500 $^\circ\text{C}$ furnace was charged with two ~ 3 cm x 1 cm pieces of Ni or Cu foil. The furnace temperature was ramped to 800 $^\circ\text{C}$ over ~ 20 min under a flow of 600 sccm of nitrogen gas and 250 sccm of hydrogen gas and then held at 800 $^\circ\text{C}$ for 20 min. The furnace temperature was then ramped to 1000 $^\circ\text{C}$, the growth temperature, in ~ 10 min. Decaborane vapors were then

carried into the growth zone from a heated container at 70-72 °C, using 10 sccm of nitrogen as the carrier gas. Hydrogen gas was then turned off, the nitrogen gas flow was reduced to 500 sccm; and an ammonia flow at 100 sccm was additionally introduced into the furnace. After a growth time of 10 min, the samples were further annealed at 1000 °C for 10 min under 100 sccm of ammonia and 100 sccm of nitrogen gas. The furnace was then cooled to room temperature under a 400 sccm nitrogen flow and a 30 sccm ammonia flow.

Sample preparation for analyses. The as-grown samples were spin-coated with PMMA on one side. The other side was cleaned with an oxygen plasma, as growth of BNNS takes place on both sides of the Ni or Cu substrates. Ni was etched with ~3 N hydrochloric acid at 60 °C and Cu was etched with ~2.5% FeCl₃ solution. The free floating PMMA coated BNNS were then washed with ~1 N HCl (Cu), followed by deionized water and then transferred to suitable substrates for further analyses.

Physical Measurements. Optical microscopy was carried out on an Olympus U-PMTVC equipped with a digital camera (Infinity Inc) and AFM was obtained on Veeco Dimension 3100 (Digital Instruments Inc.) with tapping mode. Raman spectra of the BNNS were obtained using a 514 nm excitation wavelength laser under a 100× objective. The laser power was kept at ~4 mW to avoid damage to the sample. The TEM and EELS analyses and the electron diffraction measurements were carried out using a JEOL 2010F transmission electron microscope at 200 kV.

For TEM and EELS analyses, the PMMA coated BNNS were deposited on holey carbon on copper grids, followed by removal of the PMMA with acetone. For optical microscopy and AFM, the PMMA coated BNNS were deposited on 300 nm SiO₂/Si

wafers, followed by PMMA removal with acetone. A further annealing under hydrogen at 100 sccm and argon at 300 sccm at 400 °C for 3 h was performed to remove residual carbon.

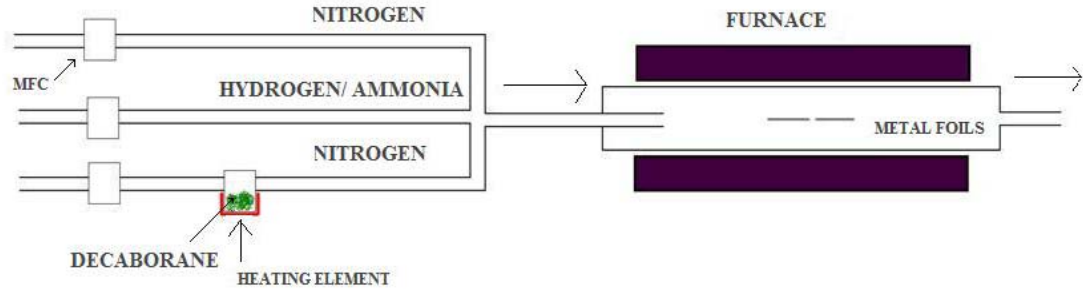


Figure S1. Schematic diagram of experimental set-up for CVD growth of BNNS on Ni or Cu foils.

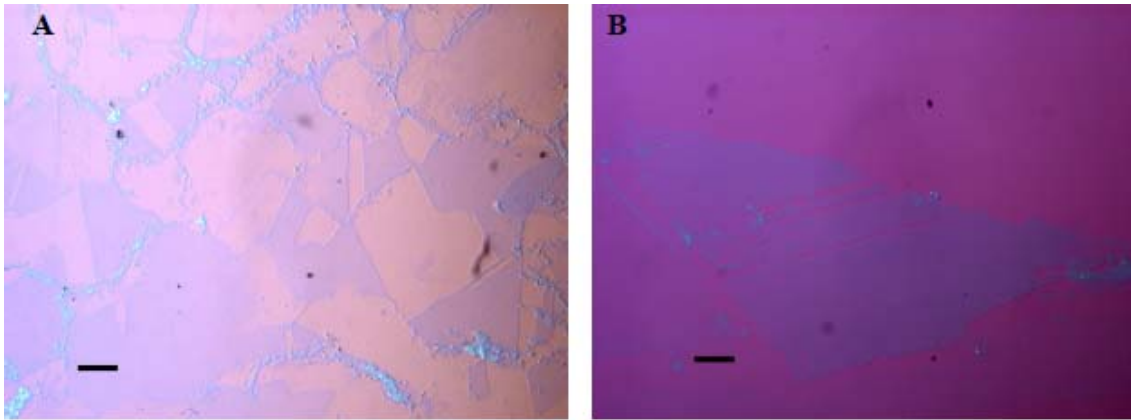


Figure S2. Optical images of BNNS grown on (A) Ni foils (B) Cu foils. Scale bar: 20 μm.

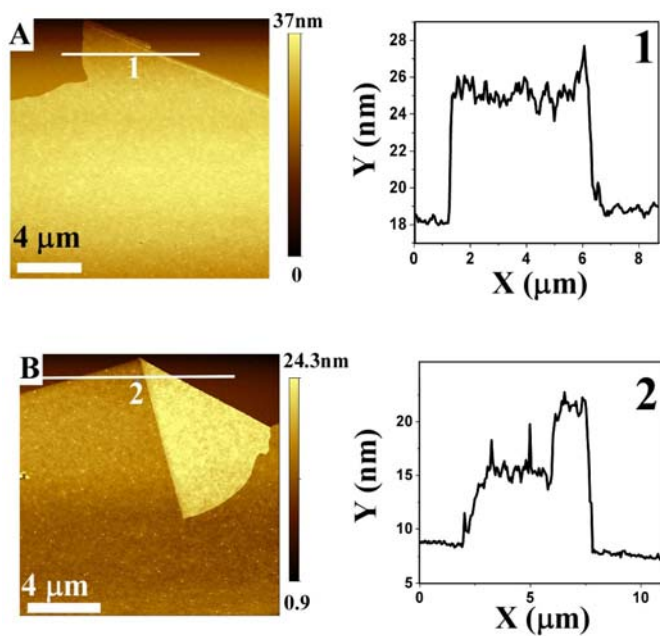


Figure S3. AFM images and height profiles of BNNS grown on Cu foils.

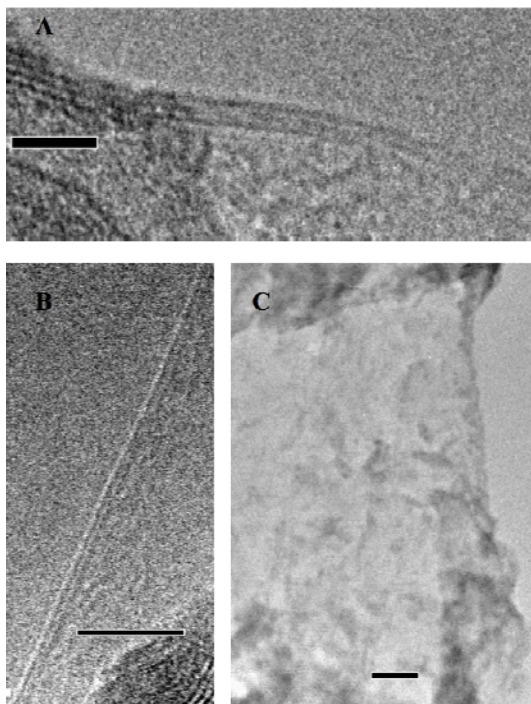


Figure S4. TEM images of BNNS grown on Cu foils. Scale bars: A and B, 5 nm; C, 0.05 μm.

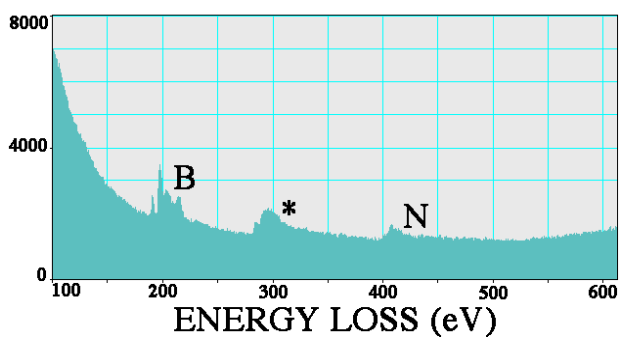


Figure S5. Electron energy loss spectrum (EELS) of BNNS showing peaks for sp^2 B and sp^2 N. The small peak * for amorphous C is from post-synthetic contaminants.

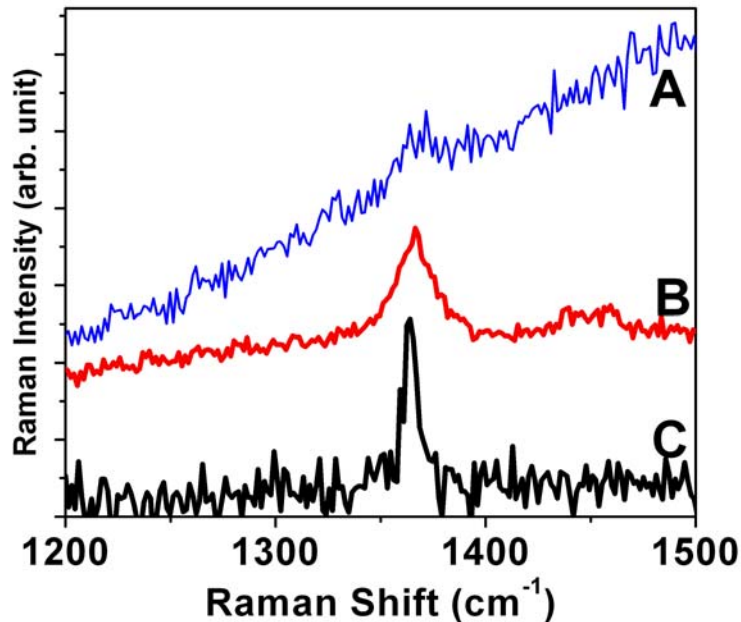


Figure S6. Raman spectra of CVD grown BNNS (on Ni substrates) with thicknesses of: (A) ~ 6 nm and (B) ~ 10 nm, and (C) Raman spectrum of BNNS obtained from exfoliated h-BN flakes.

¹ Shriver, D. F.; Drezdson, M. A. *Manipulation of Air-Sensitive Compounds*; 2nd ed.;

Wiley: New York, **1986**.