

Electronic Supporting Information

Bimetallic Catalytic Growth of Boron Nitride Nanotubes

Liangjie Wang,^{a,b} Taotao Li,^a Xiaoyang Long,^a Xiaona Wang,^a Yancui Xu,^a and Yagang Yao^{*,a}

^aDivision of Advanced Nanomaterials, Key Laboratory of Nanodevices and Applications, CAS Center for Excellence in Nanoscience, Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou 215123, China.

*E-mail: ygyao2013@sinano.ac.cn

^bSchool of Materials Science and Engineering, Shanghai University, Shanghai, 200444, China

Synthesis of Ni-Y, Ni, and Y nanoparticles

Ni-Y and Ni-Mo nanoparticles

0.2 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added into 20 mL of 10% didecyldimethylammonium bromide (DDAB)/toluene solution to form the inverse micelles. Then, 0.040 mL of 0.1 M $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution was added into the micelle solution under sonication. After that, 0.8 mL of 2.0 M lithium borohydride (LiBH_4)/THF solution was added to reduce the salts into metals after bubbling with N_2 and pumping the freeze solution with liquid nitrogen under low pressure to remove dissolved oxygen. The solution turned black immediately upon sonication. The experimental set-up diagram of the freeze solution by liquid nitrogen is shown in Figure 1. The Ni-Mo nanoparticles were prepared by similar method, just replacing $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution with $(\text{NH}_4)_2\text{MoO}_4$ aqueous solution.

Ni or Y nanoparticles

0.2 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ was added into 20 mL of 10% DDAB/toluene solution to form the inverse micelles. After that, 0.8 mL of 2.0 M LiBH_4 /THF solution was added to reduce the salts into metals after bubbling with N_2 to remove dissolved oxygen. The products were then dispersed in 2-propanol, drop-dried on a SiO_2 /Si wafer.

BNNTs Growth

Different precursor materials (B_2O_3 or B) were placed into an open-ended alumina tube, and located at the center of the heating zone (1200 °C) of the tube furnace. The substrates with and without bimetallic catalyst nanoparticles were faced down the alumina tube. Then, 200 standard cubic centimeter per minute (sccm) of N_2 and 200 sccm of H_2 were introduced into the chamber. Subsequently, the precursors were heated to 1200 °C and held for 1 h under the NH_3 gas. After that, NH_3 gas flow was stopped in order to terminate the reaction and the system was cooled down to room temperature under the N_2 flow. We further demonstrate the effectiveness of bimetallic catalyst to grow BNNTs in another way employing a mixture of B/NiO/ Y_2O_3 , B/NiO, and B/ Y_2O_3 as precursor under the same experimental conditions.

Characterizations

The products were characterized by scanning electron microscope (SEM, Hitachi S-4800), atomic force

microscopy (AFM, Dimension3100), and high-resolution transmission electron microscope (TEM, Tecnai G2 F20 S-Twin) equipped with an energy-dispersive X-ray energy dispersive spectrometer (EDS, Apollo 40SDD). Raman spectroscopy was collected over the spectral range of 1000 cm^{-1} to 2000 cm^{-1} using LabRAM ARAMIS Raman confocal microscope (HORIBA JobinYvon) equipped with a wavelength of 532 nm. The crystal structure was characterized by X-ray diffraction (XRD, D8 Advance, Bruker AXS). The UV-visible absorption spectra of the products were characterized by UV-visible absorption spectroscopy (JascoV-466 Spectrophotometer).



The experimental set-up diagram for metal nanoparticles preparation. (a) The two salts were freeze-dried before $(\text{LiBH}_4)/\text{THF}$ solution adding. (b) The photograph of nanoparticles in the flask.

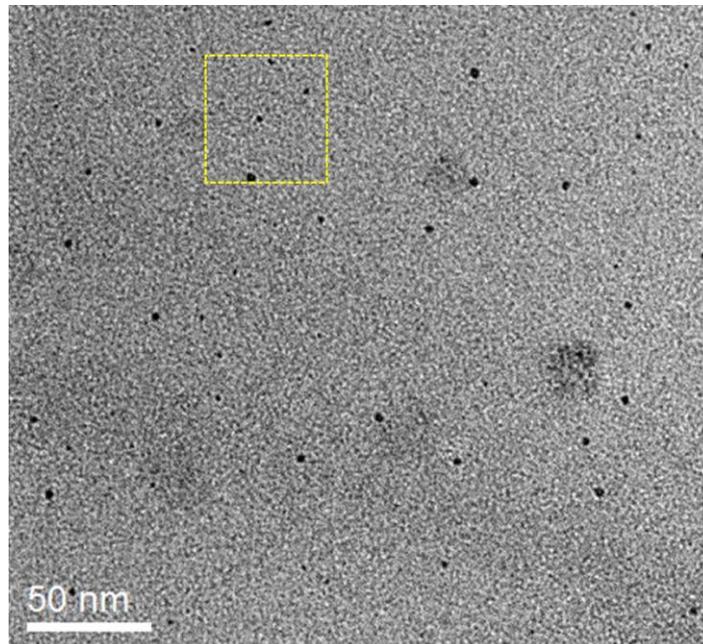


Figure S1. The TEM image of Ni-Y nanoparticles.

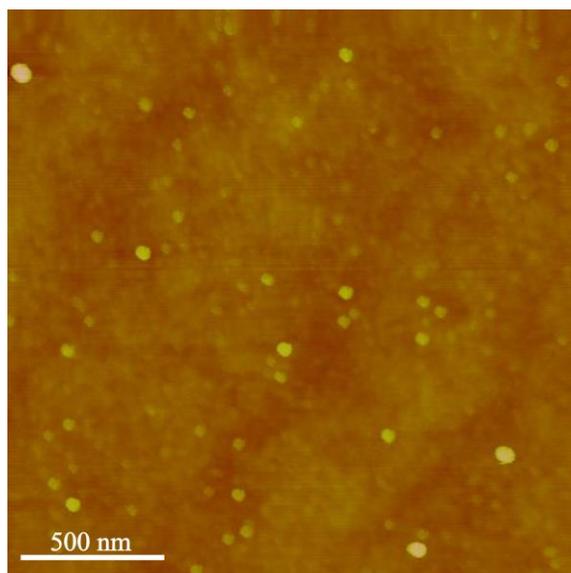


Figure S2. The magnified AFM image of as-prepared Ni-Y nanoparticles.

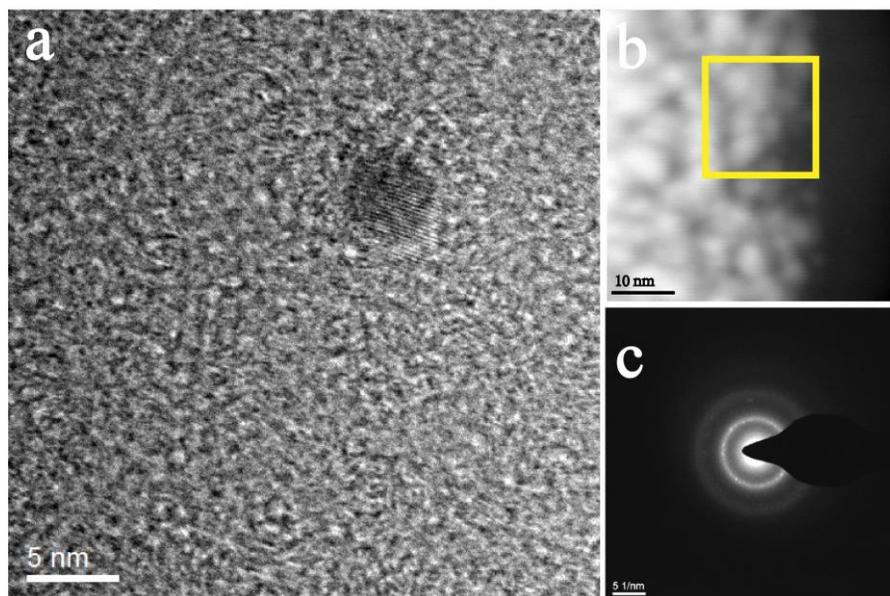


Figure S3. (a) The TEM image of Ni-Y nanoparticle. (b) The STEM image of nanoparticles and (c) the SAED pattern of several nanoparticles shown in the yellow rectangle in (b).

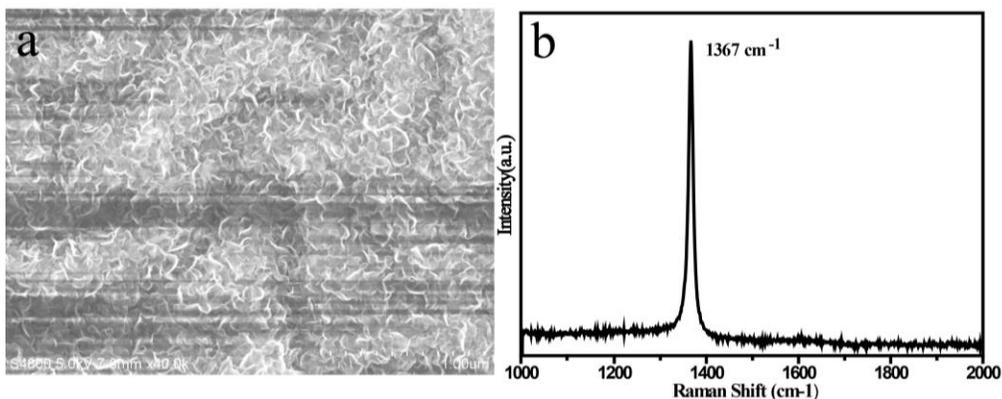


Figure S4. (a) BN nanosheets grown on the SiO₂/Si surface without Ni-Y nanoparticles. (b) Raman spectra of BNNSs.

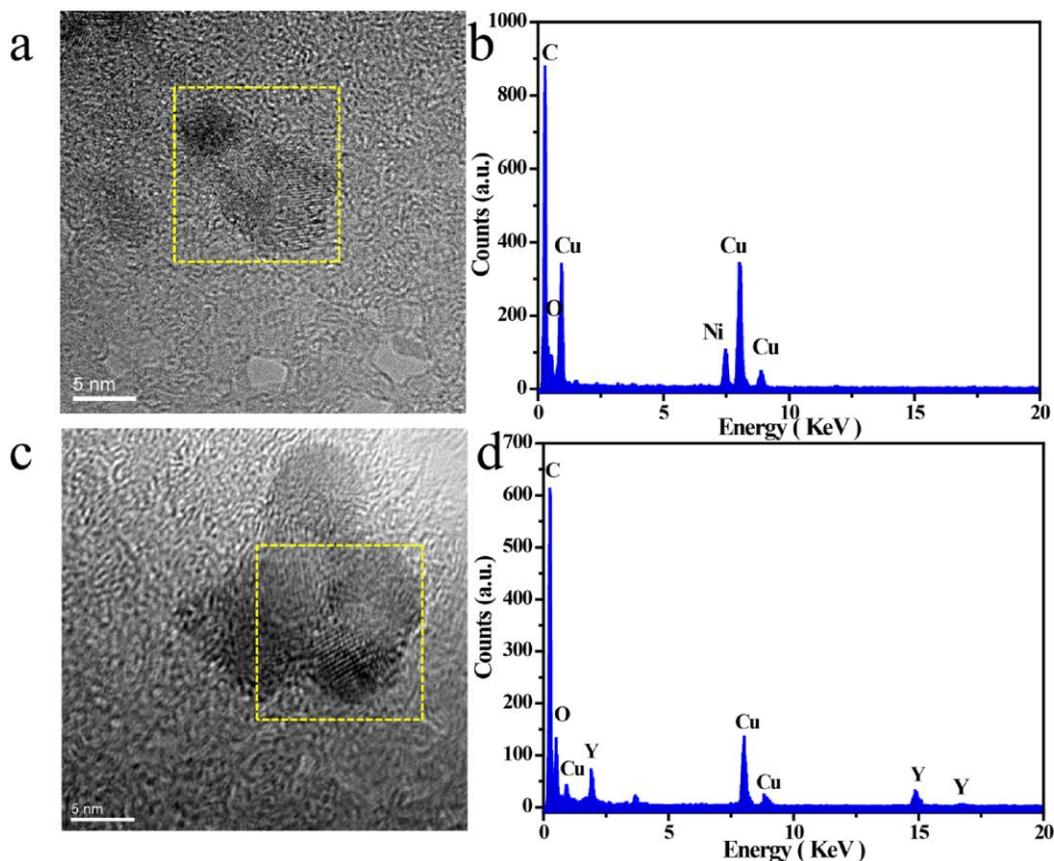


Figure S5. Ni and Y nanoparticles characterizations. (a) TEM image of Ni nanoparticles. (b) EDS spectrum of Ni nanoparticles (shown in the yellow rectangle in a). (c) TEM image of Y nanoparticles. (d) EDS spectrum of Y nanoparticles (shown in the yellow rectangle in c).

Comparing Figure 1d with S5b, we found that Ni peak at ~7.5 KeV can be discovered in Figure S5b, but Y peaks at ~1.8 and ~15 KeV are not exposed. Compare Figure 1d with S5b, we found that the Y peaks appeared in EDS spectrum as shown in Figure S5d, without Ni peaks at about 7.5 KeV. Figure 1d is EDS spectrum of the Ni-Y nanoparticles, the Ni and Y peaks appearing at the same time, which proves we successfully prepared the bimetallic nanoparticles.

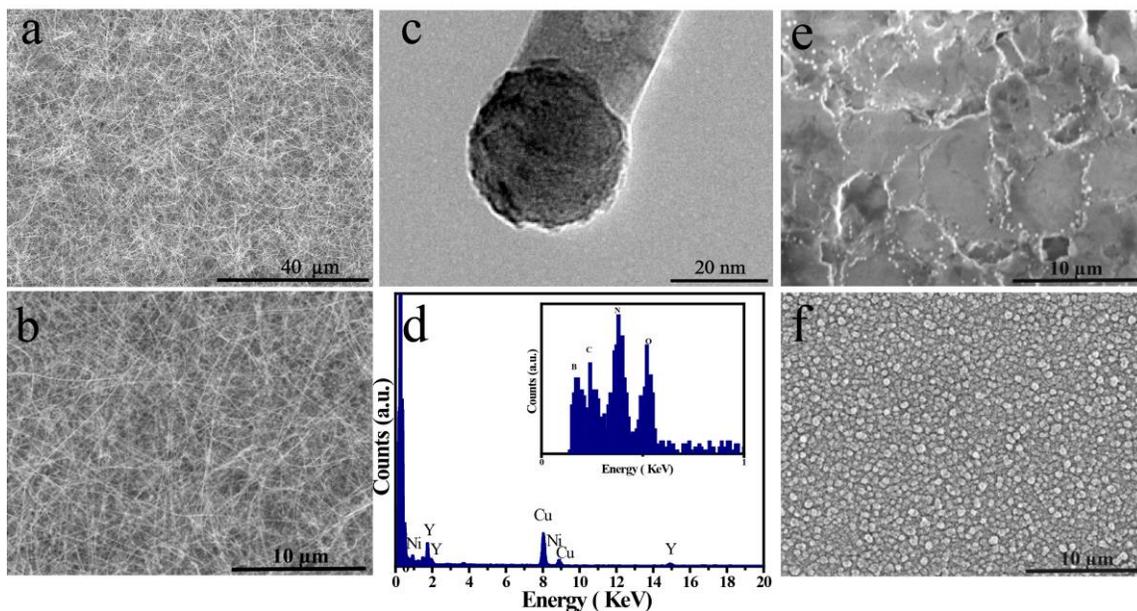


Figure S6. Morphology characterizations of as-grown BNNTs. (a) and (b) The mixture of B/Y₂O₃/NiO as precursor. (c) The image of close ended BNNT. (d) EDS spectrum of an encapsulated catalyst particle inside of as-grown BNNT. The inset exhibits the light elements of B, N, O and C. The presence of Cu and C signature in both the cases was attributed to the carbon-coated copper grid used in the sample preparation. (e) B/Y₂O₃ as precursor. (f) B/NiO as precursor.