Rebar Graphene from Functionalized Boron Nitride Nanotubes—Supporting Information

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Materials and Methods

RGBNNT synthesis. A standard 1-inch quartz tube was used as the reaction chamber and temperatures were pre-calibrated using a k-type thermocouple probe (Omega Engineering, Inc.). The typical synthesis process was as follows. A 25-µm-thick 10 cm × 10 cm Cu foil (99.8% purity, Alfa Aesar) was first pretreated using the electrochemical polishing method as described.[1] The pretreated Cu foil was cut into 1 cm × 1 cm pieces and coated with a BNNT solution using a spin-coater. See below for concentrations and spin rates. Then, the Cu foil was loaded into the furnace that served as both an annealing system and as a CVD chamber and the reaction chamber (temperature was increased to 1077 ℃ before the loading) was evacuated to ~ 16 mTorr. For graphene growth with CH_4, 500 sccm H_2 was introduced into the system and the Cu foil was moved into the hot region of the furnace by a magnetic rod and the foil was annealed for 5 min. Then an additional 1 sccm CH_4 was introduced into the system for 15 min for the graphene growth. Afterwards, the Cu foil was quickly removed from the hot region using a magnetic rod and permitted to cool to the room temperature. For graphene growth without CH_4, 50 sccm H_2 and 500 sccm Ar were introduced into the system and the Cu foil was then moved into the hot region of the furnace by a magnetic rod and the foil was annealed for 20 min. After the annealing, the Cu foil was quickly removed from the hot region using a magnetic rod and permitted to cool to the room temperature.

Preparation of functionalized BNNTs. Highly crystalline, long, few-walled BNNTs synthesized by a catalyst-free high temperature pressure (HTP) laser heating method were used as raw materials.[2] For RCO_2-functionalized BNNTs, BNNTs (10 mg) were sonicated with HNO_3 (15 mL, 70%) for 12 h, and the reaction mixture was then filtered under vacuum and washed

with 20 mL H_2O and then with 20 mL acetone, both H_2O and acetone washes were repeated three times to yield 5.0 mg of HO-BNNTs.[3] The as-produced HO-BNNTs were then reacted with 2-ethylhexanoyl chloride (5 mL, excess) at 100 °C for 120 h, and the reaction mixture was filtered under vacuum and washed with 20 mL H_2O and then with 20 mL acetone, both H_2O and acetone washes were repeated three times to yield 3.5 mg of RCO_2-BNNTs.[4] The as-produced RCO_2-BNNTs were dissolved in $CHCl_3$ at a concentration of 2 mg/mL. For Pluronic/BNNTs, BNNTs (2 mg) were dispersed together with Pluronic 127 (10 mg, Sigma-Aldrich) in DI water (10 mL). The solution was then tip sonicated (Misonix Sonicator 3000) at 30 W for 1 min to generate a homogeneous solution.

Dispersion of functionalized BNNTs onto Cu foil. For RCO_2-BNNTs solution, 100 µL RCO_2-BNNTs $CHCl_3$ solution was deposited on the surface of the pretreated Cu foil (1 cm × 1 cm) by spin coating at 500 rpm for 10 s, and the procedure was repeated 10 times. For Pluronic/BNNTs solution, the spin-coating was conducted at 1000 rpm for 40 s, and the procedure was repeated 10 times.

Polymer-free transfer of RGBNNT sheets on target substrates. The transfer protocol used was similar to the literature protocol.[5] (1) The Cu foil was etched in 100 mL 0.1 M aqueous $(NH_4)_2S_2O_8$ with 1% butanol by volume overnight, resulting in the rebar graphene film being lifted from the surface of the Cu and floating to the top of the etchant solution; (2) submerging a clean glass slide into the etchant and picking up the floating film with the glass slide, followed by transferring the film from the glass slide into 100 mL H_2O containing 1% butanol by volume overnight to wash away remaining etchants; (3) dipping a target substrate into the water and

butanol solution, and picking up the film; (4) leaving the sample overnight in the air, and then drying at 60 °C overnight at 130 Torr.

Device fabrication and measurement. RGBNNT FETs were fabricated on SiO_2 (300 nm)/ highly doped p-type Si wafers. Six-terminal electrode leads were defined with photolithography followed by the sputter deposition of Au (20 nm) and lift-off. A six-probe station (Desert Cryogenic TT-probe 6 system) was used to measure the electrical properties under a pressure of 10^{-5}-10^{-6} Torr under room temperature using an Agilent B1500A Semiconductor Device Analyzer. The mobilities of the FET devices were calculated based on the slope of current variation against gate voltage using eq 1:

$$\mu = \left(\frac{\Delta I_{ds}}{\Delta V_{gs}}\right) / \left(\frac{C_g W V_{ds}}{L}\right) \ (1)$$

where I_{ds} and V_{ds} are the source–drain current and voltage, respectively, V_{gs} is the back-gate source voltage, L and W are the effective channel length and width, respectively, and C_g is the gate capacitance of the FET device.

Calculations for using RCO_2 functional group and Pluronic F127 as carbon source for graphene growth. The surface area of single layer graphene is 2965 m^2/g (both sides).[1] Then, for a 1 cm × 1 cm Cu foil, the mass of graphene (mass of C atoms) is 7×10^{-8} g. For method 2 (RCO_2-BNNTs), the concentration of the solution is 2 mg/mL, the mass percentage of C atoms is ~ 40% as determined by XPS analysis. If only 10 μL of the solution stays on the Cu after spin coating (100 μL, 10 times), the mass of C left is 8×10^{-6} g, over 100 times larger than the amount needed. Similarly, for method 4 (Pluronic/BNNTs), the concentration of the solution is 12 mg/mL and the mass percentage of C atoms is ~ 30% as determined by XPS analysis. If only 10

µL of the solution stays on the Cu after spin coating (100 µL, 10 times), the mass of C left is 5×10^{-6} g, over 500 times larger than the amount needed. In conclusion, there should be enough C from RCO_2 functional groups or Pluronic F127 to serve as the carbon source for graphene growth.
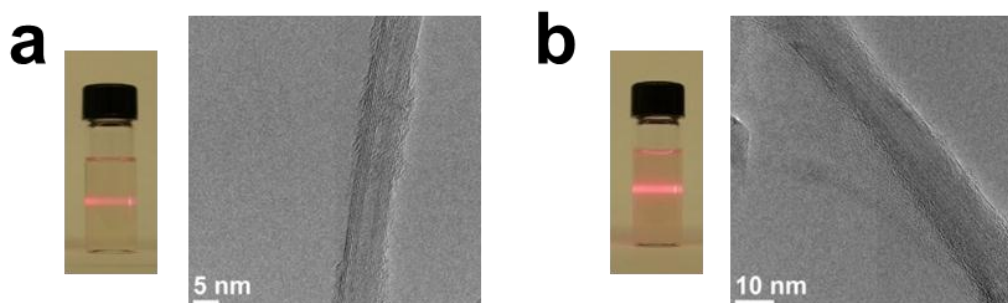

Figure S1. Photograph of raw BNNTs.

Figure S2. (a) Photograph of RCO_2-BNNTs solution (with a laser light passing through the solution) and TEM image of an isolated nanotube. (b) Photograph of Pluronic/BNNTs solution (with a laser light passing through the solution) and TEM image of an isolated nanotube.
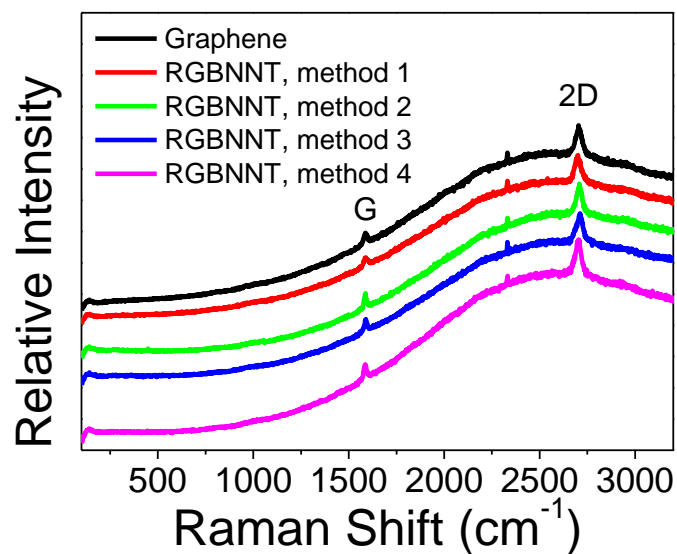
Figure S3. Raman spectra (excited with 514 nm laser) of as-grown RGBNNT on Cu. The black curve is the control of graphene synthesized without BNNTs; the red curve is RGBNNT synthesized using method 1; the green curve is RGBNNT synthesized using method 2; the blue curve is RGBNNT synthesized using method 3; the pink curve is RGBNNT synthesized using method 4.
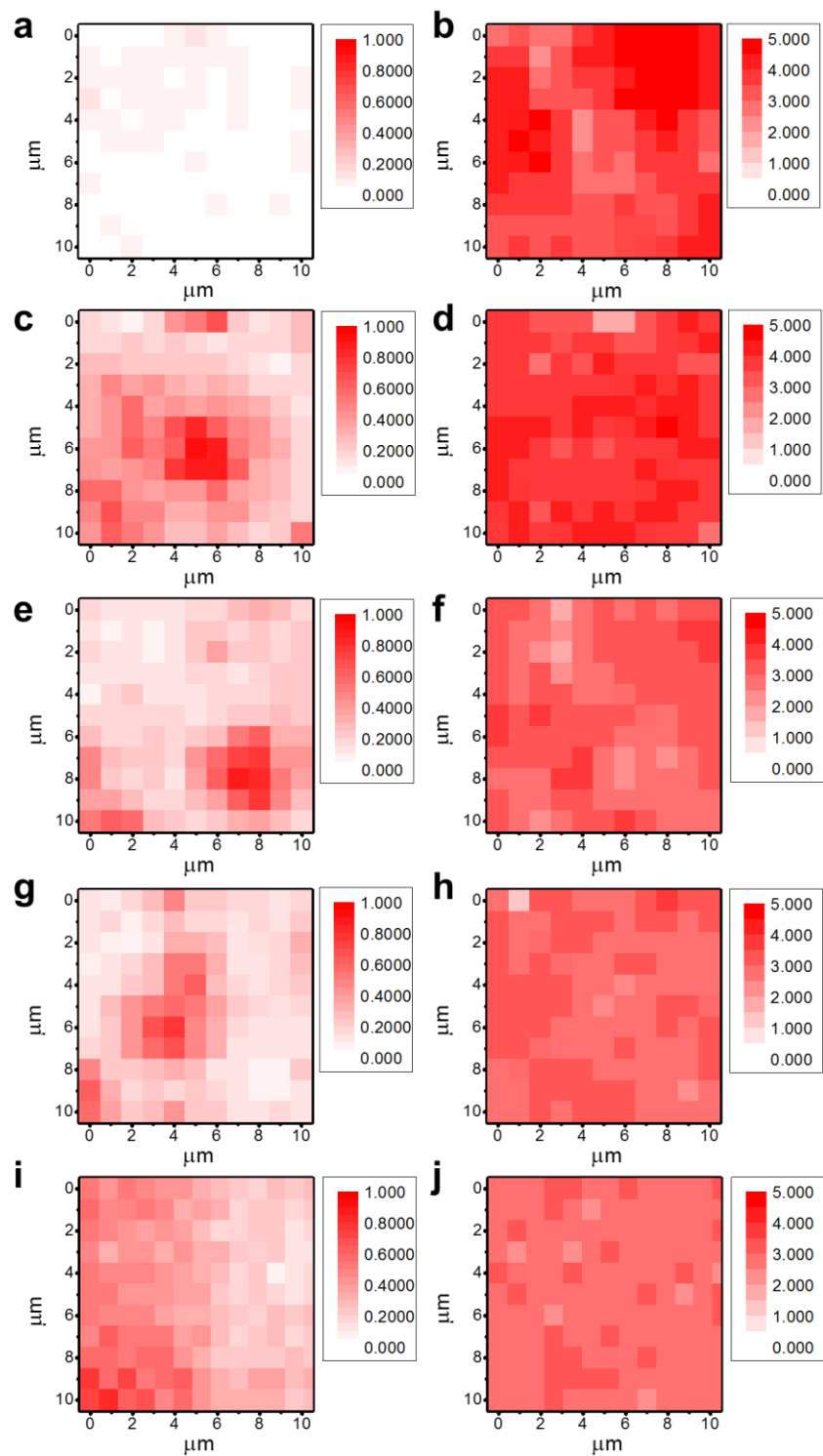
Figure S4. Raman mapping (excited with 514 nm laser) of (a,b) graphene and RGBNNT made from (c,d) method 1; (e,f) method 2; (g,h) method 3; and (i,j) method 4; on SiO_2/Si substrate.

(a,c,e,g,i) show the ratio between the intensity of the D peak over the G peak (D/G). (b,d,f,h,j) show the ratio between the intensity of the 2D peak over the G peak (2D/G).
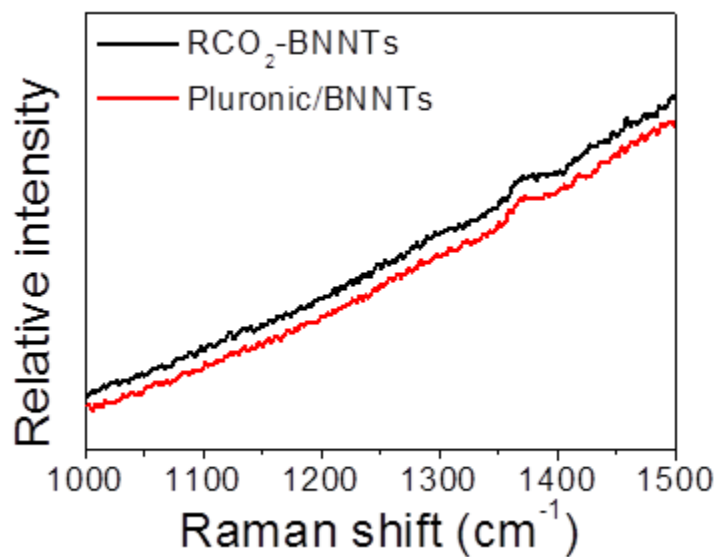

Figure S5. Raman spectra (excited with 514 nm laser) of spin-coated RCO_2-BNNTs and Pluronic/BNNTs on Cu before graphene growth.
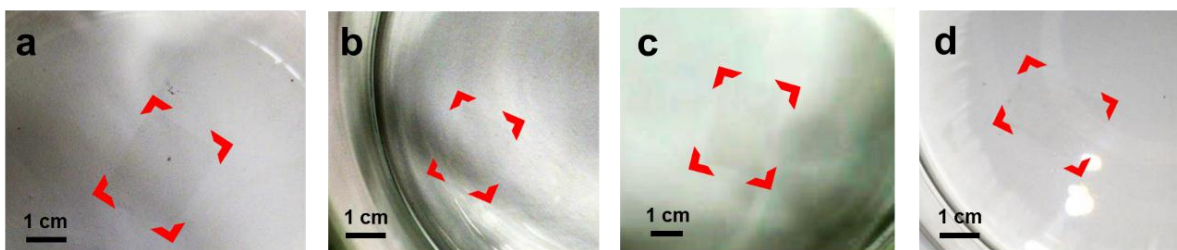
Figure S6. Photographs of free-floating RGBNNT on 1% butanol in H_2O. (a) Method 1; (b) method 2; (c) method 3; and (d) method 4. To aid visualization, the rectangular RGBNNT is highlighted in red at the corners.
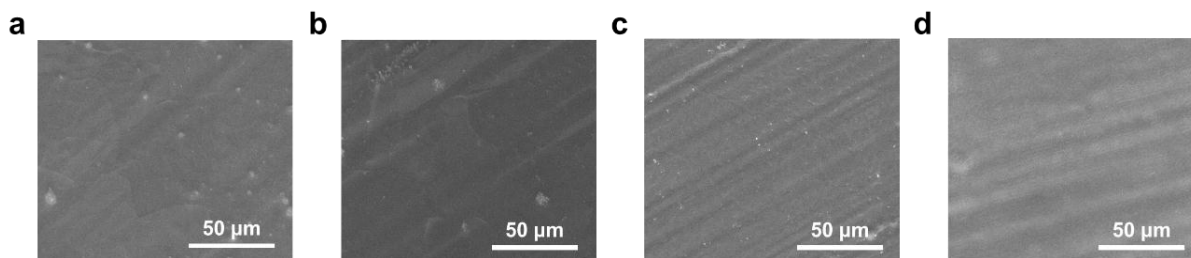
Figure S7. SEM images of RGBNNT prepared from (a) method 1; (b) method 2; (c) method 3; and (d) method 4. Very few BNNT bundles were observed.
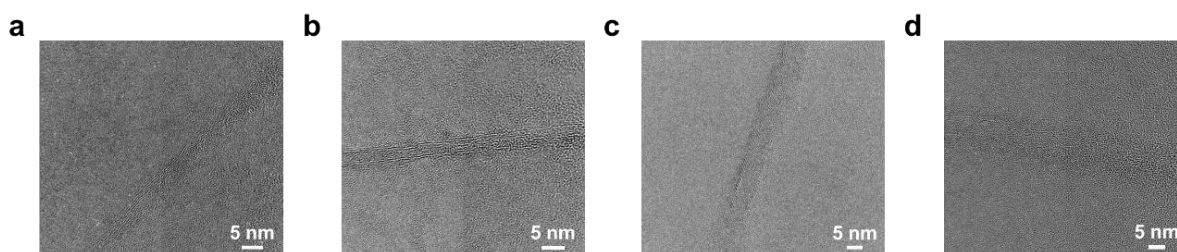

Figure S8. TEM images of a BNNT within RGBNNT prepared from (a) method 1; (d) method 2; (c) method 3; and (d) method 4.
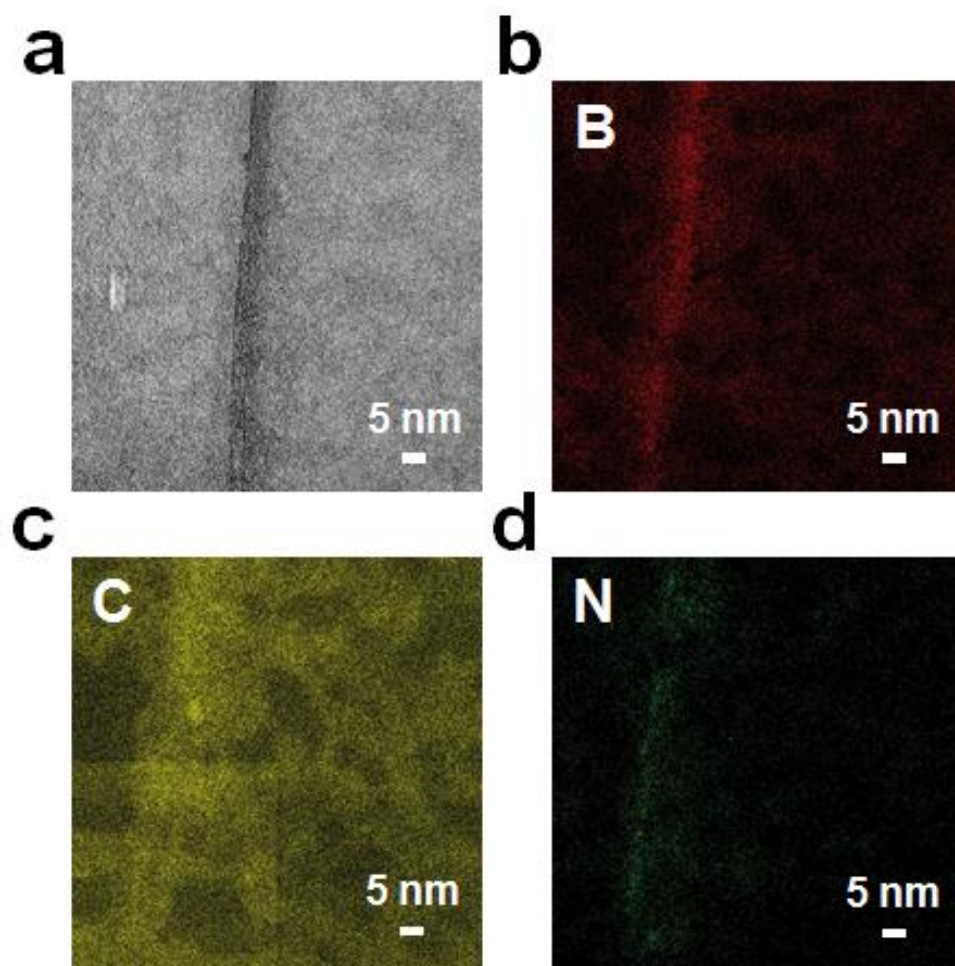
Figure S9. EELS elemental mapping of a BNNT within RGBNNT prepared from method 1. (a) TEM image of the BNNT and graphene. (b-d) Elemental distribution of B, C, N, respectively. The mismatch in BNNT position comes from the image drift during TEM imaging.
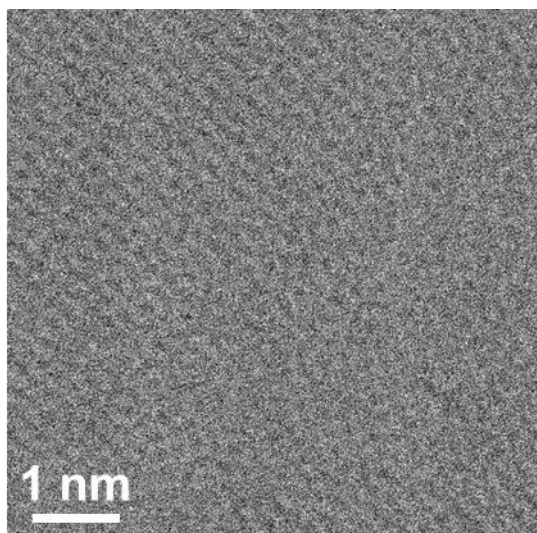
Figure S10. A BF-STEM image of RGBNNT (method 3), same image as Figure 3a but without filter.
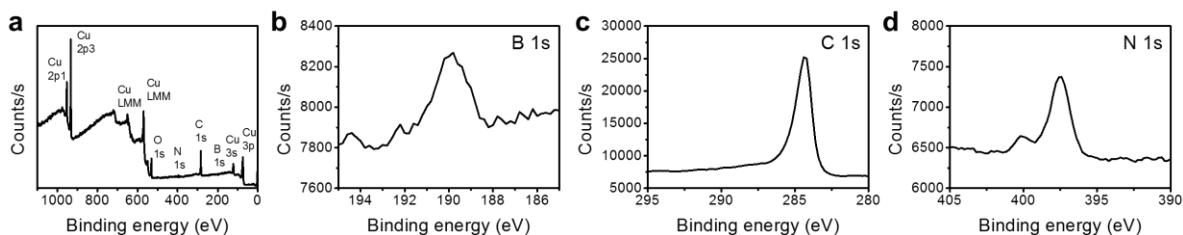

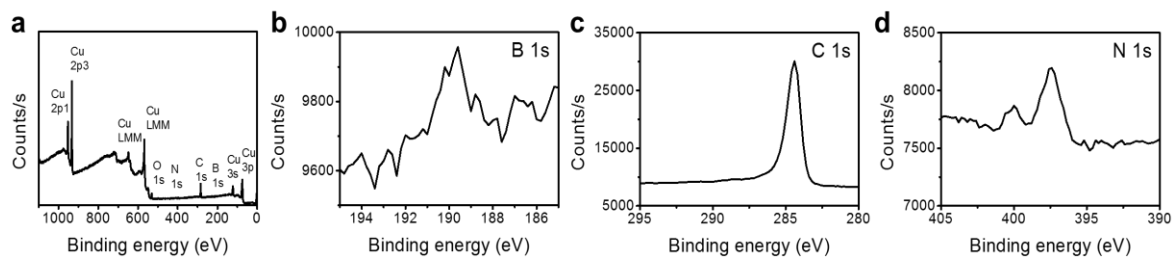**Figure S11.** The XPS spectra of RGBNNT (method 1). (a) Survey, (b) B 1s, (c) C 1s, (d) N 1s.

Figure S12. The XPS spectra of RGBNNT (method 2). (a) Survey, (b) B 1s, (c) C 1s, (d) N 1s.
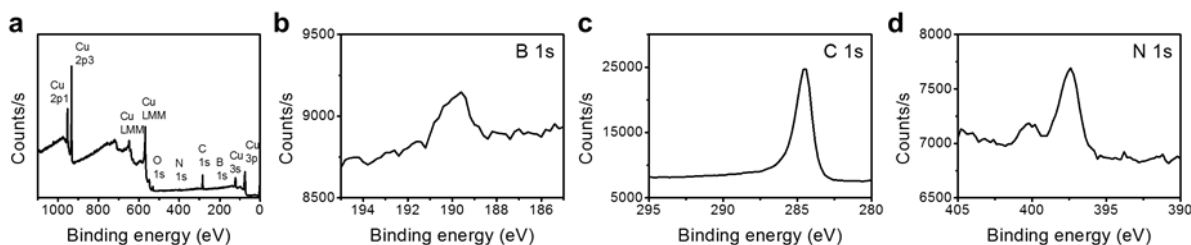
Figure S13. The XPS spectra of RGBNNT (method 3). (a) Survey, (b) B 1s, (c) C 1s, (d) N 1s.
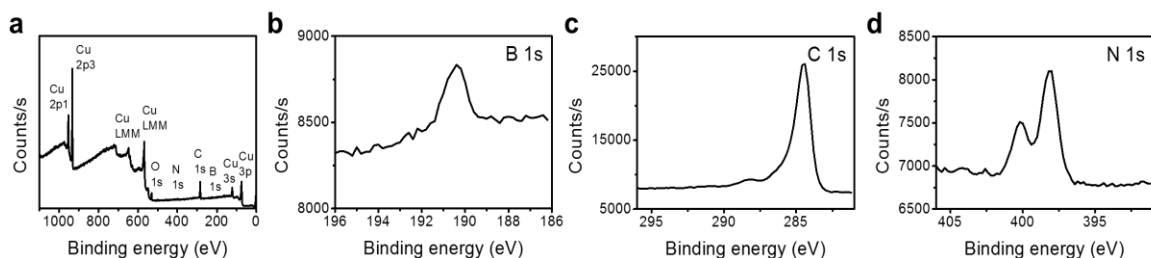

Figure S14. The XPS spectra of RGBNNT (method 4). (a) Survey, (b) B 1s, (c) C 1s, (d) N 1s.

References

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