

**Controllable boron doping carbon nanotubes with tunable dopant
functionalities: an effective strategy toward carbon materials with enhanced
electrical properties**

(Supporting information)

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1. CNT synthesis

The CNTs used in the present study were synthesized using a catalytic chemical vapor deposition (CVD). Details of the CNT growth process were similar to that previously described¹⁻². In brief, Fe films (3.0 nm thickness) and an alumina (Al_2O_3) support layer (40 nm thickness) sputtered onto 1 cm \times 1 cm polished silicon (Si) substrates with a silicon dioxide (SiO_2) layer of 600 nm were used as the catalyst films for CNT growth. The CNT were synthesized at one atmospheric pressure in a 3 inch quartz tube furnace with two process steps, including catalyst particle formation and CNT growth. For a typical catalyst particle formation experiment, we first flowed 200 sccm (sccm denotes standard cubic centimeter per minute at 1 atm) helium (He) and 1800 sccm hydrogen (H_2) for 15 minutes while ramping the temperature from room temperature to 810 °C, then keep same gas flow rates for 15 minutes to anneal the catalyst particles. Then CNT growth began for 10 minutes using a water-assisted CVD process at 810 °C with the gas mixture of 100 sccm ethylene (C_2H_4) and 900 sccm H_2 , and 100 ppm water vapor as the carbon precursor and the catalyst preserver and enhancer, respectively. Water vapor of 100 ppm was supplied by passing 1000 sccm He carrier gas through a water bubbler with deionized (DI) water at STP (STP denotes standard condition for temperature and pressure, NIST version) condition. Water vapor concentration was monitored by a single-channel moisture meter (General Electric, MMS 35-211-1-100) coupled with a moisture probe (General Electric, M2LR) installed before the CVD reactor. All gas flows were controlled by mass flow controllers that were carefully calibrated before experiments to precisely control the gas concentrations in the CVD reactor.

Table S1. Summarized reaction conditions of BCNT synthesis and the atomic percentages of different elements identified by XPS in pristine CNTs and different as-produced BCNT samples.

P denotes pristine CNTs.

Sample	Pretreatment	Temperature (°C)	Time (hour)	B (atom %)	C (atom %)	O (atom %)
P	No	1200	4	0	99.55	0.45
A1	No	1000	4	0.08	91.42	8.53
A2	No	1100	4	0.21	92.32	7.47
A3	No	1200	4	0.40	90.14	9.46
B1	Yes	1000	4	0.40	98.01	1.59
B2	Yes	1100	4	1.80	86.49	8.34
B3	Yes	1200	4	2.09	78.75	13.69
B4	Yes	1000	8	2.36	81.22	10.65
B5	Yes	1100	8	3.38	81.85	14.77
B6	Yes	1200	8	3.92	80.56	8.44

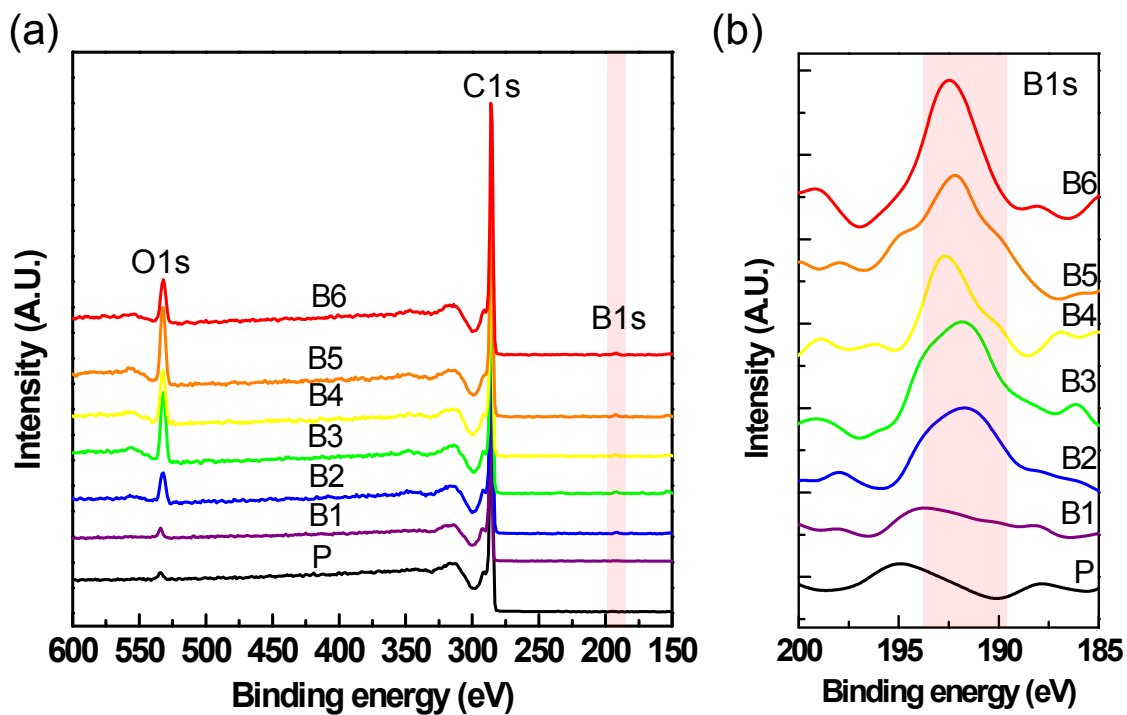


Figure S1 (a) The XPS survey spectra for the starting MWCNTs and the as-produced BCNTs prepared by the developed postgrowth substitution reaction route (Figure 1) under different reaction conditions (Table S1). The peaks assigned to B1s, C1s, and O1s are indicated. (b) The enlarged plot for B1s peaks for starting MWCNTs and the as-produced BCNTs.

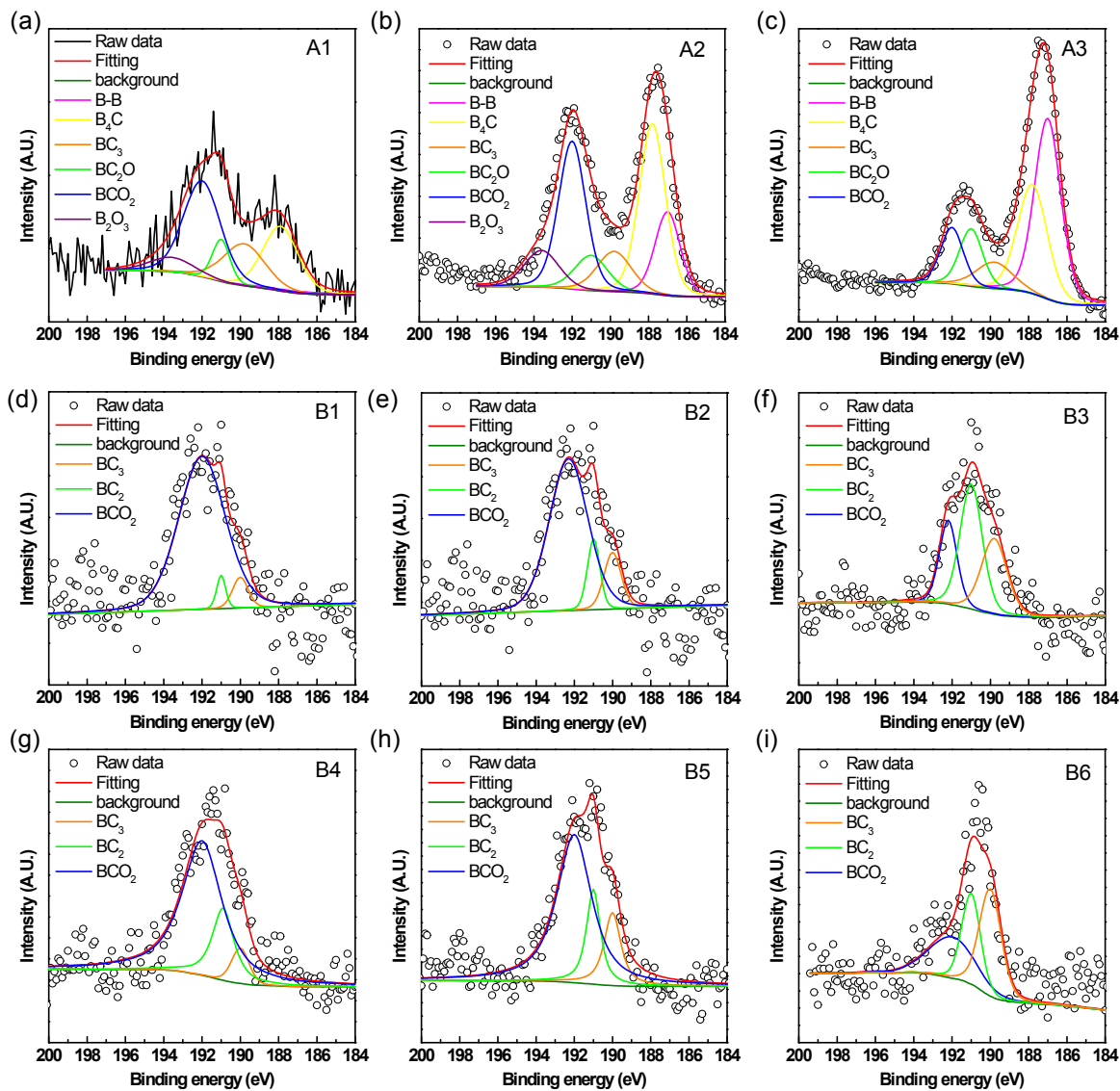


Figure S2 HRXPS spectra of B1s region of as-produced BCNTs prepared by the developed postgrowth substitution reaction route (Figure 1) under different reaction conditions (Table S1)..

Table S2 Summarized atomic percentages of B-B, B₄C, BC₃, BC₂O, BCO₂, and B₂O₃ chemical configurations identified by HRXPS in pristine CNTs and different as-produced BCNT samples.

Sample	B-B (at%)	B ₄ C (at%)	BC ₃ (at%)	BC ₂ O (at%)	BCO ₂ (at%)	B ₂ O ₃ (at%)
P	0	0	0	0	0	0
A1	0	0.02	0.01	0.01	0.02	0.01
A2	0.03	0.07	0.02	0.02	0.06	0.02
A3	0.16	0.11	0.03	0.05	0.04	0
B1	0	0	0.01	0.03	0.36	0
B2	0	0	0.23	0.20	1.37	0
B3	0	0	0.66	0.94	0.50	0
B4	0	0	0.16	0.49	1.71	0
B5	0	0	0.53	0.58	2.26	0
B6	0	0	1.25	1.12	1.55	0

Reference

1. Chiang, W.-H.; Futaba, D. N.; Yumura, M.; Hata, K., Growth Control of Single-Walled, Double-Walled, and Triple-Walled Carbon Nanotube Forests by a Priori Electrical Resistance Measurement of Catalyst Films. *Carbon* **2011**, *49*, 4368-4375.
2. Chiang, W.-H.; Futaba, D. N.; Yumura, M.; Hata, K., Direct Wall Number Control of Carbon Nanotube Forests from Engineered Iron Catalysts. *Journal of Nanoscience and Nanotechnology* **2013**, *13*, 2745-2751.