

Electronic Supplementary Information

Effect of Boron Doping on Electrical Conductivity of Metallicity–Separated Single Walled Carbon Nanotube

Kazunori Fujisawa^{1,2,*}, Takuya Hayashi¹, Morinobu Endo^{1,3}, Mauricio Terrones^{1,3,4} Jin Hee Kim^{5,7} and Yoong Ahm Kim^{6,7,*}

¹Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan.

²Department of Physics and Center for 2-dimensional and Layered Materials (2DLM), The Pennsylvania State University, University park, Pennsylvania 16802, United States.

³Institute of Carbon Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan.

⁴Department of Chemistry and Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States.

⁵Faculty of Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Republic of Korea.

⁶Department of Polymer Engineering, Graduate School, School of Polymer Science and Engineering & Department of Polymer Engineering, Graduate School, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Republic of Korea.

⁷Institute for Biomedical Sciences, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano, Japan.

Corresponding Authors

E-mail address: kuf15@psu.edu (K. Fujisawa), yak@jnu.ac.kr (Y.A. Kim)

Contents

- Raman spectra plotted with relative Raman intensity acquired from the single wall carbon nanotubes (M-SWCNTs) and semiconducting single wall carbon nanotubes (S-SWCNTs).
- Raman spectra of as-received, heat-treated and boron doped M-SWCNTs and S-SWCNTs.
- Scanning electron micrograph of pristine and boron doped M-SWCNTs and S-SWCNTs.
- Aberration corrected transmission electron micrograph of pristine and boron doped M-SWCNTs and S-SWCNTs.
- Table of chemical state of boron atom in boron doped carbon system.
- Table of measured resistivity at room temperature (297 K).

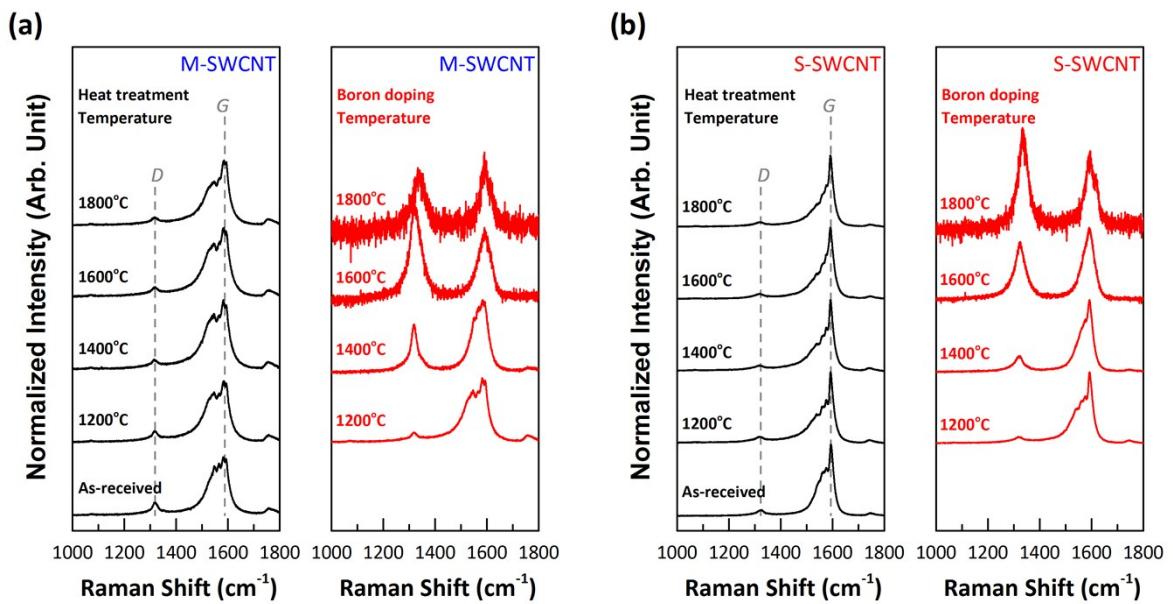


Figure S1. Raman spectra plotted with relative Raman intensity acquired from the metallic (a) and semiconducting (b) SWCNTs before and after heat-treatment, and boron doping.

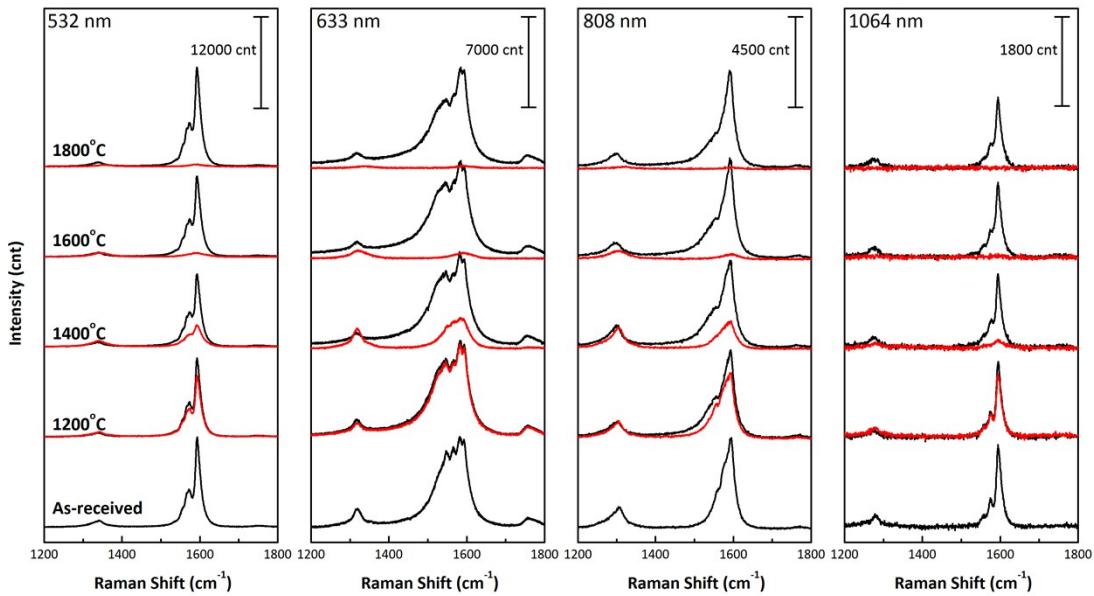


Figure S2. First order Raman spectra showing the D and G bands for the as-received, heat-treated (black line) and boron doped (red line) M-SWCNTs, taken with four different laser lines.

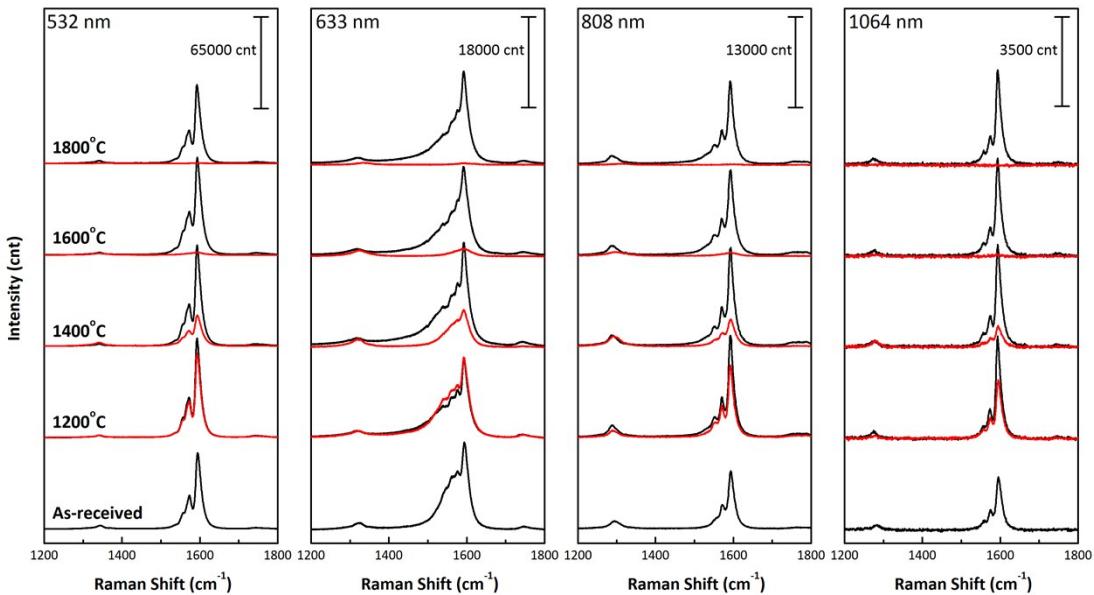


Figure S3. First order Raman spectra showing the D and G bands for the as-received, heat-treated (black line) and boron doped (red line) S-SWCNTs, taken with four different laser lines.

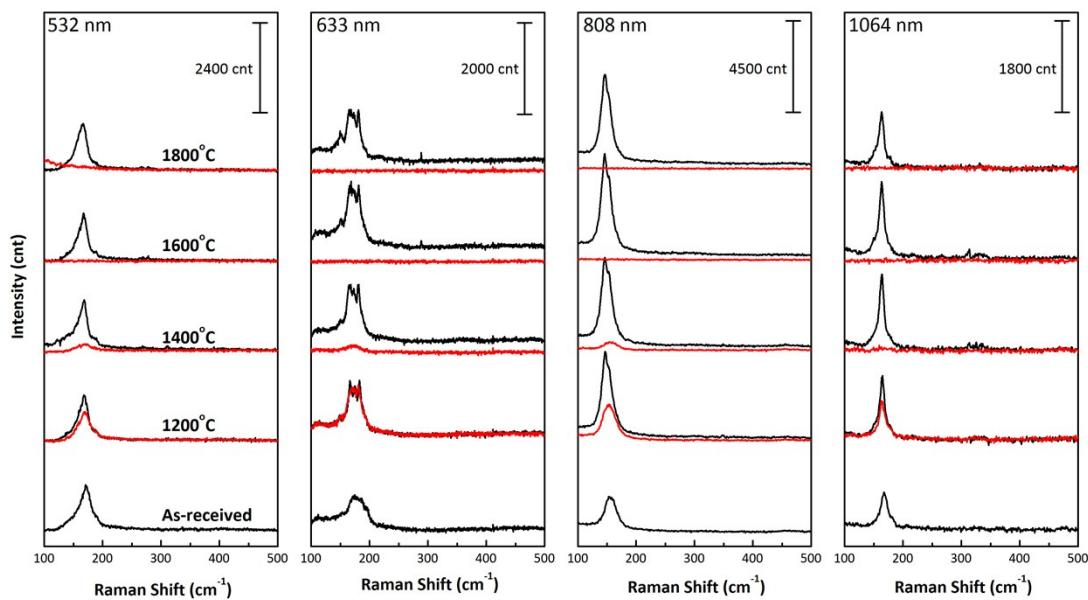


Figure S4. Low-frequency Raman spectra for the as-received, heat-treated (black line) and boron doped (red line) M-SWCNTs, taken with four different laser lines.

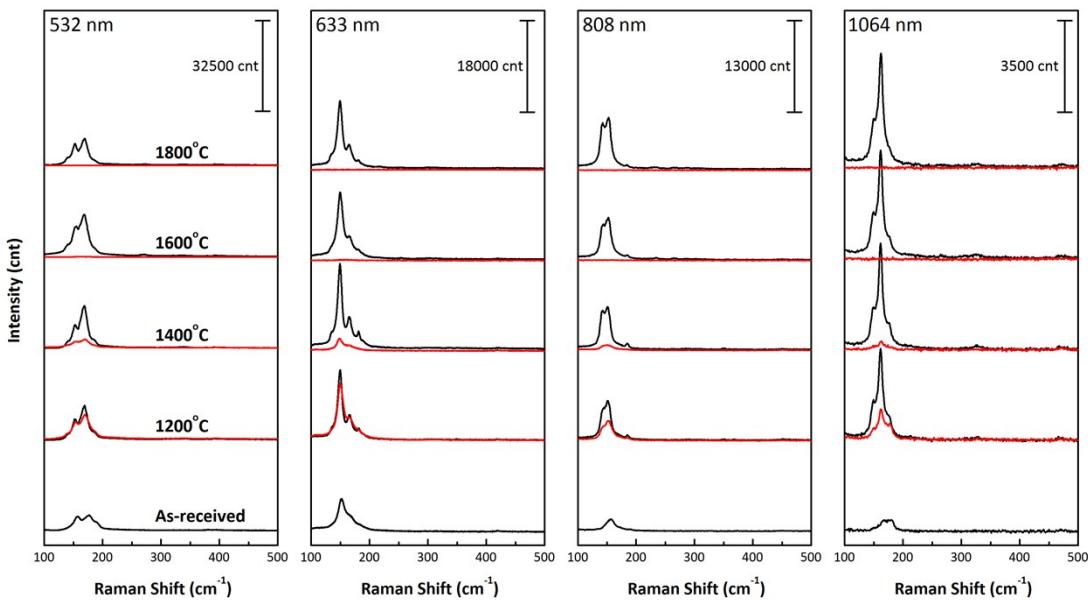


Figure S5. Low-frequency Raman spectra for the as-received, heat-treated (black line) and boron doped (red line) S-SWCNTs, taken with four different laser lines.

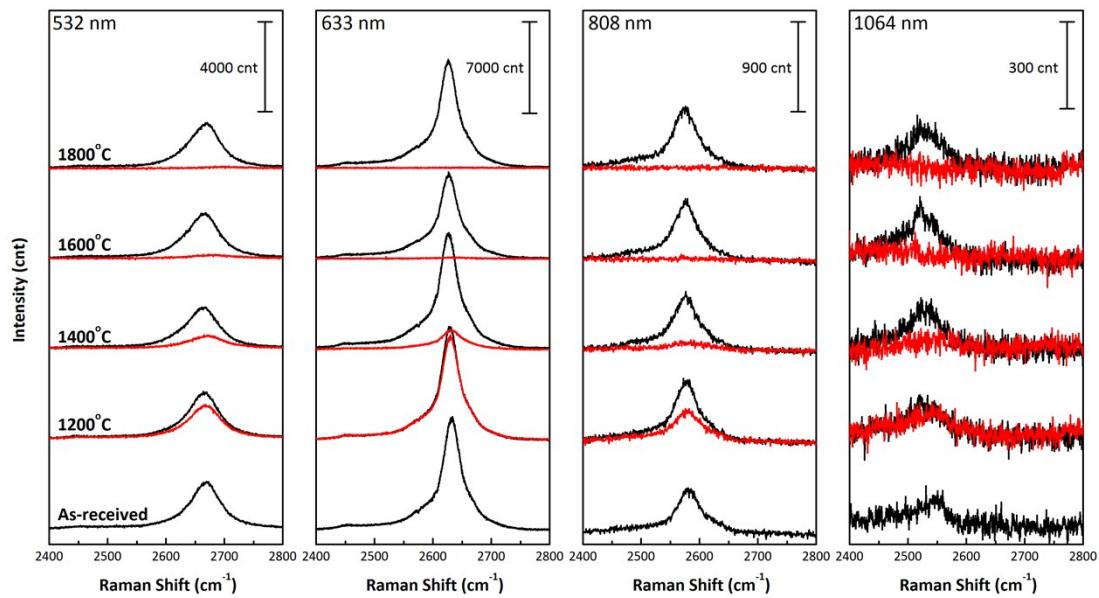


Figure S6. Second order Raman spectra for the as-received, heat-treated (black line) and boron doped (red line) M-SWCNTs, taken with four different laser lines.

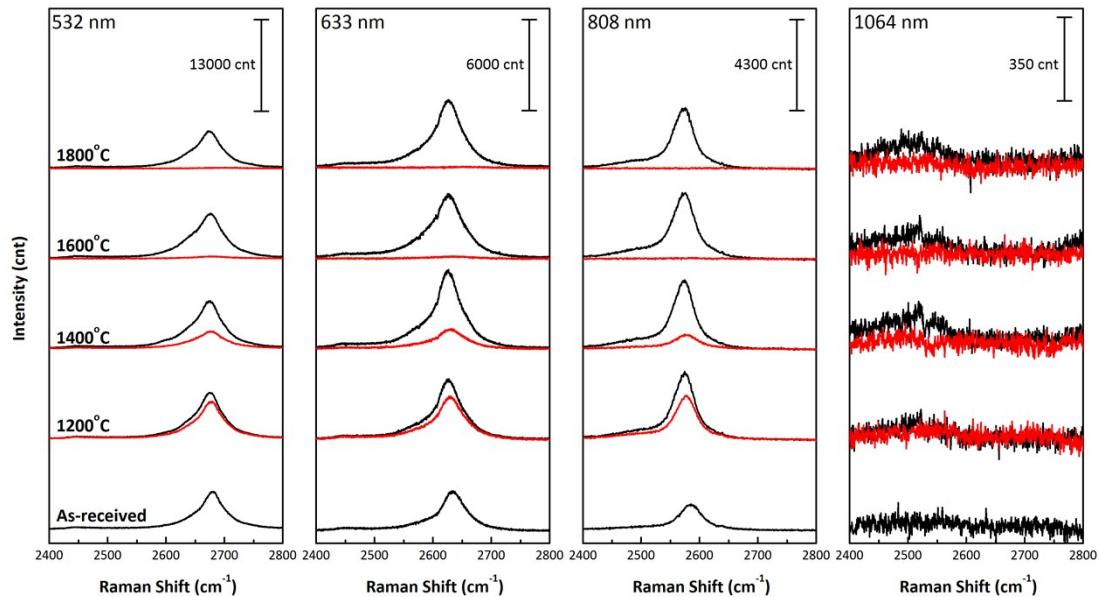


Figure S7. Second order Raman spectra for the as-received, heat-treated (black line) and boron doped (red line) S-SWCNTs, taken with four different laser lines.

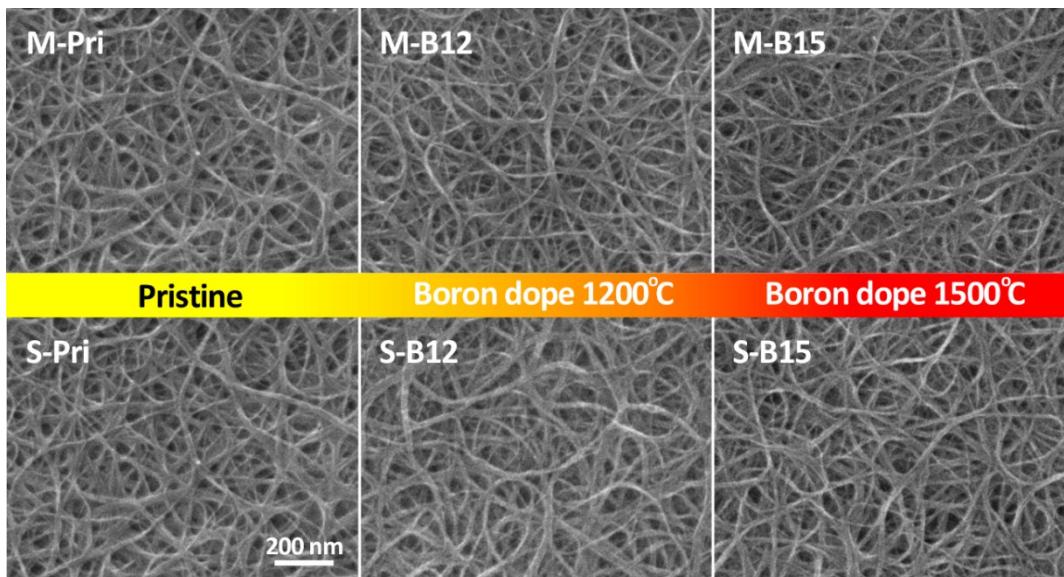


Figure S8. Scanning electron microscopic images of the pristine and boron doped M-SWCNTs and S-SWCNTs. There is no distinctive change in the surface morphology before and after boron doping.

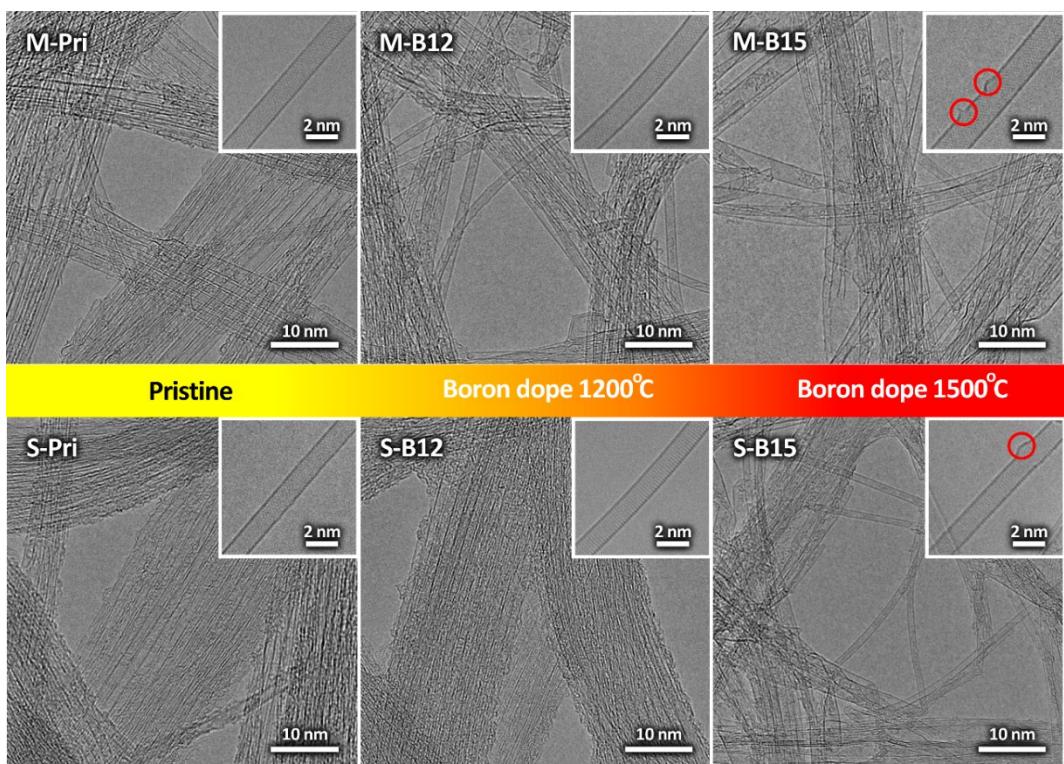


Figure S9. Aberration corrected high resolution transmission electron microscopic images of the pristine and boron doped M-SWCNTs and S-SWCNTs. The red circles in the inset for SWCNTs doped at 1500°C indicate structural defect possibly caused by the incorporation of boron atoms and the formation of BC₃ domain.

Table S1 Chemical state of boron atom in boron doped carbon system.

Material	Precursor	Peak Position	Assignment	Reference
B-pyrocarbon [1]	Boron Chloride (BCl_3)	186.5	B Cluster	
		187.8	B_4C	
		188.8	BC_3	
		190.0	BC_2O	
		192.0	BCO_2	
		193.2	B_2O_3	
B-DWCNT [2]	Borane (BH_3)	191.4	BC_3	
B-SWCNT [3]	Triisopropyl Borate ($\text{C}_9\text{H}_{21}\text{BO}_3$)	187.0	Elemental Boron	
		190.0	BC_3 in Carbon	
		191.5-192.1	BC_3 in SWCNT	Referring [2]
		198.0	-	
		199.5	-	
B-Graphene [4]	Diborane (B_2H_6), Boron-stuffed Graphite	189.0	BC_3	Referring [2]
B-Graphene [5]	Boron Oxide (B_2O_3)	187.7	B_4C	
		189.0	BC_3	
		190.4	BC_2O	Referring [2], [3]
		191.9	BCO_2	
B-Graphene [6]	Boric Acid (H_3BO_3)	186.7	B_4C	
		187.1	Elemental Boron	Referring [4]
		190.6	BC_3	
B-Graphene [7]	Trimethylboron ($\text{B}(\text{CH}_3)_3$)	189.7	B-C	Referring [2], [3]
B-Graphene [8]	Phenylboronic Acid ($\text{C}_6\text{H}_7\text{BO}_2$)	190.9	BC_3	Referring [2]
B-Graphene/ Ni(111) [9]	Triethylborane ($\text{C}_6\text{H}_{15}\text{B}$)	187.4	BC_3	
B-MWCNT [10]	Triphenylborane ($\text{C}_{18}\text{H}_{15}\text{B}$)	186.5	B Cluster	
		187.5	B_4C	
		189.5	BC_3	
		191.0	BC_2O	Referring [1]
		192.3	BCO_2	
		193.0	B_2O_3	
B-MWCNT [11]	Triphenylborane ($\text{C}_{18}\text{H}_{15}\text{B}$)	186.6	B Cluster	
		187.6	B_4C	
		189.5	BC_3	
		191.0	BCN	Referring [1]
		191.4	BC_2O	
		192.5	BCO_2	
B-MWCNT [12]	Diborane (B_2H_6)	191.0	B-C	
		187.9	B_4C	
B-DWCNT [13]	Triisopropyl Borate ($\text{C}_9\text{H}_{21}\text{BO}_3$)	189.0	BC_3	
		190.0	BC_2O	Referring [1]
		192.0	BCO_2	
		193.2	B_2O_3	
B-SWCNT [14]	CoNiB Amorphous Alloy	190.1	B-C	
		192.6	B-O	
B-SWCNT [15]	Boron Oxide (B_2O_3)	191.5	BC_3	
		192.8	B_2O_3	Referring [3]
C_{59}B [16]	Boron Nitride (BN), Boron Carbide (B_4C), Boron	188.8	BC_3	
		192.4	H_3BO_3 , B_2O_3	

Table S2. Resistivity of the pristine and boron doped SWCNT sheets measured at 297 K.

I.D.	Pristine	Resistivity at 297 K ($\Omega \cdot \text{cm}$)			
		Boron doping temperature ($^{\circ}\text{C}$)			
		1200	1300	1400	1500
Metallic	3.02×10^{-4}	3.19×10^{-4}	1.07×10^{-3}	1.27×10^{-3}	1.36×10^{-3}
Un-separated	5.60×10^{-3}	3.58×10^{-3}	3.34×10^{-3}	3.11×10^{-3}	3.17×10^{-3}
Semiconducting	2.50×10^{-1}	1.79×10^{-2}	1.03×10^{-2}	8.16×10^{-3}	5.63×10^{-3}

Reference:

- [1] S. Jacques, A. Guette, X. Bourrat, F. Langlais, C. Guimon, and C. Labrugere, Carbon N. Y. **34**, 1135 (1996).
- [2] L. S. Panchakarla, A. Govindaraj, and C. N. R. Rao, ACS Nano **1**, 494 (2007).
- [3] P. Ayala, W. Plank, A. Grüneis, E. I. Kauppinen, M. H. Rümmeli, H. Kuzmany, and T. Pichler, J. Mater. Chem. **18**, 5676 (2008).
- [4] L. S. Panchakarla, K. S. Subrahmanyam, S. K. Saha, A. Govindaraj, H. R. Krishnamurthy, U. V. Waghmare, and C. N. R. Rao, Adv. Mater. **21**, NA (2009).
- [5] Z.-H. Sheng, H.-L. Gao, W.-J. Bao, F.-B. Wang, and X.-H. Xia, J. Mater. Chem. **22**, 390 (2012).
- [6] T. Wu, H. Shen, L. Sun, B. Cheng, B. Liu, and J. Shen, New J. Chem. **36**, 1385 (2012).
- [7] Y.-B. Tang, L.-C. Yin, Y. Yang, X.-H. Bo, Y.-L. Cao, H.-E. Wang, W.-J. Zhang, I. Bello, S.-T. Lee, H.-M. Cheng, and C.-S. Lee, ACS Nano **6**, 1970 (2012).
- [8] H. Wang, Y. Zhou, D. Wu, L. Liao, S. Zhao, H. Peng, and Z. Liu, Small **9**, 1316 (2013).
- [9] W. Zhao, J. Gebhardt, K. Gotterbarm, O. Höfert, C. Gleichweit, C. Papp, A. Görling, and H.-P. Steinrück, J. Phys. Condens. Matter **25**, 445002 (2013).
- [10] L. Yang, S. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Wang, Q. Wu, J. Ma, Y. Ma, and Z. Hu, Angew. Chemie **123**, 7270 (2011).
- [11] Y. Zhao, L. Yang, S. Chen, X. Wang, Y. Ma, Q. Wu, Y. Jiang, W. Qian, and Z. Hu, (2013).
- [12] R. B. Sharma, D. J. Late, D. S. Joag, A. Govindaraj, and C. N. R. Rao, Chem. Phys. Lett. **428**, 102 (2006).
- [13] S. C. Lyu, J. H. Han, K. W. Shin, and J. H. Sok, Carbon N. Y. **49**, 1532 (2011).
- [14] B. Wang, Y. Ma, Y. Wu, N. Li, Y. Huang, and Y. Chen, Carbon N. Y. **47**, 2112 (2009).
- [15] B. Anand, R. Podila, P. Ayala, L. Oliveira, R. Philip, S. S. Sankara Sai, A. A. Zakhidov, and A. M. Rao, Nanoscale **5**, 7271 (2013).
- [16] H.-J. Muhr, R. Nesper, B. Schnyder, and R. Kötz, Chem. Phys. Lett. **249**, 399 (1996).