

Aqueous Noncovalent Functionalization and Controlled Near-Surface Carbon Doping of Multiwalled Boron Nitride Nanotubes

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Boron nitride nanotubes (BNNTs), known as the III–VI homologue of carbon nanotubes (CNTs), are structurally identical to CNTs except that the C atoms are replaced by alternating B and N atoms.¹ Similar to their C counterpart, BNNTs have remarkable mechanical properties and thermal conductivity.¹ But in contrast to the uncontrollable metallic or semiconducting behaviors of CNTs, BNNTs possess a uniform electronic bandgap (~ 5.5 eV) that is independent of the tube diameter and chirality.^{1,2} Further band gap tuning of BNNTs is also possible through, for example, applying transverse electric field,³ deformation,⁴ and doping.^{1,5} Of particular interest is the substitutional C-doping. In light of the marked structural similarities between BNNTs and CNTs and the possibilities to create a whole range of B–C–N ternary phases by controlling the doping levels, there is a fairly wide scope for the BNNT bandgap engineering through C-doping.^{1,5a,b}

The opportunity to exploit the applications of nanotube materials relies largely on their successful manipulation; in many cases, sidewall chemical functionalization is an important first step.⁶ Over the past decade, while the CNT chemistry has been extensively studied,⁶ the chemical functionalization of BNNTs has remained relatively unexplored.⁷ Herein, we report the noncovalent functionalization of BNNTs in aqueous solution through π -stacking of an anionic perylene derivative, namely perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS, Figure 1a). PTAS functionalization affords a well-controlled modification of nanotube surfaces with the carboxylate functional groups and thus imparts aqueous solubility to BNNTs. On the basis of PTAS functionalization, an innovative methodology for the controlled near-surface C-doping of BNNTs was further demonstrated: through controlled vacuum-annealing of the functionalized nanotubes, thermal degradation of the grafted PTAS molecules will lead to the generation of tiny graphitic C species which can be incorporated into the outmost tube-shells of host BNNTs (multiwalled) through a slow C/BN substitution reaction process.^{1,8} Transport experiments revealed that, as a consequence of C-doping, the electronic properties of BNNTs had been delicately modified.

High-purity multiwalled BNNTs were grown by a chemical vapor deposition (CVD) method.⁹ A representative transmission electron microscopy (TEM) image of BNNTs is displayed in Figure 1b. By simple ultrasonication of BNNTs in an aqueous solution of PTAS followed by filtration, washing, redispersing, and dialysis to remove any unbound free PTAS molecules (see Supporting Information), we obtained the PTAS-functionalized BNNTs (denoted as PTAS-BNNTs hereafter). While the pristine BNNTs show no solubility in water, the functionalized nanotubes are easily soluble in aqueous

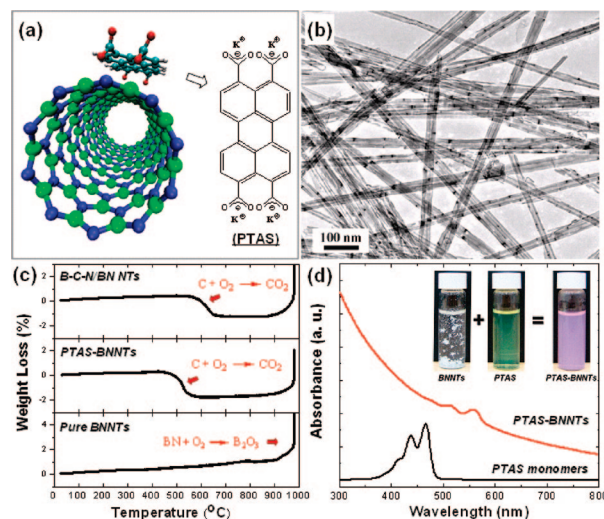


Figure 1. (a) Schematic of PTAS functionalization of BNNTs. (b) A representative TEM image of the starting pure BNNTs. (c) Comparative TGA curves of pure BNNTs, PTAS-BNNTs, and C-doped B–C–N/BN tubes, measured in air at a heating rate of 10 °C/min. (d) UV–visible absorption spectra of PTAS-BNNTs and the monomeric PTAS in a dilute aqueous solution; inset shows optical photographs of pure BNNTs, PTAS, and PTAS-BNNTs in aqueous solution.

solution, with accessible concentrations up to ~ 0.3 mg/mL. Thermogravimetric analyses (TGA) of PTAS-BNNTs revealed a steady mass loss between ca. 450 and 550 °C in a manner typical of sidewall functionalization,⁶ as shown in Figure 1c. According to TGA, the amount of attached PTAS was estimated to be around 2 wt %, regardless of the initial PTAS concentration in solution.

The easy grafting of BNNTs by PTAS implies that there are strong π – π interactions between the molecules and nanotubes. This is manifested in a ~ 102 nm bathochromic shift of the chromophore absorption band of PTAS-BNNTs relative to that of PTAS monomers (Figure 1d). Such a distinct red-shift can only be rationalized in terms of the substantially strong electronic interactions between PTAS and BNNTs in the ground state.^{6c,7d} Also noteworthy is the observation that, upon binding with BNNTs, the PTAS fluorescence is almost entirely quenched by the nanotubes (Figure S2), indicative of the efficient electron and/or energy transfer between the excited PTAS molecules and BNNTs.^{6c,7d}

The aqueous solubility of PTAS-BNNTs is a consequence of the presence of plenty of surface-attached COO^- functional groups, which create a cloud of negative charge around the nanotubes. The carboxylate functionalities not only impart solubility to BNNTs but also make the functionalized nanotubes chemically active. As expected, PTAS-BNNTs are pH-responsive in aqueous solutions

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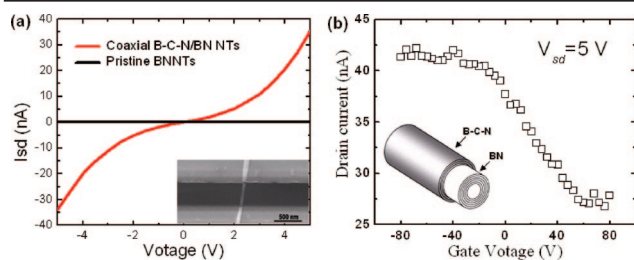


Figure 2. (a) Two-terminal I - V curves recorded from an individual pristine BNNT and a coaxial B-C-N/BN nanotube. Inset shows a scanning electron micrograph of the B-C-N/BN nanotube with Ti/Au metal contacts. (b) Transfer characteristic of the prototype B-C-N/BN nanotube FET. Inset is a schematic illustration of the B-C-N/BN coaxial nanotubes.

and exhibit superior metal binding ability with a large variety of aqueous metal ions (Figures S3 and S4). The carboxylic functionalization of CNTs has long been known,⁶ and herein carboxylate-functionalized BNNTs are reported for the first time. We thus believe this work may open a new avenue for BNNTs chemical processing and application.

The conversion of PTAS-BNNTs to the C-doped BNNTs was realized by controlled vacuum heating (2 °C/min) of the nanotube samples to 1180 °C and isothermal annealing at this temperature over ~2 h.¹⁰ The first evidence of the formation of C-doped BNNTs comes from the TGA results. As shown in Figure 1c, the oxidation of the graphitic carbon within doped BNNTs takes place at 590–650 °C. This temperature range is much higher than in the case of molecular C in PTAS-BNNTs and is well in line with the previously reported TGA data for B-C-N nanotubes.¹¹ As expected, the Raman spectra of doped BNNTs (Figure S5) show the activation and broadening of G and D bands, which, as documented in previous studies,¹² are characteristic Raman scattering features of the B-C-N nanotubes. Besides the G and D bands, also seen from the Raman spectra of doped nanotubes is the retained E_{2g} band of the BN phase.⁷ Keeping in mind that the starting BNNTs are multishelled, this result means that C-doping is occurring only within the outermost few tube shells, while leaving the inner BN layers intact. In other words, the present C-doped BNNTs are composed of the BN core layers and the coaxial B-C-N outer layers. Further analyses of the spatial distribution of B, C, and N species by the spatially resolved EELS technique (Figure S6) have convincingly confirmed that the doped nanotubes indeed possess the heterogeneous B-C-N/BN structure with a defined core-shell geometry.¹³ High-resolution TEM (HRTEM) examination of the heterogeneous B-C-N/BN nanotubes revealed that they had preserved the nonbuckled tube-wall structures (Figure S7), similar to the starting BNNTs.

Conclusive evidence for the successful doping of C into BNNTs was further provided by the transport experiments.¹⁴ Figure 2a displays the comparative I - V curves recorded from individual pristine and doped nanotubes. In line with the previous theoretical and experimental results,^{1,5} the pristine BNNT is electrically insulating and exhibits a resistance of more than 10 G Ω . By contrast, the doped B-C-N/BN tube reveals a dramatically enhanced transport, suggestive of a semiconducting material, with an electrical resistance 2 orders of magnitude lower than that of pure BNNTs. Through further measurements on the prototype field-effect transistors (FETs), the semiconducting B-C-N/BN nano-

tubes were identified to be of p -type (Figure 2b). This result is reminiscent of the previously reported ternary BC₂N films that were also found to be p -type semiconductors.¹⁵ Here it is worth noting that, due to a relatively thick SiO₂ gate dielectric layer (~500 nm) used in the present B-C-N/BN nanotube FETs, the observed gate voltage response for transport modulation was still rather weak. The FET design optimization by integrating thin high- κ dielectric gate oxide layers is now being pursued.

To sum up, the results presented in this study highlight two major findings: (i) noncovalent functionalization of BNNTs in the aqueous solution, through which the carboxylate-functionalized BNNTs have been prepared for the first time, and (ii) an innovative methodology for the controlled near-surface C-doping of BNNTs. As a result of doping, novel B-C-N/BN coaxial nanotubes have been fabricated on a large scale, and their p -type semiconducting behaviors were elucidated through gate-dependent transport measurements.

Acknowledgment. Financial support from MEXT of Japan and NSF (No. 50702074) of China is acknowledged.

Supporting Information Available: Experimental details, EELS and fluorescence spectra of PTAS-BNNTs, pH and metal ion response of PTAS-BNNTs, Raman and spatially resolved EELS spectra, and a representative HRTEM image of the coaxial B-C-N/BN nanotubes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Golberg, D.; Bando, Y.; Tang, C. C.; Zhi, C. Y. *Adv. Mater.* **2007**, *19*, 2413, and references cited therein.
- (2) Blase, X.; Rubio, A.; Louie, S. G.; Cohen, M. L. *Europhys. Lett.* **1994**, *28*, 335.
- (3) Ishigami, M.; Sau, J. D.; Aloni, S.; Cohen, M. L.; Zettl, A. *Phys. Rev. Lett.* **2005**, *94*, 056 804.
- (4) Bai, X. D.; Golberg, D.; Bando, Y.; Zhi, C. Y.; Tang, C.; Mitome, M.; Kurashima, K. *Nano Lett.* **2007**, *7*, 632.
- (5) (a) Miyamoto, Y.; Rubio, A.; Cohen, M. L.; Louie, S. G. *Phys. Rev. B* **1994**, *50*, 4976. (b) Golberg, D.; Dorozhkin, P.; Bando, Y.; Dong, Z.-C. *MRS Bull.* **2004**, *29*, 38. (c) Tang, C.; Bando, Y.; Huang, Y.; Yue, S.; Gu, C.; Golberg, D. *J. Am. Chem. Soc.* **2005**, *127*, 6552.
- (6) (a) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105. (b) Hirsch, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853. (c) Guldi, D. M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1400.
- (7) (a) Zhi, C.; Bando, Y.; Tang, C.; Xie, R.; Sekiguchi, T.; Golberg, D. *J. Am. Chem. Soc.* **2005**, *127*, 15996. (b) Xie, S.-Y.; Wang, W.; Shiral Fernando, K. A.; Wang, X.; Lin, Y.; Sun, Y.-P. *Chem. Commun.* **2005**, 3670. (c) Zhi, C.; Bando, Y.; Tang, C.; Honda, S.; Sato, K.; Kuwahara, H.; Golberg, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7932. (d) Huang, Q.; Sandanayaka, A. S. D.; Bando, Y.; Zhi, C.; Ma, R.; Shen, G.; Golberg, D.; Zhao, J.; Araki, Y.; Ito, O.; Gao, L. *Adv. Mater.* **2007**, *19*, 934.
- (8) (a) Han, W.; Bando, Y.; Kurashima, K.; Sato, T. *Appl. Phys. Lett.* **1998**, *73*, 3085. (b) Golberg, D.; Dorozhkin, P.; Bando, Y.; Hasegawa, M.; Dong, Z. C. *Chem. Phys. Lett.* **2002**, *359*, 220.
- (9) Tang, C.; Bando, Y.; Sato, T.; Kurashima, K. *Chem. Commun.* **2002**, 1290.
- (10) Here we emphasize that, to successfully obtain the C-doped BNNTs, it is critical to control the thermal degradation behavior of PTAS on the BNNT surfaces by applying a well-controlled slow heating rate such as 1–2 °C/min. See Supporting Information for details.
- (11) Han, W. Q.; Mickelson, W.; Cumings, J.; Zettl, A. *Appl. Phys. Lett.* **2002**, *81*, 1110.
- (12) (a) Zhi, C. Y.; Bai, X. D.; Wang, E. G. *Appl. Phys. Lett.* **2002**, *80*, 3590. (b) Piazza, F.; Nocua, J. E.; Hidalgo, A.; Jesus, J. De; Weiss, B. L.; Morell, G. *Diamond Relat. Mater.* **2005**, *14*, 965.
- (13) Kim, S. Y.; Park, J.; Choi, H. C.; Ahn, J. P.; Hou, J. Q.; Kang, H. S. *J. Am. Chem. Soc.* **2007**, *129*, 1705.
- (14) Keeping in mind the coaxial core-shell geometry of B-C-N/BN nanotubes, transport measurements only probed the outermost B-C-N shells which are actually in contact with the metal leads.
- (15) Watanabe, M. O.; Itoh, S.; Mizushima, K.; Sasaki, T. *J. Appl. Phys.* **1995**, *78*, 2880.

JA8020878