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Isolation of Individual Boron Nitride Nanotubes via Peptide Wrapping

Zhenghong Gao,[†] Chunyi Zhi,[‡] Yoshio Bando,[‡] Dmitri Golberg,[‡] and Takeshi Serizawa*[,†]

Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan and International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received December 4, 2009; E-mail: t-serizawa@bionano.rcast.u-tokyo.ac.jp

Boron nitride nanotubes (BNNTs), a rising wide band gap semiconductor, have been given considerable attention, since they were theoretically predicted in 1994.[1] BNNTs have an analogous structure to carbon nanotubes (CNTs) but exhibit properties different from those of CNTs in many aspects. BNNTs possess a wide band gap, ca. 5.5 eV, independent of chirality and diameter,[1] superb elasticity and strength,[2] high thermal conductivity,[3] good electrical insulation,[1] unique luminescence,[4] high resistance to oxidation,[5] and biocompatibility.[6] Therefore, BNNTs have the most promising application perspectives in nanocomposite materials,[7] nanoscale electrical devices,[1,8] biomedical fields,[6] and optical systems working under extreme conditions.[7]

However, there are several key obstacles hindering their applications. First, similar to CNTs, almost all forms of BNNTs are insoluble in any solvents.[7] Second, the isolation of individual BNNTs is a prime challenge, because it is a fundamentally unavoidable step for any further applications.[9] In addition, the development of practical methods for functionalizing BNNTs is also necessary for various technologies. In the case of CNTs, many efforts have been undertaken with respect to dispersion, isolation, and functionalization. Regarding environmentally and biomedically favorable aqueous systems, wrapping CNTs with biomolecules such as peptides,[10] DNAs,[11] and lipids[12] has been reported in detail. This led to good individual dispersion[10−12] and potential hierarchical self-assembly.[13] However, the interactions between BNNTs and biomolecules including proteins,[14] DNAs,[14] and cells[6] in which the $\pi-\pi$ interactions are considered to play an important role have just started to draw attention recently. Herein, we present how to disperse BNNTs into aqueous media and how to isolate individual BNNTs applying a novel combinational method of peptide wrapping and sonication procedures, and we also exploit the strong $\pi-\pi$ interactions between BNNTs and peptides using fluorescence (FS), Fourier-transformed infrared (FT-IR), and ultraviolet−visible (UV/vis) absorption spectroscopies. This new pathway not only may be effective for isolating BNNTs in aqueous media but also may offer potential opportunities for functionalizing BNNTs and expanding their future applications.

Highly pure multiwalled BNNTs were synthesized by a carbon-free chemical vapor deposition method, as reported elsewhere.[15] A peptide named B3 (HWSAWWIRSNQS) and previously selected for CNTs from a phage-displayed peptide library was rich in aromatic groups.[16] This peptide strongly interacted with CNTs via $\pi-\pi$ interactions. We anticipated that B3 could also interact with BNNTs via the same interactions. In a typical experiment, 1.5 mg of BNNTs were added into aqueous solutions containing 100 μM B3 with a total volume of 3 mL and then the mixed solution was sonicated for 3 h, followed by centrifugation at 2000 rpm for 25 min to remove insoluble materials. The supernatants were slightly turbid (Figure 1a) and could be kept for several weeks at ambient environment. Experimental details are summarized in the Supporting Information.

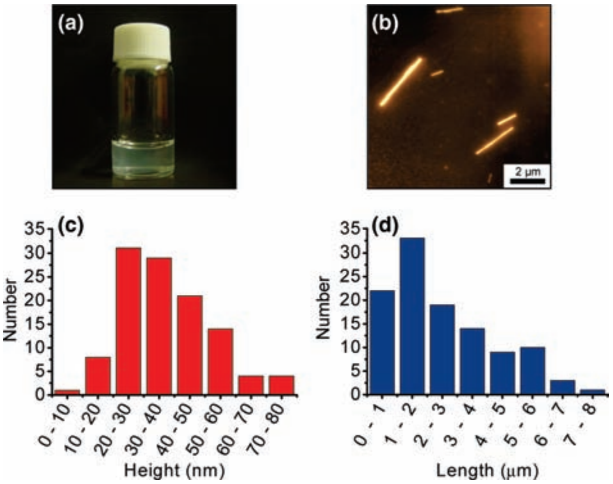

Figure 1. (a) Dispersed solution of B3/BNNT complexes, (b) AFM image of the complexes, and statistical AFM (c) height and (d) length analyses of the complexes collected from 50 different images (the total number of BNNTs was 112).

The B3/BNNT complexes were investigated by atomic force microscopy (AFM). AFM images displayed excellent dispersion of the needle objects on the mica surface (Figure 1b). The statistical analyses indicated the objects with heights less than 80 nm and lengths up to 8 μm (Figure 1c and 1d). The heights were slightly greater than those for the original BNNTs (20−50 nm),[7] suggesting that BNNTs were wrapped with B3. The lengths were slightly shorter than those for the original BNNTs (up to 10 μm);[7] this difference may have originated from partial tube damaging during the sonication procedure. These observations suggest that the needle objects were individual BNNTs wrapped with B3, which were isolated in the aqueous phase.

Circular dichroism (CD) spectra of B3 (Figure S1) revealed that the main chain tended to form the α-helical conformation in the aqueous solution. The spectra did not change in the presence of BNNTs. The structural optimization of B3 based on molecular mechanics resulted in an amphiphilic α-helix, in which all indole groups derived from three tryptophan residues could be located on the same face (Figure S2). It was therefore suggested that these tryptophan residues cooperatively interacted with the hydrophobic BNNT surface via $\pi-\pi$ interactions.

To confirm the importance of $\pi-\pi$ interactions, each tryptophan residue was mutated into alanine. Significantly, any mutation resulted in poor BNNT dispersion (Figure S3), confirming the

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[†] The University of Tokyo.
[‡] National Institute for Materials Science.

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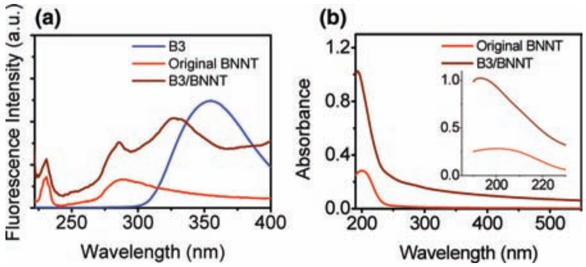

Figure 2. (a) Comparative FS spectra of B3, the original BNNTs, and the complexes and (b) comparative UV/vis absorption spectra of the original BNNTs and the complexes. The inset shows an enlarged portion of the UV/vis absorption spectra between 185 and 240 nm.

cooperative contribution of three tryptophan residues. CD spectra revealed that the α-helix contents of the mutants were smaller than B3 (Figure S4), also suggesting an essential requirement of the conformation. In addition, the shuffled B3 (HWARISNWSQWS) showed poor BNNT dispersion (Figure S3), indicating the importance of the primary sequence.

FS was used to gain insights into the mechanism of $\pi-\pi$ interactions (Figure 2a). Before measurements, we employed a dialysis process against milli-Q water for 24 h to further remove unbound B3. Interestingly, significant changes were observed for peaks assigned to B3 and the BNNT. The peak assigned to the tryptophan residues appeared at 355 nm, while it appeared at 346 nm for the complexes. Importantly, the broad peak at ~290 nm, which should be attributed either to impurities and defect centers or to radiative excitonic dark states,[17] became sharper and its maximum slightly shifted from 289 to 286 nm. It is noteworthy that the sharper profile suggests individualized BNNTs in the aqueous phase. All changes in the relative peak positions suggested that strong charge transfers were indeed presented between B3 and the BNNT due to the anticipated $\pi-\pi$ interactions.

Further investigation was conducted by FT-IR absorption spectroscopy (Figure S5). Specifically, the peaks assigned to the original BNNTs appeared at 771 cm^{-1} and 1347 cm^{-1}, which were assigned to respective E1u (TO) and E1u (LO) modes (TO: transverse optic; LO: longitudinal optic),[4,18] while they appeared at 820 cm^{-1} and 1376 cm^{-1} for the complexes. Meanwhile, the peaks at ~743 cm^{-1}, which were assigned to the strongly infrared active hydrogen out-of-plane in phase bending mode of the benzene ring of the tryptophan residues,[19] disappeared for the complexes. These variations in FT-IR absorption spectra also supported the $\pi-\pi$ interactions existing between the tryptophan residues and the hydrophobic BNNT surface.

It was surprising that a notable blue shift of the UV/vis absorption peak for the BNNT was observed when the spectra were acquired to clarify how the $\pi-\pi$ interactions between B3 and the BNNT affect the electrical structure of BNNTs (Figure 2b). A sharp peak assigned to a band gap transition of BNNTs appeared at 200 nm for the original BNNTs, while it appeared at 193 nm for the complexes. This shift evidenced that the electrical structure of BNNTs was affected by the strong charge transfer derived from the strong $\pi-\pi$ interactions between the BNNT and B3, thereby resulting in the band gap widening. This observation indicates that B3 on the BNNT surface may behave as dopants; the detailed mechanism is going to be investigated more deeply.

In summary, a facile and novel approach for the dispersion and isolation of individual BNNTs from the raw material has been demonstrated by combining peptide wrapping with sonication procedures. AFM observations revealed the excellent isolation of peptide-wrapped BNNTs in aqueous phases. FS and FT-IR absorption spectra indicated that the strong $\pi-\pi$ interactions took place between B3 and BNNT. UV/vis absorption spectra showed a blue shift of 7 nm for the absorption peak. The peptide/BNNT complexes may have promising applications in electronics, optical devices, and biological fields due to excellent dispersion and unique physical properties.

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Supporting Information Available: Detailed experimental procedures and supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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