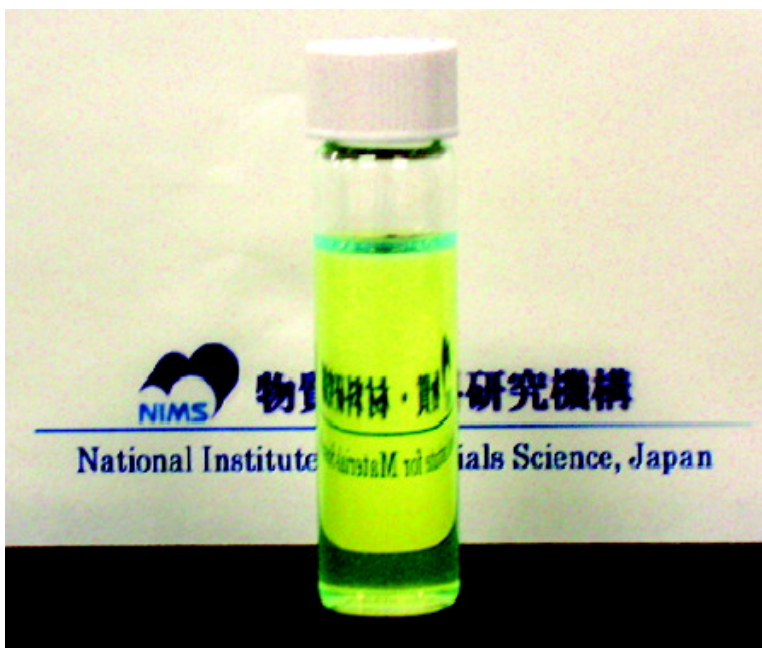## Communication

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Perfectly Dissolved Boron Nitride Nanotubes Due to Polymer Wrapping

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Over the past decade, a significant emphasis has been put onto the research of boron nitride nanotubes (BNNTs) due to their potential applications in prospective electronic and mechanical devices. According to theoretical calculations, BNNT is a wide band gap semiconductor independent of tube radius, chirality, and other geometrical factors.[1] BNNTs have excellent mechanical properties,[2] high thermal conductivity,[3,4] resistance to oxidation, and chemical stability,[5] which makes them most valuable in devices working in hazardous and high-temperature environments.

However, all currently known forms of a BNNT material are insoluble in organic solvents. This has hindered the applications in many prospective fields. For example, the studies of BNNT composites have been lacking since it is extremely difficult to obtain highly pure BNNTs in large quantities. For carbon nanotubes (CNTs), much effort has been put into functionalization and solubilization.[6−8] On the basis of the existing breakthroughs in this field, the applications of CNTs in polymeric composites[9] and compatibility with biological systems[11] have recently been explored in detail. The similar progress on BNNT solubility is awaited.[12] Recently, BNNTs were dissolved via functionalization with poly-(ethyleneglycol).[13] However, carbon contamination could not be avoided since CNT substitution reaction was used to fabricate BNNTs. In addition, the detailed characterization of the solution was absent. In the present communication, highly pure BNNTs were synthesized at high yield by a carbon-free method.[14] BNNTs were further dissolved in various organic solvents through wrapping them with a polymer. Importantly, such wrapping fully preserves the BN nanotube's intrinsic properties due to the sole noncovalent functionalization. A BNNT−polymer composite film was then fabricated, and the interactions between BNNTs and a polymer were investigated. The ultraviolet−visible (UV−vis) absorption spectra of the composite films and well-dispersed uniform BNNT films prepared from BNNT solutions serve as convincing experimental evidences that the soluble BNNTs have a band gap of approximately 5.5 eV.[1]

BNNTs were synthesized by a carbon-free chemical vapor deposition method.[14] A mixture of MgO, FeO, and boron powder was used to in situ produce a catalyst and a boron oxide vapor. Then BNNTs were grown due to the vapor reaction with an ammonia gas at a high temperature. The as-grown BNNTs were further washed with HNO_3 in order to remove the remaining catalyst particles. The purified BNNTs have a pure white color appearance. All peaks of an X-ray diffraction spectrum can be solely attributed to h-BN, which indicates a highly pure boron nitride phase. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigations reveal a perfect crystalline structure of BNNTs with a diameter of 20−50 nm and a length of
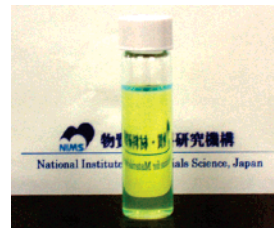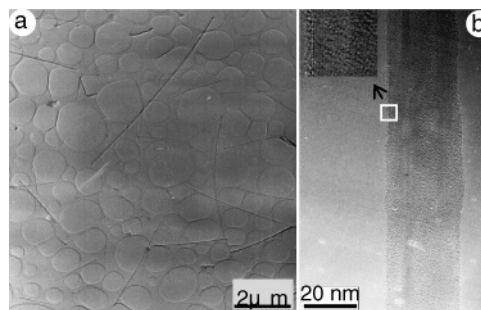
Figure 1. Dilute solution of BNNTs.

Figure 2. (a) Low-magnification TEM image of perfectly dispersed BNNTs. (b) High-resolution TEM image of BNNTs wrapped by PmPV. The inset is the enlarged image of a wrapped BNNT wall fragment.

up to 10 μm. The purity of the present BNNTs can be better than 90 vol %.[15]

The BNNTs were then solubilized via wrapping BNNTs with a conjugated polymer, poly[m-phenylenevinylene-co-(2,5-dioctoxy-p-phenylenevinylene)] (PmPV).[9] The experimental process is simple and thus may be easily scaled up. In a typical experimental run, first, 5 mg of PmPV was dissolved in 20 mL of chloroform, and second, 5 mg of BNNTs was added into the solution. The mixture was sonicated over 2 h at room temperature, followed by centrifugation (2000 rpm) in order to remove insoluble materials. Then a homogeneous solution was obtained, in which no precipitation was observed during a long time keeping at ambient conditions. Dilute BNNT solution is highly transparent, as shown in Figure 1. For this particular solution, the amounts of PmPV, BNNTs, and chloroform were 5 mg, 0.2 mg, and 20 mL, respectively (the yellow color originates from PmPV). The PmPV-wrapped BNNTs were fully soluble in chloroform, N,N-dimethylacetamide, tetrahydrofuran, etc., whereas they were insoluble in water, ethanol, etc.

The dilute BNNT solution was further analyzed by TEM. A drop of pellucid solution was dripped on a carbon-film-coated copper grid, followed by the solvent evaporation. BNNTs in solution exhibited very good dispersion, as shown in Figure 2a. Due to sonication, most soluble BNNTs have a length at 2−6 μm, slightly shorter than that of the original BNNTs. The BNNTs covered by polymer still retained a perfect crystalline structure, as shown in Figure 2b. Typically, BNNTs are nonwetted by most materials.
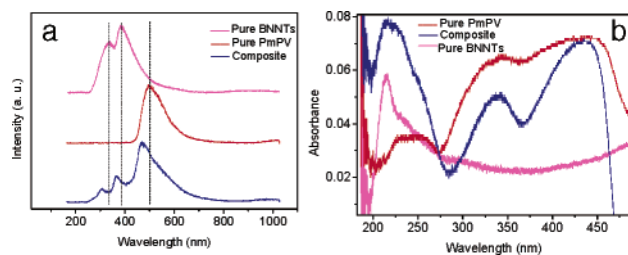
Figure 3. (a) Comparative CL spectra and (b) UV−vis absorption spectra of pure BNNTs, pure PmPV, and a composite made of them.

PmPV has a modified structure of common polyphenylenevinylene (PPV). The chain of this kind of polymer tends to coil, thus forming a helical structure. Similar to the case of CNTs, it is assumed that the coiled polymer conformation allows the nanotubes to be totally wrapped with the polymer. This, in turn, can lead to the intermolecular proximity and occurrence of the prominent $\pi-\pi$ interactions.[7,9,10] It is thought here that these $\pi-\pi$ interactions provide the perfect adhesion between the polymer and the present BNNTs.

The luminescence spectroscopy fully confirmed the significant $\pi-\pi$ interactions between the polymer and BNNTs. Given the fact that BNNTs have light emission in the ultraviolet region,[15] cathodoluminescence (CL) is a good tool to investigate the luminescence properties of the prepared BNNT−PmPV composites. To do so, a few BNNT solution drops were dripped onto a clean silicon wafer. A uniform composite film was then obtained after solvent evaporation. The CL experiment was performed with the use of a field emission SEM. The comparative CL spectra of pure BNNTs, pure PmPV, and the composite made of them are shown in Figure 3a. Two peaks are visible in the spectrum of pure BNNTs, which are thought to originate from B or N vacancies.[18] A single peak at 500 nm dominates the spectrum of pure PmPV. It is surprising that the large blue shifts were observed for the composite−20 and 30 nm for BNNT-related peaks and PmPV-related peaks, respectively. Additional CL experiments demonstrated that the values of blue shifts did not change in a wide composition ratio range between PmPV and BNNTs. It is suggested that the peak shifts arose from the efficient charge transfer between the BNNT and polymer. The charge transfer between the polymer and CNTs is well-known.[7,9] Curran et al.,[9b] while investigating the photoluminescence of PPV/CNT composites, found only a drop in the luminescence intensity, whereas the peak position was kept constant. It seems that BNNTs have even much stronger interactions with a polymer, as compared with CNTs. The detailed features of the present strong $\pi-\pi$ interactions between BNNTs and PmPV require further studies.

It is unfortunate that UV−vis absorption experiments cannot be performed using a solution sample since most of the organic solvents are totally opaque to the light of a wavelength shorter than 250 nm (4.96 eV), while a BNNT has a band gap at approximately 5.5 eV according to the computations. Therefore, a PmPV−BNNT composite was prepared for the UV−vis absorption experiments. Figure 3b shows the UV−vis absorption spectra of a pure polymer and the composite. Three broad peaks are visible in the spectrum of pure PmPV. Note that the highest energy peak becomes broader for the composite spectrum. To reveal the features of BNNTs more clearly, a uniform 2−5 μm thick film made of BNNTs was fabricated through heating the composite to 700 °C in air.[15] This treatment solely removed PmPV, retaining the nanotube fraction.[15] A new peak centered at 5.8 eV appears. This peak is thought to

originate from a band gap transition of BNNTs. Considering the results of CL at a low temperature,[15] the present band gap can be estimated to be between 5.2 and 5.5 eV.[16,17] Finally, it should be noted that the present sample is composed of multi-walled BNNTs. This presumes a mixture of BNNTs of different diameters and chiralities. Therefore, the present experimental results serve as convincing evidence of BNNT band gap independence of geometrical factors.

In summary, BNNTs were functionalized by wrapping them with PmPV. The wrapped BNNTs were soluble in many organic solvents. TEM and CL characterization indicated the strong $\pi-\pi$ interactions between BNNTs and PmPV. UV−vis absorption analysis of BNNT−PmPV composites and thin BNNT films prepared from solution revealed a band gap of approximately 5.5 eV, which is consistent with the theoretical calculations. The newly prepared polymer-wrapped soluble BNNTs may have numerous potential applications in composites[19] and optical devices due to good dispersion and unique luminescence properties.

Supporting Information Available: A photo of 1 g of pure BNNTs (Figure S1); SEM image of BNNTs (Figure S2); X-ray diffraction spectrum of BNNTs (Figure S3); comparative thermogravimetric analysis of BNNT and CNT (Figure S4); low-temperature CL spectrum of BNNTs (Figure S5); SEM image of BNNT film (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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