

Solubilization of boron nitride nanotubes

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A successful attempt in the functionalization and solubilization of boron nitride nanotubes is reported, and a functionalization mechanism based on interactions of amino functional groups with nanotube surface borons is proposed.

There has been much recent interest in boron nitride nanotubes (BNNTs) for their electronic,^{1–3} thermal,^{4–6} and mechanical properties,^{7,8} which are in many cases different from and/or superior to those of carbon nanotubes.⁹ For example, BNNTs are semiconductors with a wide band-gap (4–5 eV) independent of the nanotube chirality or morphology.^{1–3} The thermal conductivity, oxidation resistivity, thermal and chemical stability, and yield resistance of BNNTs are higher than those of their carbon analogs. Among widely discussed unique applications of BNNTs are their use as nanoscale semiconductors operating in oxidative environments at high temperatures^{5,6} and as insulating nanocomposites of high thermal conductivity.^{6,10}

Most investigations in the literature were focused on BNNTs in the solid state, because these nanotubes, like their carbon counterparts, are generally insoluble in common organic and aqueous media.¹¹ For carbon nanotubes, the research efforts on their functionalization and solubilization have stimulated and enabled the exploitation of the properties and applications that are not accessible in the solid state, such as the dispersion of carbon nanotubes in polymeric nanocomposites and the compatibilization with biological systems.^{12,13} Similarly significant effects on the research of BNNTs may be expected from the introduction of the nanotubes into homogeneous solution. We report here a successful attempt in the solubilization of BNNTs.¹⁴ The solubilization was based on interactions of amino groups in oligomeric diamine-terminated poly(ethyleneglycol) (PEG) with the BNNT surface, conceptually similar to those proposed in the solubilization of carbon nanotubes.^{15,16} The solubilization procedure and results from the characterization of BNNTs before and after the solubilization are presented and discussed.

BNNTs were synthesized by the carbon nanotube substitution reaction,^{17–19} in which purified multiple-walled carbon nanotubes (MWNTs, Nanostructure & Amorphous Materials, Inc.) were used as a template to react with boron oxide (powder, 99.8%, Alfa Aesar) and anhydrous ammonia (National Welders Supply Company) in a quartz chamber at high temperature (1200 °C), followed by thermal treatment (780 °C) in low-pressure air to remove the residual carbon from the sample.⁴ The X-ray photoelectron spectroscopy (XPS, Kratos AXIS 165) analysis of the sample yielded a B:N ratio of 1.05:1, with the slight excess of

boron due to residual boron oxide. Upon further purification by repeated washing with hot water to remove boron oxide, the content of BNNTs in the sample was at least 75% by weight, comparable with those reported in the literature.^{17–20}

The thermogravimetric analysis (TGA, Mettler-Toledo TGA/SDAT851e) result of the sample in air is shown in Fig. 1. The weight increase at high temperatures was due to the oxidation of boron in the BNNTs,⁴ and the amount of increase (~25%) was consistent with the estimated BNNT content in the sample.

The presence of BNNTs in the sample was confirmed by scanning (SEM, Hitachi S-4700) and transmission electron microscopy (TEM, Hitachi HD-2000) characterization. The SEM image in Fig. 2 (top) shows abundant nanotubes. The TEM results suggest that the BNNTs are mostly long tubes of around 20 nm in diameter (Fig. 2, bottom), with generally thinner walls than those in the starting MWNTs and also with a distorted layer structure in the wall.

The BNNTs were solubilized *via* functionalization† with amine-terminated oligomeric poly(ethyleneglycol) (PEG_{1500N}, Scheme 1). In a typical experiment, a sample of BNNTs (42 mg) was mixed with PEG_{1500N} (800 mg), and the mixture was heated to 100 °C and kept at that temperature for 3 days under nitrogen protection. Upon cooling to ambient temperature, the reaction mixture was extracted repeatedly with deionized water, coupled with centrifuging at 3000 g. According to the weight of the solid residue, the majority (more than 55%) of the starting BNNTs were solubilized in water as a result of the functionalization with PEG_{1500N} (Scheme 1).

The functionalized BNNTs are soluble in water and organic media compatible with PEG_{1500N}. While BNNTs are colorless, the attachment of PEG_{1500N} in the functionalized BNNTs changed the sample color to brown (Fig. 3). Both the functionalization and

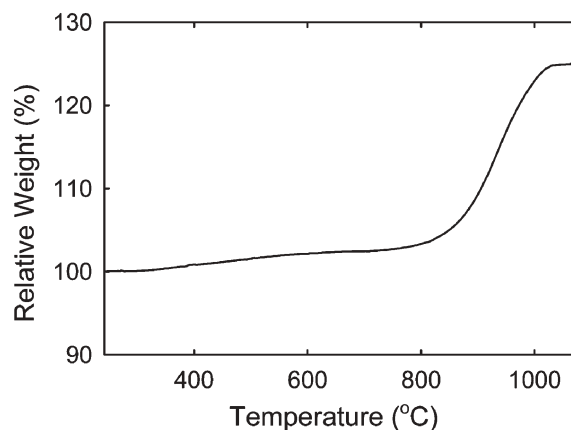


Fig. 1 A TGA trace of the BNNT sample (air, 10 °C min⁻¹), where the weight increase is due to the addition of oxygen.

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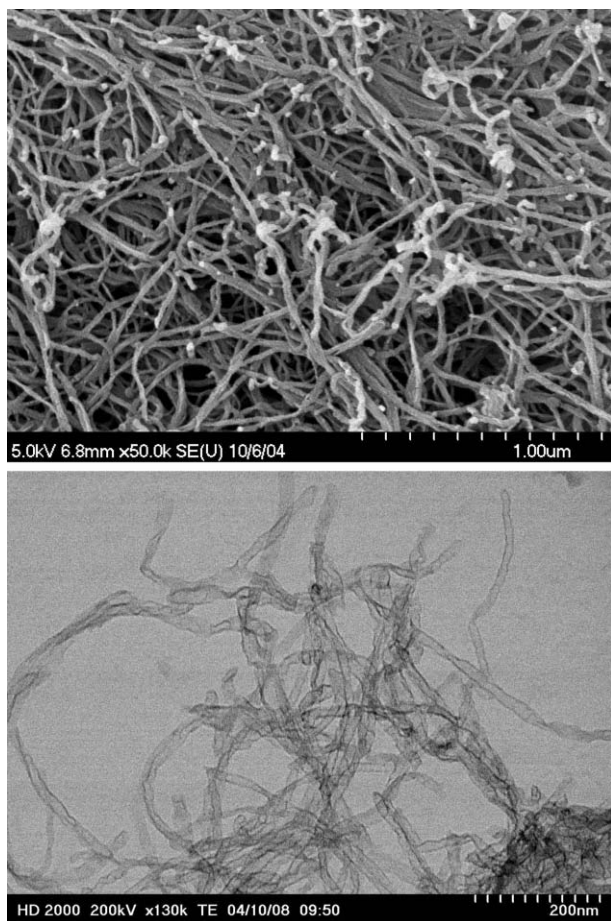
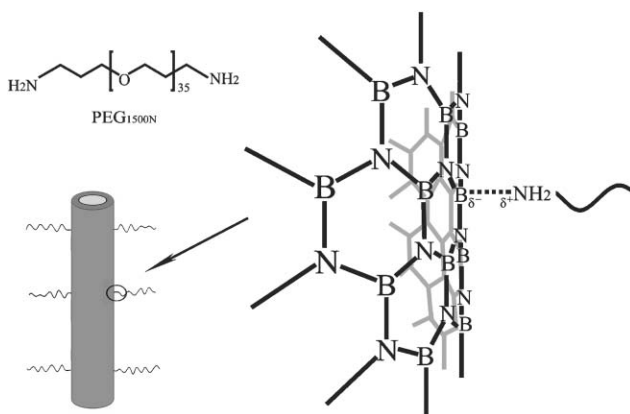


Fig. 2 SEM (top) and TEM (bottom) images of the purified BNNTs.



Scheme 1

the solution color are likely due to interactions of the PEG_{1500N} amino groups with nanotubes, as proposed in Scheme 1. According to results from control experiments, the amino moiety in the functionalization agent is necessary for the functionalization and solubilization of BNNTs. In fact, there was no solubilization at all when the nanotube sample was simply heated in neat deionized water under the same experimental conditions. Similarly, no meaningful solubilization was found with the use of alcohol-terminated or methoxy-terminated PEG (PEG_{1500OH} and PEG_{1500OCH₃}, respectively) as the functionalization agent.

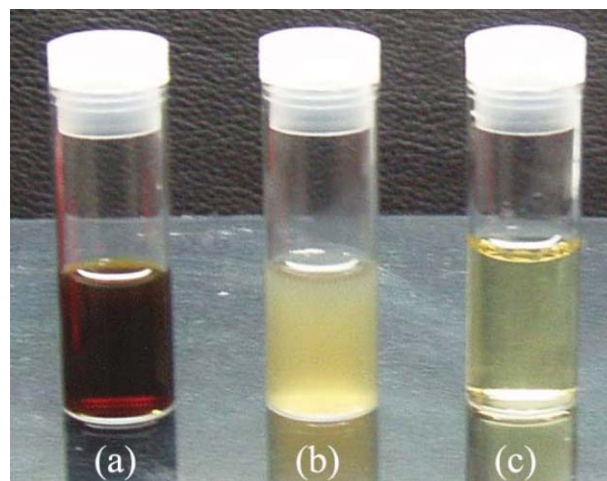


Fig. 3 (a) An aqueous solution of the PEG_{1500N}-functionalized BNNTs. (b) The suspension from the dialysis of the solution in (a) against water. (c) The supernatant from the low-speed centrifuging of the suspension in (b).

The functionalization of BNNTs with PEG_{1500N} was reversible. The brown-colored solution of PEG_{1500N}-functionalized BNNTs was placed in a membrane tubing (molecular weight cutoff ~12000) for dialysis against fresh deionized water. In less than 3 days, the color disappeared and the solution turned into a suspension (Fig. 3), from which colorless BNNTs were recovered almost quantitatively *via* simple low-speed centrifuging. As shown in Fig. 4, the FT-IR (Thermal-Nicolet Nexus 670) spectral features of the recovered BNNTs are generally the same as those of the starting BNNTs (except for several small peaks due to residual PEG_{1500N}), with the characteristic peaks at 1380 cm⁻¹ and 800 cm⁻¹ due to B–N vibrations parallel and perpendicular to the nanotube axis, respectively.²¹

Additional experiments were performed to confirm that the solution color was indeed associated with the PEG_{1500N}–BNNT interactions. One was to precipitate the PEG_{1500N}-functionalized BNNTs from the brown-colored solution *via* high-speed centrifuging. At 25000 g for 30 min, brownish precipitates were observed, and the solution became only slightly yellowish, suggesting that the color was attached to the nanotubes. In

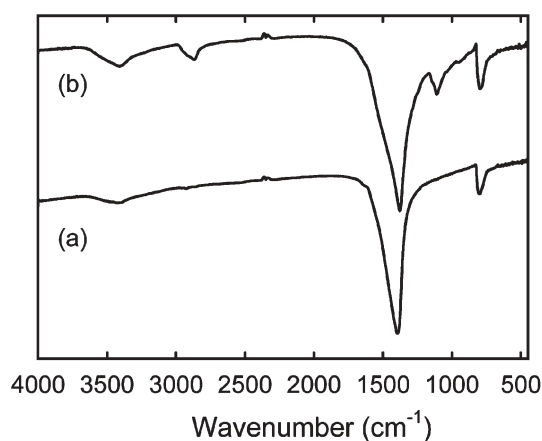


Fig. 4 The FT-IR spectra of the starting (a) and recovered (b) BNNT samples in a KBr matrix.

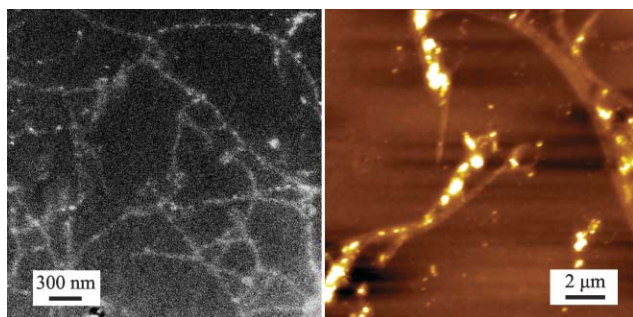


Fig. 5 TEM (left) and AFM (right) images of the PEG_{1500N}-functionalized BNNTs.

another experiment, the PEG_{1500N}-functionalized BNNTs were dialyzed against an aqueous solution of the PEG_{1500N} with matching concentration. No meaningful precipitation or change in solution color were observed after the dialysis. Thus, the color must be a part of the functionalization, as proposed in Scheme 1.

The dispersion of the PEG_{1500N}-functionalized BNNTs was examined by both TEM and AFM (Molecular Imaging PicoPlus). For the TEM specimen, a small drop of an aqueous solution of the functionalized BNNTs was placed on a holey-carbon-coated copper grid, followed by solvent evaporation. As shown in the TEM image in Fig. 5, the nanotubes are well-dispersed. The sample for AFM measurement was deposited on a mica substrate. However, the presence of abundant functional group PEG_{1500N} made the imaging somewhat difficult. Thus, the specimen was treated at 400 °C in air for 1 h to remove some of the attached PEG_{1500N} molecules from the sample. The subsequent AFM image of the thermally treated specimen exhibits island-like structures on the nanotube surface (Fig. 5), which may be attributed to the remaining PEG_{1500N} functional groups.

In summary, BNNTs could be introduced into homogeneous aqueous and organic solutions *via* the functionalization with oligomeric PEG molecules bearing amino moieties. The color change of the sample from colorless to brown upon the functionalization was identified as being associated with interactions between the PEG amino groups and the nanotube surface. Both the solubilization and the color change were found to be reversible, which could be interpreted mechanistically as being due to the formation and dissociation of amine–boron ionic bonds. The solubilization *via* functionalization may add a new dimension in applications of BNNTs, such as their homogeneous dispersion in nanocomposite materials for unique thermal and optical properties.

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Notes and references

† The largely ionic interactions in the solubilization, as discussed later in the manuscript, are more chemical (acid–base reactions) than physical, thus may still be classified as “functionalization”.

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