

Amine-functionalized boron nitride nanotubes

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Abstract

The surface of boron nitride nanotubes (BNNTs) has been functionalized with amine groups via ammonia plasma irradiation. The functionalized tubes were characterized by Fourier transform infrared spectroscopy and electron energy loss spectroscopy. Amine-functionalized BNNTs were found to be highly dispersible in chloroform, and are predicted to form the basis of a new class of chemically reactive nanostructures. © 2007 Elsevier Ltd. All rights reserved.

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Boron nitride nanotubes (BNNTs) show excellent mechanical and thermal properties similar to those of carbon nanotubes (CNTs) [1–6]. However, in contrast to CNTs which exhibit variable metallic and semiconducting characteristics, BNNTs are uniform semiconductors with a wide bandgap (~ 5.5 eV) [7]. In addition, BNNTs have a high resistance to oxidation and are structurally stable [8]. These properties make BNNTs potentially attractive candidates for numerous applications involving nanomaterials. However, for some applications, chemically modified (i.e. functionalized) nanotube surfaces are desirable. Although numerous functionalization schemes exist for CNTs [9–12], little has been reported on the functionalization of BNNTs [13,14]. This is in large part due to the inherent low chemical reactivity of the surface of well-crystallized BNNTs, which inhibits many traditional solution-based reactions.

Here we describe the successful functionalization of BNNTs with amine functional groups. The groups were generated at the surface of the BNNTs using an aggressive non-equilibrium ammonia glow plasma treatment. The functionalized BNNTs were characterized by Fourier transform infrared (FT-IR) spectroscopy and electron energy loss spectroscopy (EELS).

Plasma treatment renders BNNTs dispersible in the common organic solvent chloroform.

BNNTs used in this study were synthesized on Si substrates by thermal decomposition of B and MgO powders in an ammonia environment at 1200 °C in an electric furnace [15]. Fig. 1(a) shows a typical scanning electron microscopy (SEM) image of the as-synthesized BNNTs. Average diameters and lengths of the tubes are 20 nm and over 10 μm , respectively.

Amine functional groups were then introduced at the surface of the BNNTs using an ammonia plasma treatment in a microwave plasma generator. Fig. 1(b) shows a schematic of the microwave plasma generator. The system was equipped with a 1.5 kW microwave generator (Applied Science and Technology, Inc. Model SXRH), a DC power supply for the carbon substrate holder, and an ammonia gas line. After the BNNTs/Si substrate was placed on the holder, the stainless steel chamber was pumped down to less than 0.3 Pa. The ammonia gas (10 sccm) was then introduced into the chamber under a pressure of 400 Pa. An ammonia plasma was generated by applying 200 W of microwave power through the quartz window equipped at the top of the chamber and a -100 V bias to the substrate holder for 10 min at room temperature. After the plasma generation, the substrate temperature was about 200 °C due to plasma bombardment of the holder. The dose under these conditions is estimated to be 1.3×10^{15} ions/cm².

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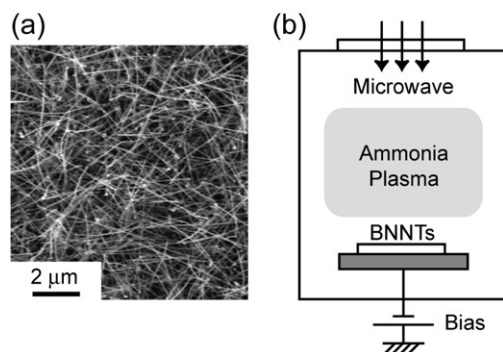


Fig. 1. (a) Typical SEM image of pristine BNNTs on Si substrate as a specimen for plasma treatment. (b) Schematic illustration of the microwave plasma system used in this study.

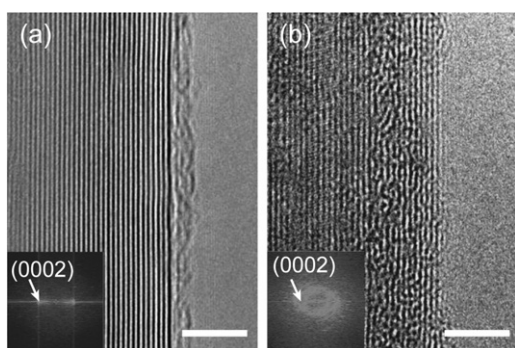


Fig. 2. High-resolution TEM images and Fourier transform images of the wall of (a) pristine BNNT and (b) ammonia plasma-treated BNNT. Scale bar, 4 nm.

Following plasma treatment, the resultant BNNT material on the Si substrate was recovered by sonicating the substrate in deionized water (10 mL).

Fig. 2(a) and (b) show high-resolution transmission electron microscopy (HR-TEM) images of the wall of a BNNT before and after ammonia plasma treatment, respectively, where the longitudinal direction of both images is the nanotube axis. These images were obtained using a Philips CM200 microscope operating at 200 keV. Insets show Fourier transform images of the BNNT at the edge region. Without plasma treatment straight BN lattices are clearly observed. The Fourier transform image also depicts two sharp spots corresponding to the BNNT (0002) plane. It is noted that the defocused structure at the surface in Fig. 2(a) is residual amorphous BN material. After plasma treatment, as shown in Fig. 2(b), the outermost 6–8 BN shells (namely 2–3 nm thickness), are transformed into a defective wavy structure, which includes lattice bending and atomic vacancies. The Fourier transform image exhibits a halo pattern around (0002) spots. This indicates the existence of local defects in the BN walls compared to the pristine BNNT shown in Fig. 2(a).

During the ammonia plasma treatment of the BNNTs, the substrate temperature was approximately 200 °C. Although BNNTs have previously been shown to be extremely stable at similarly low temperatures, even in an oxygen environment [8], in this case, as shown in Fig. 2(b), wavy layers were observed at the surface layers of the BNNTs following the ammonia

plasma irradiation. As the thermal effect on the BN lattice is negligible in this study, the effect of ions and radicals in the ammonia glow plasma must dominate. According to optical emission spectroscopy (OES) studies of typical low-temperature ammonia glow plasmas, the primary excited species in an ammonia plasma are N_2 , N_2^+ , NH_2 , NH , and H atoms [16]. Among these species, the N_2^+ ion is likely to be attracted to BNNTs due to the negative bias applied. Other positive ions, NH^+ , NH_2^+ and NH_3^+ , would be rare in this plasma because their ionization energies are typically above 10 eV, which is larger than the electron temperature in the plasma [17]. Since the kinetic energy of N_2^+ ions around the substrate is about 100 eV, much larger than the cohesive energy of a hexagonal B–N bond (7–8 eV) [18], defects could be created at the BNNT surface by ion collision and displacement of some B and/or N. Radicals such as NH_2^* or H^* could be expected to terminate the resulting vacancies at the surface of the BNNTs. Based on bond ionicity considerations, we propose that NH_2^* radicals attach to B atoms, whereas the H^* radicals attach to N atoms. The dynamic repetition of defect creation by positive ions and the termination of vacancies by radicals would produce BNNT surfaces functionalized with amine groups. From the evidence afforded by the TEM analysis it is apparent that stable and strong BN bonds of BNNTs can be substantially modified by low-temperature ammonia plasma irradiation.

Amine-functionalized BNNTs (AF-BNNTs) provide a versatile platform for further chemical functionalization. Indeed, we have found that AF-BNNTs are far more amenable to wet chemistry manipulation than pristine BNNTs. To investigate the dispersibility of the AF-BNNTs, both AF-BNNTs (2 mg) and pristine BNNTs (2 mg) were mixed with chloroform (2 mL) and sonicated in a bath sonicator (VWR International, 50 W and ~40 kHz) for 5 min to completely suspend the material. After the procedure, the suspension was allowed to stand for periods varying from several hours to several days.

Following sonication of both the AF-BNNTs and pristine BNNTs in chloroform and standing for 5 h, the AF-BNNTs were found to exhibit significantly greater dispersibility in chloroform than pristine BNNTs as shown Fig. 3. Since the suspension of AF-BNNTs maintained its milky appearance after standing for 7 days, the supernatant BNNTs were extremely well dispersed in chloroform, indicating excellent dispersibility. The corresponding control experiment carried out with pristine BNNTs exhibited no dispersibility of the nanotubes. In particular, following sonication of the pristine BNNTs and standing for 5 min, significant quantities of pristine BNNTs precipitated out of the dispersion. After 30 min, the supernatant solution appeared transparent. TEM observation of both supernatant solutions showed that the AF-BNNT solution contained many nanotubes, while nanotubes were rarely found in the pristine BNNT solution. In addition, defective BNNTs formed by Ar plasma bombardment of pristine BNNTs exhibited a degree of dispersibility in chloroform (data not shown). Thus, the reason for the dispersibility of AF-BNNTs in chloroform is likely to be a result of the atomic degradation of the crystallinity. The ability to suspend the AF-BNNTs in

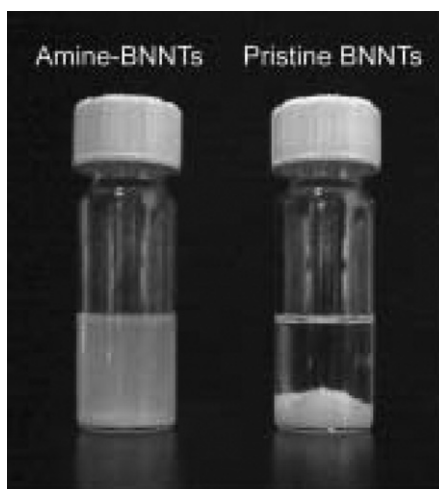


Fig. 3. Photographs of vials containing the AF-BNNTs (left-hand side) and the pristine BNNTs (right-hand side) in chloroform after standing for 5 h.

a useful organic solvent such as chloroform has significant implications for the solution-based chemistry that may be carried out using these materials.

To demonstrate further chemical functionalization of plasma-treated BNNTs, molecules of 3-bromopropanoyl chloride (BPC) were coupled to the AF-BNNTs. The coupling of the BPC molecule with the surface of the AF-BNNTs was achieved via sonication of the AF-BNNTs in the liquid BPC reagent. Amide formation between the acid chloride groups of the BPC molecules and the amine groups occurs on contact to form BPC-modified BNNTs (BPC-BNNTs). The materials were stirred for several hours and were then isolated using membrane filtration followed by extensive washing with ethanol.

Fig. 4 shows the FT-IR spectra of pristine BNNTs, AF-BNNTs, the free BPC molecule, and BPC-BNNTs. The spectrum of the pristine BNNTs exhibits two distinct peaks at 1391 cm^{-1} and 815 cm^{-1} which are attributed to the in-plane B–N transverse optical mode of the BNNTs and the B–N–B out-of-plane bending vibration perpendicular to the axis of the nanotube. These values are in good agreement with a number of reports concerning the FT-IR spectra of BNNTs [19,20]. The spectrum of the AF-BNNTs was found to exhibit essentially the same peaks as those seen in the spectrum of the pristine BNNTs. We believe this is due to the heterogeneity of the surface of the BNNTs as shown by HRTEM, and the different environments of the amine groups at the surface of the BNNTs. This would be expected to cause a spread in the vibrational modes of the amine groups making their identification particularly difficult.

The spectrum of the free molecule BPC [21] shows peaks attributed to the carbonyl stretch of the acid chloride and a bending mode of the Br–CH₂ at 1795 cm^{-1} and 1268 cm^{-1} , respectively. The peaks attributed to the stretching and bending vibrations of the methylene groups are believed to be present in the regions $3070\text{--}2840\text{ cm}^{-1}$ and $1480\text{--}1370\text{ cm}^{-1}$, respectively. In the spectrum of the BPC-BNNTs, the peaks due to the B–N axial vibrations and vibrations perpendicular to the

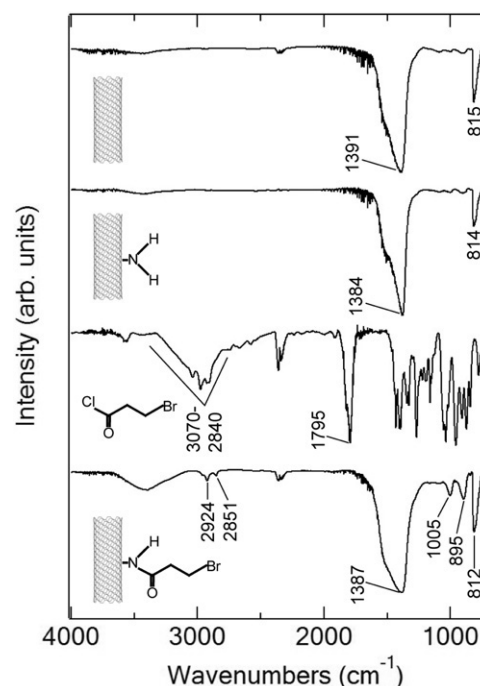


Fig. 4. FTIR spectra of pristine BNNTs, the AF-BNNTs, the free acid chloride molecule (BPC), and the BPC-BNNTs.

axis of the tubes are identified at 1387 cm^{-1} and 812 cm^{-1} , respectively. In contrast to the spectrum of the free BPC molecules in which the exact position of the methylene groups of the alkyl chain cannot accurately be identified, the spectrum of the BPC-BNNTs shows peaks at 2924 cm^{-1} and 2851 cm^{-1} , which are assigned to the asymmetric and symmetric stretching vibrations of the methylene groups of the BPC moieties. The appearance of two peaks at 1005 cm^{-1} and 895 cm^{-1} are tentatively assigned to the C–N stretch and the N–H out of plane wagging, respectively, of the amide of the BPC molecules at the surface of the BNNTs. While the identification of these peaks seems reasonable it is noted that the precise assignment of peaks in this region is nontrivial. While the stretching vibration of the carbonyl group of the acid chloride of BPC is clearly seen at 1795 cm^{-1} , the corresponding peak is absent in the spectrum of the BPC-BNNTs. This may be explained by amide formation that causes a significant shift in the position of the carbonyl group leading to its overlap with the stretching vibration attributed to the transverse optical mode of the BNNT between 1700 cm^{-1} and 1220 cm^{-1} , and therefore the carbonyl group is not visible in the spectrum. Overall, the IR data provides support for the assertion that the bromopropyl moieties are covalently bound to the surface of the BNNTs.

EELS (Gatan Model 766) equipped with TEM was also employed as an additional means by which the presence of BPC molecules at the surface of a single BPC-BNNTs could be confirmed. This was done by recording the EELS spectra of an isolated BNNT exposed to BPC molecules either following ammonia plasma treatment or without ammonia plasma treatment as shown in Fig. 5(a) and (b), respectively. BNNTs exposed to BPC following plasma treatment exhibited a Br peak at about 1550 eV , suggesting that the attachment of

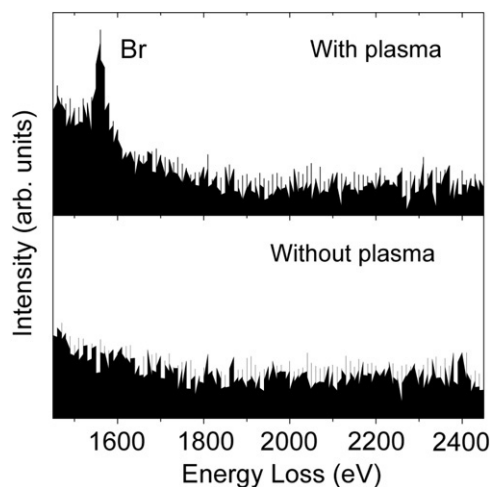


Fig. 5. Electron energy loss spectrum of isolated BPC-BNNTs (a) with and (b) without ammonia plasma treatment.

the BPC molecules at the surface of the nanotubes had indeed taken place. The control experiment carried out with BNNTs not treated by an ammonia plasma but subjected to the same exposure to BPC molecules showed no Br peak in the EELS spectrum. Combining this evidence with the data available from the FT-IR analysis, we can conclude that the BNNTs are covalently modified with the BPC molecules and hence that amine-functionalization of the BNNTs can be achieved by plasma treatment.

In conclusion, we have demonstrated the amine-functionalization of BNNTs by irradiation with an ammonia plasma. The presence of the amine groups at the surface of the BNNTs and their chemical reactivity was confirmed by the covalent coupling of reactive BPC molecules to the amine groups via amide formation and the characterization of the molecules using FT-IR spectroscopy and EELS. We have also shown that the AF-BNNTs are suspended in chloroform. Thus, the AF-BNNTs fabricated in this study have the potential to be utilized as building blocks for the formation of nanoscale structures and composite materials since the amine functional groups present on the modified tubes can be used as binding sites for the immobilization of small molecules, polymers, and condensed phase materials. In addition, the functionalization of materials using plasma irradiation demonstrated in this study has more potential since plasma parameters such as type of gas, pressure, and temperature, are controllable. Such approaches may provide

a means to precisely control the surface functionality and the composition of nanoscale materials.

Acknowledgments

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