Nanotubes

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Covalent Functionalization: Towards Soluble Multiwalled Boron Nitride Nanotubes**

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In many respects, a boron nitride nanotube (BNNT) has advantageous properties when compared to a standard carbon nanotube (CNT). For example, BNNTs are stable wide-band-gap semiconductors, independent of diameter and chirality.[1] In contrast, the electrical performance of a CNT is a complex function of many structural parameters, which are difficult to control.[2] BNNTs exhibit excellent mechanical properties, high thermal conductivity, and superb resistance

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to oxidation.[3–8] Therefore BNNTs are thought to be primarily useful in nanoscale semiconductors working in oxidative or hazardous environments at high temperatures, and as an additive in composites that leads to the improvement of mechanical properties and thermal conductivity of the matrix.

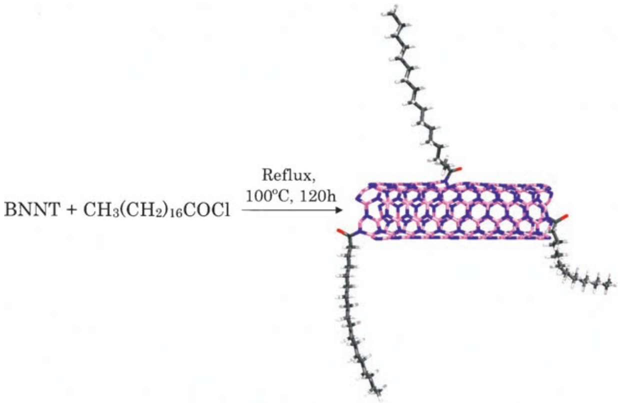
However, to date there has been a lack of notable progress in the above-mentioned fields. Many unanswered questions, such as how to adjust the electronic structure of BNNTs, how dispersible BNNTs are in a solvent, and how to produce clean BNNTs in high yield, has hampered the expected breakthroughs.

The functionalization of CNTs is a vital tool in tailoring their properties and engineering devices, and significant efforts have been undertaken with respect to this functionalization. Intense research has been carried out on soluble CNTs, CNT composites, and CNT compatibility with biological systems.[9–13] As for the BNNT system, only recently Xie et al. have obtained good BNNT dispersion through their functionalization with amine-terminated oligomeric poly(ethylene glycol).[14] The functionalized BNNTs were easily retracted, which indicates that the interactions between the amino groups and the BNNTs are noncovalent. In addition, contamination with carbon was a major concern as the BNNTs were produced by a CNT substitution reaction.[8] To date, the covalent-bond chemistry of BNNTs and related functionalization has long been awaited but not reported. The ability to functionalize BNNTs with covalently bonded groups should allow the tailoring of their properties and of the materials made out of them.

Herein, we report how pure multiwalled BNNTs are synthesized in high yield by carbon-free chemical vapor deposition (CVD).[15,16] A mixture of boron and metal oxide served as the reactant during the synthesis and an original approach was then developed to functionalize BNNTs with an organic residue through the formation of a covalent bond. This method led to highly soluble products. Cathodoluminescence (CL) and UV/Vis absorption experiments revealed variations in the electronic structure of the BNNTs after functionalization, which may pave a way to tune the band gap of the BNNTs.

The functionalization methodology is based on the chemical reaction between the COCl group of stearoyl chloride and amino groups on the BNNTs, as shown in Scheme 1. A similar reaction has been widely applied to modify CNTs.[9] In contrast to the starting material (multiwalled BNNTs), which is insoluble in organic solvents, the functionalized BNNTs (f-BNNTs) are soluble in solvents such as chloroform, *N*,*N*-dimethylacetamide, tetrahydrofuran, *N*,*N*-dimethylformamide, acetone, toluene, and ethanol. The solubility of f-BNNTs in *N*,*N*-dimethylacetamide is $>0.5\,\mathrm{g\,L^{-1}}$. Very dilute BNNT solutions are almost totally transparent and white concentrated BNNT solutions are visually nonscattering. No precipitation was observed when the sample was kept over a long period under ambient conditions.

Transmission electron microscopy (TEM) was used to confirm the presence of BNNTs in solution and to check the morphology of the f-BNNTs. The results are shown in Figure 1. f-BNNTs in solution are well dispersed and retain a characteristic 1D tubular morphology. An amorphous layer can be observed on their surface. On average, the f-BNNTs are slightly shorter than the original BNNTs, which is caused by stirring of the reaction mixture for a long period during functionalization.



Scheme 1. Schematic representation of the designed reaction to give a functionalized nanotube.

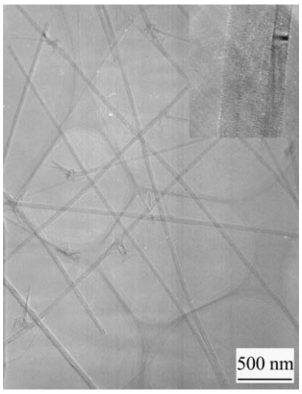


Figure 1. TEM images of f-BNNTs. Inset: a high-magnification TEM image revealing a tubular structure of the f-BNNT and an amorphous layer on its surface.

To reveal the functionalization mechanism, Fourier-transformed infrared (FTIR) spectroscopy was used to compare the original BNNTs with f-BNNTs (Figure 2. The absorptions corresponding to C=O (1774 and 1630 $\mathrm{cm^{-1}}$) and C–H bonds (bending vibrations: 1016, 1078, 1163, and 1193 $\mathrm{cm^{-1}}$, stretching vibrations: 3033 2959 and 2925 $\mathrm{cm^{-1}}$(weak)) can be clearly identified in the FTIR spectrum of f-BNNTs, which indicates that long alkyl chains are bonded to the BNNTs. It is worth noting that for stearoyl chloride, the peaks related to C=O appear at 1712 and 1807 $\mathrm{cm^{-1}}$, while they appear at 1774 and 1630 $\mathrm{cm^{-1}}$ for the f-BNNTs. This shift implies that the COCl functional group participates in the chemical reaction. As a reductive NH_3 gas is used during the CVD synthesis of BNNTs from boron and metal oxide,[15,16] we assume that there are some amino groups present on the side walls of the BNNTs, as well as at their open ends. Their presence ensures that long alkyl chains can bond through the chemical reaction between COCl and the amino groups. The effect is similar to that observed in CNTs, whose defects can be oxidized to form

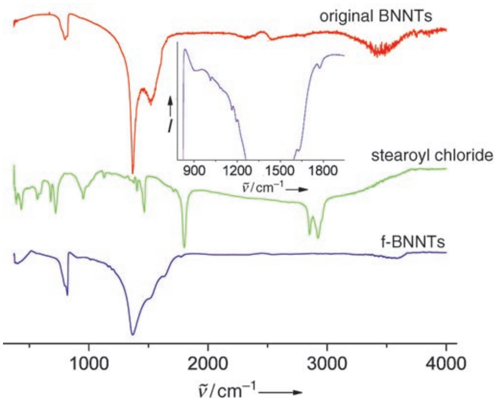


Figure 2. Comparative FTIR spectra of original BNNTs, stearoyl chloride, and f-BNNTs. Inset: an enlarged profile of additional peaks that only appear in the spectrum of f-BNNTs.

reactive groups, and subsequently long-chain alkyl amines can be coupled to carboxy groups activated with $SOCl_2$.[17] In addition, the chemical reaction also induces notable variations in BNNT-related FTIR peaks, namely, the disappearance of peaks corresponding to multiphonon processes (2313 and 2530 cm^{-1}) and abatement of splitting of the E_{1u}(TO) and E_{1u}(LO) modes (TO: transverse optic; LO: longitudinal optic).[18] An investigation into the detailed mechanism that causes these changes is underway.

Given that variations in the optical properties have also been observed for CNTs after functionalization[19,20] and that UV emission has been observed for BNNTs,[18] we performed CL measurements on the f-BNNTS. A f-BNNTs powder was chosen as the sample to be analyzed as solutions are not suitable for CL experiments. Figure 3 compares the room-temperature CL spectrum of original BNNTs with that of f-BNNTs. As previously reported, the spectrum of original BNNTs shows a dominant peak at about 3.25 eV and a shoulder at about 4.05 eV, which is thought to originate from B or N vacancies.[18] Peaks related to the band transition should appear at about 5.5 eV, which can only be observed from low-temperature CL experiments. In the spectrum of the f-BNNTs, there is a new shoulder at about 2.50 eV. One possible explanation for this emission is that a new defect-related band is introduced into the energy gap of BNNTs. This, in turn, implies that a long alkyl chain protruding from a side wall or open end of a BNNT may lead to a dopant effect. The dopant effect may be induced by a charge transfer between the BNNT and the alkyl chain.[9] Another possibility is that the shoulder at about 2.50 eV may solely originate from the long alkyl chains, which means that we detect a kind of surface-state luminescence. If so, the intensity of the shoulder emission may provide a way to estimate the density of alkyl chains on the surface of a BNNT.

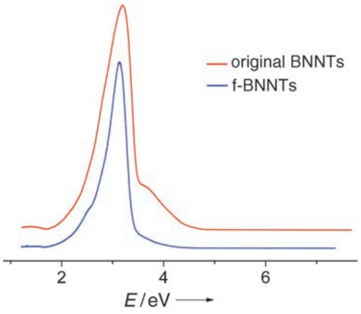


Figure 3. Comparative CL spectra of original BNNTs and f-BNNTs.

To probe the influence of long alkyl chains on the electronic structure of BNNTs, UV/Vis absorption experiments were performed. A solution sample cannot be used for these experiments as most organic solvents are totally opaque to wavelengths shorter than 250 nm (4.96 eV), and a BNNT has an even larger band gap according to a previous study.[1] Therefore, BNNT films were used as samples. Figure 4 compares the UV/Vis absorption spectrum of BNNTs with that of f-BNNTs. The peak at 5.80 eV dominates the BNNT spectrum; it corresponds to the band-gap transition and indicates a band gap in the range of 5.2 to 5.5 eV.

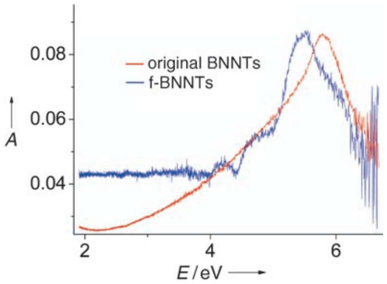


Figure 4. Comparative UV/Vis absorption spectra of original BNNTs and f-BNNTs.

More features appear in the spectrum of the f-BNNT. First, the dominant peak shifts to about 5.45 eV and displays a shoulder at 5.8 eV. This shoulder clearly corresponds to the peak of the band-gap transition mentioned above. Second, new peaks at about 4.68 and 4.20 eV appear. The shift of the main peak indicates that some new electronic states are present in the energy-gap region of the f-BNNTs. If the long alkyl chain acts as a carbon dopant, it may be that the additional electronic states appear in the top of the valence band and the bottom of the conduction band. It was reported that in boron carbonitride (BCN) nanotubes, the carbon content may affect the band gap. Typically in BCN nanotubes, the width of the band gap decreases with an increase in carbon concentration.[21] However, it is difficult to control precisely the atomic concentration of carbon within BCN nanotubes at the stage of tube growth.

In contrast, the process of postsynthesis chemical modification of BNNTs may be easily controlled. Specifically, the density of alkyl chains on the BNNT surface can be adjusted by controlling the reaction time and temperature. Alternatively, a defunctionalization process could be developed to further adjust the alkyl-chain density as with CNTs.[22] The peaks at 4.68 and 4.20 eV imply that the dopant effect of alkyl chains on BNNTs is real. This doping is crucial for the engineering of the wide band gap. Chen et al. have used a long alkyl chain to decorate single-walled CNTs.[9] Variations in the band structure of the decorated CNTs have indeed been observed in absorption experiments. The influence of an alkyl chain on BNNTs may be even larger than that on CNTs as carbon atoms are already present in CNTs but are heteroatomic for BNNTs. This factor makes the modification of BNNTs with organic groups highly promising.

In summary, an original methodology has been developed to functionalize multiwalled BNNTs with long alkyl chains and the resultant functionalized BNNTs are soluble in many organic solvents. The CL and UV/Vis absorption experiments indicate that long alkyl chains may induce drastic changes in the band structure of BNNTs. These findings may be the beginning of significant progress in the chemistry of BNNTs and their functionalization paves the way to controllable tailoring of their electronic structure and to band-gap engineering.

Experimental Section

An induction furnace was used to synthesize multiwalled BNNTs. The detailed procedure is described elsewhere.[15,16] The as-prepared BNNTs were heated to about 1900 °C in nitrogen to remove impurities and metal catalysts. For functionalization, the BNNTs were immersed in stearoyl chloride, the mixture was stirred, heated to 100 °C, and annealed over 120 h. After centrifugation, the remaining solid was washed with chloroform and *N*,*N*-dimethylformamide repeatedly to afford f-BNNTs.

The microstructure was analyzed by using a JEOL-3000F high-resolution field-emission TEM operated at 300 kV. FTIR spectra were collected by using a Perkin Elmer FTIR spectrometer with a laser wavelength of 1024 nm. The CL spectra were recorded in a charge-coupled device (spectra view 2D; Jobin Yvon, France).

The UV/Vis absorption experiments were performed by using a Hitachi U-4100 spectrometer. The f-BNNTs were dissolved firstly in chloroform, a few drops of the solution were dripped onto a clean quartz wafer, then the solvent was allowed to evaporate. A uniform compact film suitable for UV/Vis absorption experiments was thus obtained. For the original BNNTs, a technique developed in our previous studies was used to make a film.[23] Briefly, a conjugated polymer, poly(*m*-phenylenevinylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene), was used to wrap the BNNTs, which allows them to be dissolved. Composite films were first made by dripping a solution of the BNNTs onto a quartz wafer; the original uniform BNNT film was obtained by heating the composite film to 700 °C in air to remove the polymer.

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