

Functionalization and solubilization of BN nanotubes by interaction with Lewis bases

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By interaction with a trialkylamine or trialkylphosphine, BN nanotubes can be dispersed in a hydrocarbon medium with retention of the nanotube structure.

Boron nitride (BN) is an important ceramic material with a wide range of applications. BN crystallizes in a graphite-like structure and can be viewed as replacing the C–C pair in a graphene sheet with the isoelectronic B–N pair. BN does not, however, form five- or seven-membered rings. BN nanotubes have been prepared by several methods.^{1–10} During the last year, much interest has been evinced in the functionalization and solubilization of BN nanotubes.^{11–15} For example, poly(*m*-phenylenevinylene-co-(2,5-dioctoxy-*p*-phenylenevinylene)) has been used to solubilize BN nanotubes in organic solvents, the polymer wrapping around the BN nanotubes leading to its solubilization. Water-soluble BN nanotubes have been prepared by using amine-terminated poly(ethylene glycol).¹² BN nanotubes have been covalently functionalized using stearoyl chloride and subsequently dissolved in organic solvents.¹³ Cycloaddition of dimethyl sulfoxide to BN nanotubes is suggested to weaken the B–N bond and help in the peeling of the nanotubes.¹⁴ BN nanotubes have also been fluorinated.¹⁵ The literature procedures for the functionalization and solubilization of BN nanotubes appear somewhat difficult and we, therefore, felt that there should be a simpler way to accomplish the desired results. We, therefore, considered it desirable to exploit the inherent electron deficiency of boron compounds. If we consider the boron site in BN nanotubes to act as a Lewis acid, it should be possible to form adducts with Lewis bases such as alkylamines and phosphines, which should then enable one to disperse them in suitable solvents. In this communication, we demonstrate that this does indeed happen through a study of the interaction of BN nanotubes with two tri-*n*-alkylamines and a tri-*n*-alkylphosphine.

BN nanotubes were prepared by a standard literature procedure.⁷ BN nanotubes were prepared by the reaction of B₂O₃ with multi-walled carbon nanotubes (MWNTs) in the presence of ammonia at 1250 °C for 3 h. A grey spongy product was obtained after the reaction indicating the presence of unreacted MWNTs along with BN nanotubes. The product was washed with hot water to remove excess B₂O₃. The excess carbon present in the product was removed by oxidation at 800 °C in low-pressure air (20 mPa). Scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX) were performed with

a Leica S-440I microscope fitted with a Link ISIS spectrometer. Transmission electron microscope (TEM) images were obtained with a JEOL JEM 3010 instrument fitted with a Gatan CCD camera operating at an accelerating voltage of 300 kV. In Fig. 1(a), we show a representative SEM image of the BN nanotubes prepared by us. The nanotubes have diameters in the 80–200 nm range with lengths of tens of microns. BN nanotubes have either bamboo-like or worm-like structures as revealed by the TEM image shown in Fig. 1(b). Raman spectra of the BN nanotubes were recorded using a JobinYvonHoriba HR800 Raman spectrometer using a HeNe laser (632 nm). The spectrum of purified BN nanotubes did not show the D-band (1340 cm⁻¹) or the G-band (1600 cm⁻¹) of carbon nanotubes. The nanotubes exhibit a Raman band centered at 1370 cm⁻¹ as shown in Fig. 2(a), this band is assigned to the E_{2g} tangential mode.^{9,16}

In a typical functionalization/solubilization experiment, 2 ml of trialkylamine or trialkylphosphine were added to 5 mg of purified BN nanotubes. The mixture was warmed at 70 °C for 12 h and subsequently sonicated for a few minutes. The functionalized BN

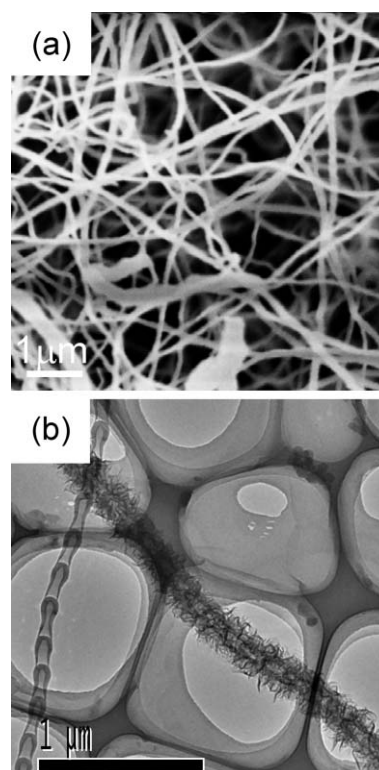


Fig. 1 (a) SEM image of purified BN nanotubes. (b) TEM image of BN nanotubes.

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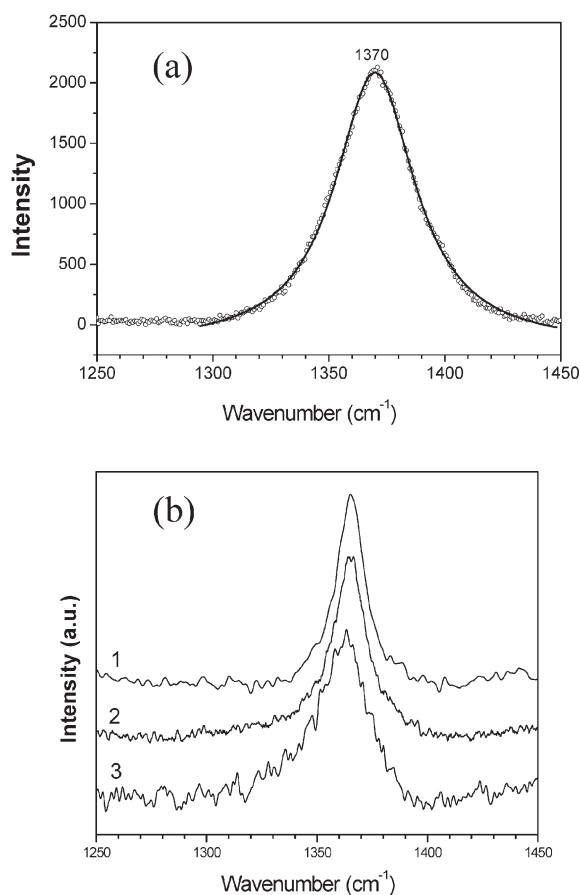


Fig. 2 (a) Raman spectrum of BN nanotubes. (b) Raman spectra of the dispersions of BN nanotubes functionalized with tributylamine (1), trioctylamine (2) and trioctylphosphine (3).

nanotubes were then dispersed in toluene (8 ml) or other hydrocarbons such as benzene, at room temperature. The dispersions were stable over long periods of time. It is not essential to interact the nanotubes with an amine or phosphine at 70 °C. Interaction at laboratory temperature for a long period yielded the same result. In Fig. 3(a), we show a photograph of a toluene dispersion of BN nanotubes treated with trioctylamine. In Fig. 4(a), we show a TEM image of the BN nanotubes obtained by taking a drop of the dispersion on the electronic microscopy grid. We see images of

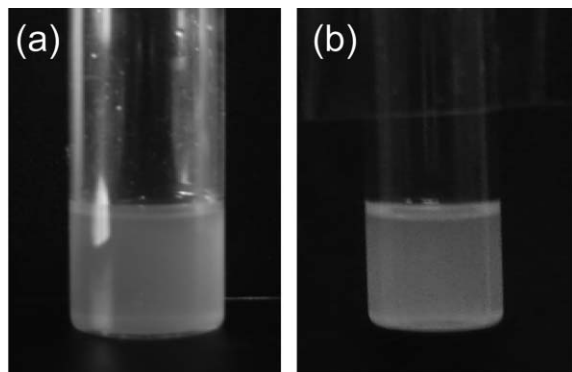


Fig. 3 Photographs of dispersions of BN nanotubes obtained after interaction with (a) trioctylamine and (b) trioctylphosphine.

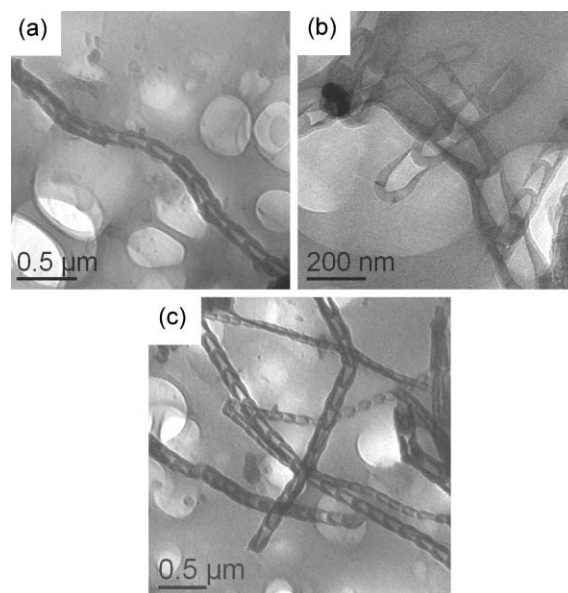


Fig. 4 TEM images of the dispersions of BN nanotubes functionalized with (a) trioctylamine, (b) tributylamine and (c) trioctylphosphine.

nanotubes similar to those in the starting material shown in Fig. 1(b). We could obtain a stable dispersion of BN nanotubes using tributylamine as well. A TEM image of the nanotubes obtained from this dispersion is shown in Fig. 4(b).

Evidence for the interaction between tributylamine and BN nanotubes has been obtained by nuclear magnetic resonance spectroscopy. We have studied the ^1H and ^{13}C NMR spectra of tributylamine-functionalized BN nanotubes in comparison with the spectra of tributylamine. We observe a small increase in the ^1H chemical shift by ~ 0.02 ppm in the amine–BN adduct. In the case of ^{13}C NMR spectra, we observe a significant increase in the chemical shifts of the γ and δ carbons by ~ 0.4 ppm and a decrease in the chemical shift of the β carbon atom by ~ 0.3 ppm. The chemical shift of the α carbon is also higher in the amine–BN adduct by ~ 0.1 ppm. The changes in the ^1H and ^{13}C spectra of tributylamine found on interaction with BN are comparable to those reported in the literature for similar complexes.^{17,18}

We have also carried out solubilization experiments using the as-prepared BN nanotubes containing carbon nanotubes as impurity. Initially, a grey dispersion containing both carbon and BN nanotubes was obtained, but the carbon nanotubes settled to the bottom within a few hours leaving the BN nanotubes in the solution. This indicates that there is no significant interaction between the Lewis base and the carbon nanotubes.

Encouraged by the results obtained with the two trialkylamines, we interacted the BN nanotubes with trioctylphosphine at 70 °C for 12 h or at 30 °C for a longer period. We could disperse the product in toluene as can be seen in the photograph in Fig. 3(b). A TEM image of the nanotubes from the dispersion is shown in Fig. 4(c). Raman spectra of the dispersions of BN nanotubes were recorded after interacting them with an amine or a phosphine. For this purpose, a drop of the dispersion was placed on a glass slide and the spectrum recorded. In Fig. 2(b), we show Raman spectrum of BN nanotubes treated with trioctylphosphine. We observe a band due to the tangential mode at 1361 cm^{-1} , similar to the starting material. Raman spectra of the toluene dispersions of

BN nanotubes treated with tributylamine and trioctylamine showed a band due to the tangential mode around 1367 cm^{-1} . These results suffice to demonstrate that the interaction of BN nanotubes with Lewis bases helps to solubilize them in nonpolar solvents. We should note that in the absence of interaction with an amine or a phosphine, BN nanotubes could not be dispersed in toluene and the nanotubes settled to the bottom in a short period.

In conclusion we have successfully demonstrated that the Lewis acid nature of boron in BN nanotubes can be exploited to functionalize and solubilize their nanostructures through interaction with Lewis bases. The solubilized nanotubes retain the nanotube features and the hydrocarbon dispersions are stable up to a few days. It is noteworthy that the interaction of the BN nanotubes with the Lewis bases at room temperature suffices to provide good dispersions of the BN nanotubes in hydrocarbon solvents. We also note that any carbon impurity due to carbon nanotubes used as templates in the preparation of the BN nanotubes settles to the bottom after interaction of the BN nanotubes with a Lewis base, thereby providing a means of separation of carbon and BN nanotubes.

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