Communication

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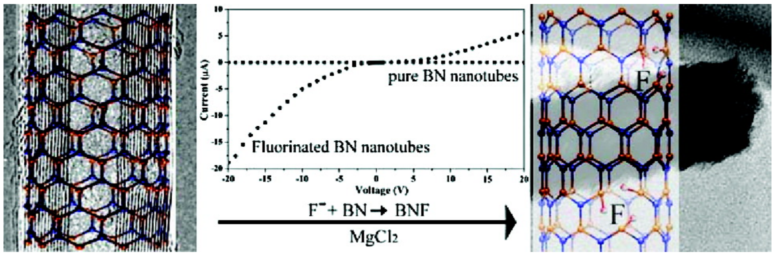

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Fluorination and Electrical Conductivity of BN Nanotubes

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The studies on BN nanotubes have been initiated due to the striking structural similarity between graphitic carbon and hexagonal BN.[1] The comparison between the two systems is of significant interest with respect to the development of functional nanomaterials and nanodevices. Due to the ionic origin of a BN band gap,[2] the electronic structure of BN nanotubes differs significantly from that of carbon nanotubes. Importantly, theoretical calculations[3] have demonstrated that BN nanotubes possess a very stable gap of ~5.5 eV, almost independent of tube diameter, helicity, and of whether a nanotube is single- or multiwalled. The electronic structure of doped BN nanotubes is primarily determined by the chemical composition.[4] Relative uniformity of electronic properties in the BN nanotubes, combined with its chemical inertness, may be the key advantage for the nanoelectronic applications. In fact, there is no need to control the diameter and helicity of BN-based nanoelectronic devices, which is extremely difficult to fulfill in the case of carbon nanotubes.[5] In this context, the uniformly doped BN nanotubes obtained through chemical modification would be a prospective object for tailoring the electronic properties.

Previous studies on functionalization of BN nanotubes have mainly focused on the B−N−C system through the control of a C content.[6] However, the helicity influence on the band gap has still been in effect.[7] Recently, Han et al.[8] used a simple chemical route to coat BN nanotubes with a conductive stannic oxide for the sensor applications, although the tube surface has been affected only. This fact reflects the well-known chemical inertness and poor wetting of BN nanotubes. To obtain the entire doping or functionalization, a novel feasible strategy is required that relies on the simultaneous nanotube growth and introduction of foreign species during a single experiment run.

In this study, we selected fluorine-functionalized BN nanotubes in order to pursue applications in nanoelectronics. Fluorination is one of the most effective pathways to affect transport properties. Since fluorine is a highly electronegative element and has the excessive valence electrons compared to B and N, the functionalization should be easily performed and should reliably yield an n-type semiconductor. First, we examined the direct reaction between BN nanotubes and fluorine or hydrogen fluoride. Although we were able to obtain F doping of BN nanotubes via a long-time reaction at a low temperature, the fluorine atoms only attached to the nanotube surface. Most unfortunately, this attachment was considerably unstable. The doped fluorine escapes easily when the tube is exposed to air or under standard beam irradiation in the electron microscope.

In this communication, we describe a novel original route toward the synthesis of F-doped BN nanotubes through the introduction of F atoms at the stage of tube growth. Basic BN crystal was synthesized by means of a traditional chemical vapor deposition (CVD) from a BF_3/NH_3 mixture system. The following chemical reactions that have been commonly used in the fabrication of a BN film were involved:[9]

$$2BF_3 + 9NH_3 \rightarrow B_2(NH)_3 + 6NH_4F \qquad (1)$$

$$B_2(NH)_3 \rightarrow 2BN + NH_3 \qquad (2)$$

The reactions were carried out in a tubular reactor made of sintered BN. The reactor was placed inside a silica tube heated electrically. The reaction system was first heated to 925 °C in a nitrogen gas flow. BF_3 and NH_3 were then separately introduced into the tube and mixed in the hot reactor zone. In the present experimental runs, a significant modification to the traditional method has been adopted: a lump of $MgCl_2$ (~30 mg) was placed into the high-temperature area of the reactor, acting as a CVD substrate. The introduction of $MgCl_2$ is intended for the catalyzed nanotube growth, based on our previous experimental results that a magnesium-containing impurity could promote the one-dimensional growth.[10] The fluorination may be accomplished through the NH_4F reaction on the freshly grown BN nanotubes:

$$NH_4F \rightarrow F^- + H^+ + NH_3 \qquad (3)$$

After the synthesis over 1 h, a colorless wool-like layer, ~10 mg in weight, appeared on the surface of the slightly sintering lump.

X-ray diffraction analysis indicates that the starting $MgCl_2$ has fully been converted to MgF_2 after the reaction. The wool-like product is solely made of a hexagonal BN. The strong diffraction peak (002) locates at $d = 0.330$ nm, slightly smaller than the parameter of 0.333 nm of pure BN nanotubes. Due to the close electronegativity, the doped fluorine should preferentially occupy nitrogen positions. The observed ~1% lattice contraction relates to the smaller covalent radius (64 pm) of fluorine compared to the 70 pm of nitrogen. The covalent feature of the dopant was further confirmed by a Fourier transformation infrared spectrum. The spectrum shows a sharp absorption peak of the B−N−B out-of-plane bending vibration and an extremely broad peak of the in-plane B−N transverse vibration, indicating a highly disordered atom arrangement in the hexagonal BN layers. Additional peaks located approximately at 930, 1020, 1670, and ~3200 cm^{-1} can be detected, peculiar to the primary vibrational features of a covalent B−F mode.[11]

Examinations by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) indicate that the fluorine-doped BN crystals possess a nanotube-like morphology with considerably disordered walls, having a high aspect ratio with the lengths up to several micrometers and diameters of a few tens of nanometers (Figure 1a). High-resolution TEM images indicate that the disordered BN layers are composed of highly curled continuous BN sheets, suggesting that the six-numbered BN atomic rings within

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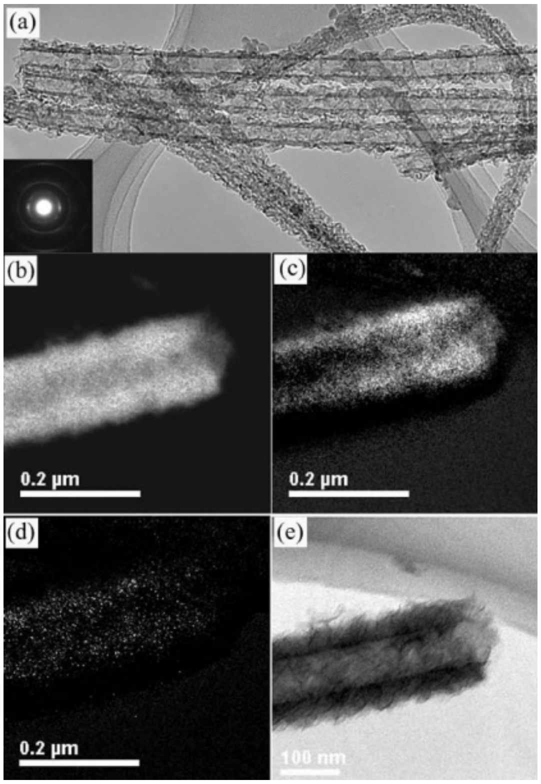

Figure 1. Low-magnification TEM image (a) and elemental maps of F-functionalized BN nanotubes synthesized using the BF_3/NH_3 system in the presence of $MgCl_2$ substrate: (b) B map; (c) N map; (d) F map, and (e) bright-field TEM image. Inset in (a): electron diffraction pattern taken from an individual tube, highlighting the disordered BN layer.

the BN sheets are strongly destroyed. This is quite different from the case of collapsed BN nanotubes when a six-membered ring structure is retained even under high temperature annealing in the presence of noble metals.[12] Energy-dispersion X-ray (EDX) analysis reveals that the elemental composition of BN_xF_y slightly changes from nanotube to nanotube, with statistic average values of $x \approx 0.97$ and $y \approx 0.07$. No traces of magnesium could be found. Electron energy loss spectra (EELS) of the sample reveal the B and N concentration as close to 1:1 stoichiometries and the F concentration of ~4 atom %. Considering the corresponding errors of EDX and EELS analyses, we would define the doping concentration as approximately 5%. We have also noticed that the concentration does not change when the sample is exposed to air or is electron-irradiated under TEM. The fluorine within the BN nanotubes is thus suggested to bond tightly. EELS mapping on the fluorinated BN nanotubes indicates the uniform fluorine distribution within the nanotubes. Representative elemental maps are shown in Figure 1b−e.

For the electrical measurements, we fabricated a standard four-terminal system (Figure 2a). The current−voltage ($I-V$) characteristics (Figure 2b) of an individual F−BN and an undoped and impurity-free BN nanotube may be compared; the latter has been synthesized by an in situ catalytic growth method.[10] The $I-V$ curve of the F−BN nanotube is nonlinear due to the Schottky barriers between the F−BN nanotube and the electrodes. The resistance of the F−BN nanotube is approximately $(2-4) \times 10^6$ Ω. Since the F−BN nanotube is <100 nm in diameter and ~5 µm in length, the resistivity of the individual F−BN is estimated as 0.2−0.6 Ω·cm, indicating a typical heavy-doped semiconductor. For comparison, we also measured the $I-V$ characteristic of an individual pure BN nanotube using the same experimental setup. Shown in Figure 2b is the corresponding $I-V$ curve. It is symmetrical and linear due to the ohm contacts between the BN and electrode, and the currents are notably lower. In fact, the resistance and resistivity of the single BN nanotube are estimated as ~2 × 10^9 Ω and ~300 Ω·cm, respectively, which differ by 3 orders of magnitude compared to those of the doped BN nanotube.

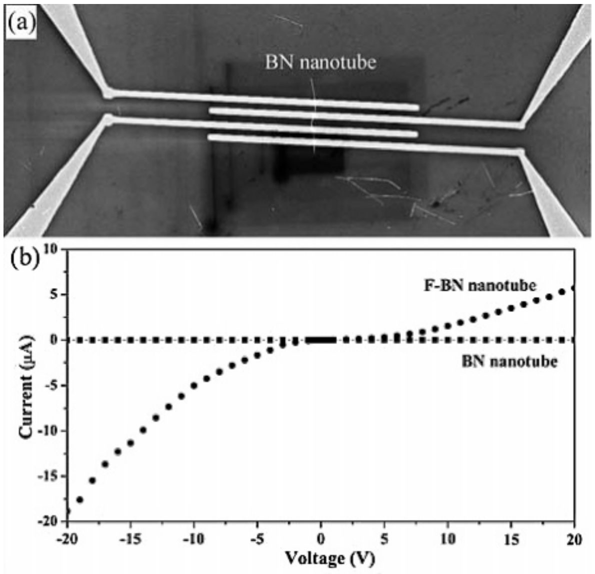

Figure 2. Four-probe measurement setup (a) for the comparative $I-V$ curve recording of a F-functionalized BN nanotube and an individual impurity-free BN nanotube (b).

In summary, fluorination of BN nanotubes results in highly curled tubular BN sheets and makes insulating BN nanotubes semiconducting. The phenomenon is assumed to be particularly important for the applications in the future nanoscale electronic devices with tunable properties.

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Supporting Information Available: Experimental description, SEM images, XRD pattern, FTIR spectrum, high-resolution TEM image, and EELS and EDX spectra of the F−BN nanotubes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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