Wet-Chemistry-Assisted Nanotube-Substitution Reaction for High-Efficiency and Bulk-Quantity Synthesis of Boron- and Nitrogen-Codoped Single-Walled Carbon Nanotubes

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ABSTRACT: We present an innovative wet-chemistry-assisted nanotube-substitution reaction approach for the highly efficient synthesis of boron- and nitrogen-codoped single-walled carbon nanotubes (B_xC_yN_z-SWNTs) in bulk quantities. The as-synthesized ternary system B_xC_yN_z-SWNTs are of high purity and quality and have fairly homogeneous B and N dopant concentrations. Electrical transport measurements on SWNT-network thin-film transistors revealed that the B_xC_yN_z-SWNTs were composed primarily of the semiconducting nanotubes, in contrast to the starting pristine C-SWNTs, which consisted of a heterogeneous mixture of both semiconducting and metallic types.

Figure 1. Schematic illustration of the wet-chemistry-assisted nanotube-substitution reaction process for B_xC_yN_z-SWNT synthesis, which involves exfoliation of the bundled C-SWNTs in an IL, wrapping of the exfoliated SWNTs with boric acid, and carbothermal substitution reaction at elevated temperature.
Detailed TEM investigations revealed that the ternary B\textsubscript{x}C\textsubscript{y}N\textsubscript{z}-SWNTs have fairly homogeneous elemental compositions.

Complementary evidence for the substitutional incorporation of B and N dopants into the tube-shell lattice of the C-SWNTs was also provided by X-ray photoelectron spectroscopy (XPS) characterization. As shown in Figure S4 in the SI, from the curve-fitted XPS spectra of B 1s, C 1s, and N 1s core-level electrons, the existence of sp\textsuperscript{2}-bonded B–C, B–N, and C–N bonding structures can be clearly identified, and the portions of B–C and C–N bonds rival that of the B–N bonds, suggesting that the constituent B, C, and N elements have a real ternary bonding nature within the tube-shell lattice.\textsuperscript{11b,c,12} IR spectroscopy was also useful for obtaining qualitative insight about the formation of hexagonal B\textsubscript{x}C\textsubscript{y}N\textsubscript{z}(h-BCN) ternary phases.

Figure 3a shows typical Fourier transform IR (FT-IR) spectra of C-SWNTs before and after B and N dopant incorporation. As can be seen, whereas the starting pristine C-SWNTs are essentially infrared-inactive (because graphic C networks do not support a static dipole moment),\textsuperscript{13} the IR spectrum of the doped B\textsubscript{x}C\textsubscript{y}N\textsubscript{z}-SWNTs clearly shows the qualitative features characteristic of h-BCN.\textsuperscript{11b,c,12} Specifically, the broad, strong IR absorption band over the range 1120–1600 cm\textsuperscript{−1} (with the main peak centered at 1392 cm\textsuperscript{−1}) corresponds to the in-plane stretching vibrations between atoms within the fused B\textsubscript{x}C\textsubscript{y}N\textsubscript{z} heteroatoms, and the minor absorption band at 710–830 cm\textsuperscript{−1} is ascribed to the corresponding out-of-plane bending modes (see Figure S1b for more details).\textsuperscript{13} Apart from the IR results, the Raman spectrum of the B\textsubscript{x}C\textsubscript{y}N\textsubscript{z}-SWNTs also shows distinct differences from that of the starting C-SWNTs, namely, much stronger disorder-induced D-band scattering and an appreciable line broadening for the tangential G band, as depicted in Figure 3b. These Raman features can be rationalized as a consequence of the substitutional doping of C-SWNTs with B and N heteroatoms, which leads to relaxation of the Raman selection rule for K-point phonons and a breakdown of the selection rule for zone-center phonon excitation.\textsuperscript{14}
In our present study, the temperature of the substitution reaction is a crucial factor that sensitively affects the substitutional B/N doping process of C-SWNTs. As mentioned above, the optimized temperature was found to be ~1000 °C, and it turned out that a decrease in the reaction temperature to 900 °C resulted in minor or no doping of the starting C-SWNTs. On the other hand, when the temperature was increased to 1150 °C, the single-shell tube structure was found to deteriorate severely, causing the majority of the SWNTs to collapse and be transformed into highly defective but much more heavily doped thick $B_xC_yN_z$-SWNTs (see Figure S5). It is important to note that similar structural degradation behavior was also reported by Golberg and co-workers in prior studies of carbothermal substitution reactions using bundled C-SWNT ropes as starting materials, but the corresponding processing temperature was much higher than in our case for the debundled SWNTs. In fact, in our study, we also conducted several control experiments employing bundled C-SWNTs as the precursor for the carbothermal substitution reaction, and neither SWNT deformation nor efficient B/N doping was observed to occur at the highest tested temperature of 1150 °C. These results suggest that the debundled C-SWNTs are much more susceptible to the substitution reaction than the bundled C-SWNT ropes and therefore highlights the key importance of the initial IL-based SWNT debundling step.

To determine whether B/N codoping successfully modified the electronic properties of the C-SWNTs and to demonstrate their applicability in nanoelectronic devices, we comparatively investigated the electrical transport properties of the SWNTs before and after B/N doping through fabrication of SWNT-network thin-film transistors (TFTs) (Figure 4a) according to a published procedure (see the SI for experimental details). As shown in Figure 4c, a dense percolating network of the starting C-SWNTs displayed the typical undepletable transfer characteristics with a low on/off ratio of ~5 due to the presence of both semiconducting and metallic nanotubes. In contrast, the $B_xC_yN_z$-SWNT network with nearly the same tube density and device geometry exhibited clear p-channel transistor behavior with on/off ratio as high as 100, indicating that the as-synthesized $B_xC_yN_z$-SWNTs were composed primarily of semiconducting nanotubes. These results are in line with our previous studies of CVD-grown $B_xC_yN_z$-SWNTs, verifying that B/N codoping is a realistic and promising way to produce purely semiconducting SWNTs and thereby to tackle the problem of electronic-type heterogeneity in pristine C-SWNTs.

To sum up, by exploiting the exfoliation and dispersion of C-SWNTs in imidazolium-based room-temperature ILs, we have innovatively improved the nanotube-substitution reaction methodology for achieving the high-efficiency synthesis of ternary $B_xC_yN_z$-SWNTs in bulk quantities. Combined TEM and EELS analyses together with XPS, FT-IR, and Raman spectroscopic studies confirmed the true substitutional incorporation of B and N dopants into the graphitic tube-shell lattice, with the single-layered nanotubular topology being well-preserved. As a consequence of B/N codoping, the electronic properties of the pristine C-SWNTs were successfully modified, and the thin-film electrical devices built from $B_xC_yN_z$-SWNTs exhibited good electrical performance characterized by semiconducting behavior. Finally, we remark that the present wet-chemistry-assisted substitution reaction strategy is not limited only to nanotubes; the capability of this approach potentially can also be extended to B/N doping of graphene-related materials. Ongoing studies along this line are now underway.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details; supplementry IR, Raman, and XPS characterization results; and the combined TEM and EELS results showing the deformation and collapse of the SWNTs at 1150 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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