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Large-scale synthesis and HRTEM analysis of single-walled B- and N-doped carbon nanotube bundles

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Abstract

Bundles of B- and N-doped single-walled carbon nanotubes (SWNTs) containing up to ~10 at% B and up to ~2 at% N were synthesized at high yields under thermo–chemical treatment of pure C SWNT bundles and B_2O_3 in a flowing nitrogen atmosphere. The bundles were characterized by means of high-resolution transmission electron microscopy and electron energy loss spectroscopy. The effects of synthesis temperature (1503–1773 K) and time (30–240 min) on the B and N contents and yield of the SWNT bundles were determined. The maximum yield of the B- and N-doped SWNT bundles was obtained under synthesis at 1553 K over 30 min. Atomic structure and morphology of individual SWNTs in the bundles, in particular, packing of doped SWNTs, helicity distribution, encapsulation of fullerene-like clusters, diameter and shell number variations were studied. The synthesized SWNTs in the bundles were stacked in a honeycomb array with the uniform inter-tube spacing of ~0.3 nm. No preferable orientation for the graphene-like tubular shells was found, i.e. both zigzag and armchair edges were observed with approximately equal proportions. Frequently, diameter increase took place for the outer tubes in a bundle and for isolated SWNTs. C-based or BN-based fullerene-like encapsulates were observed in individual SWNTs. Carbon oxidation by the B_2O_3 vapor and B and N substitution for C is thought to underlie the doping of C SWNTs. The substitution reaction temperature–time limits with respect to the morphological stability of B- and N-doped SWNT bundles are finally elucidated.

Keywords: A. Doped carbons; Carbon nanotubes; C. Transmission electron microscopy (TEM); electron energy loss spectroscopy (EELS); D. Microstructure

1. Introduction

Nanotubes made of carbon [1] are expected to bring significant breakthroughs in the technology of electronic and engineering materials of the next millennium. For applications, single-walled nanotubes (SWNTs) are preferred over other nanotubular structures [2], since the number of structural defects in them, which can dramatically affect the properties, is significantly reduced. Doping of C nanotubes with B and/or N [3–8] or preparing sandwich-like structures made of C and BN layers [9] may allow to tailor nanotube electronic [10,11] and mechanical properties [12]. For instance, B-doped nanotubes were found to exclusively exhibit metallic conductivity [10] in contrast to undoped nanotubes whose properties vary between metallic and semiconducting depending on helicity and diameter [13]. N-doped nanofibres were also expected to be metallic [8]. In addition, B-doping was found to improve graphitization of multi-walled carbon nanotubes (MWNTs) [4]. Also, it is known that B enhances the oxidation resistance of graphite and conventional carbon fibers [14] which is important for applications.

Doping of C MWNTs and preparation of composite B–C–N MWNTs are usually achieved by arc-discharge [4] or laser ablation [6] by changing the chemical composition of starting electrodes or targets, respectively. Both processes occur in the highly non-equilibrium conditions which negatively influence the chemical and structural homogeneity of the product. An alternative way of effecting C MWNT chemical composition variations has recently been discovered: A general chemical substitution reaction during which C atoms in the nanotubular network are substituted with B or B and N atoms under nanotube oxidation by the B_2O_3 vapor in an argon or nitrogen atmosphere [15,16]. Later on, this method has been

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successfully applied for changing chemical composition of C SWNT bundles by the present authors [17]. However, the limited yield and insufficient chemical homogeneity of the doped SWNT product are serious drawbacks which so far have made a detailed characterization of B- and N-doped SWNT bundles difficult [17]. The present paper reports on the pioneering of large-scale synthesis of B- and N-doped C SWNT bundles by optimization of the synthesis parameters during the substitution reaction and detailed analysis of the resultant doped SWNT product by means of high-resolution transmission electron microscopy paired with electron energy loss spectroscopy.

2. Experimental

Bundles of pure C SWNTs produced by Nd:YAG laser ablation either by CarboLex (USA) or JST-ICORP (Japan) were heated together with B_2O_3 in a flowing nitrogen atmosphere at 1503–1773 K over 30–240 min. The heating was carried out in a vertical induction furnace with a susceptor made of graphite [15–17]. The B_2O_3 powder was placed in an open sintered graphite crucible and then covered with C SWNTs. The experimental set-up is shown in Fig. 1. The N_2 gas was introduced into the chamber at the ambient pressure from the upper and lower inlets (Fig. 1) and its flows were maintained at 3 l/min (upper flow) and 0.2 l/min (lower flow) during the synthesis. The synthesis temperature was monitored using an optical pyrometer with the accuracy of ±10 K.

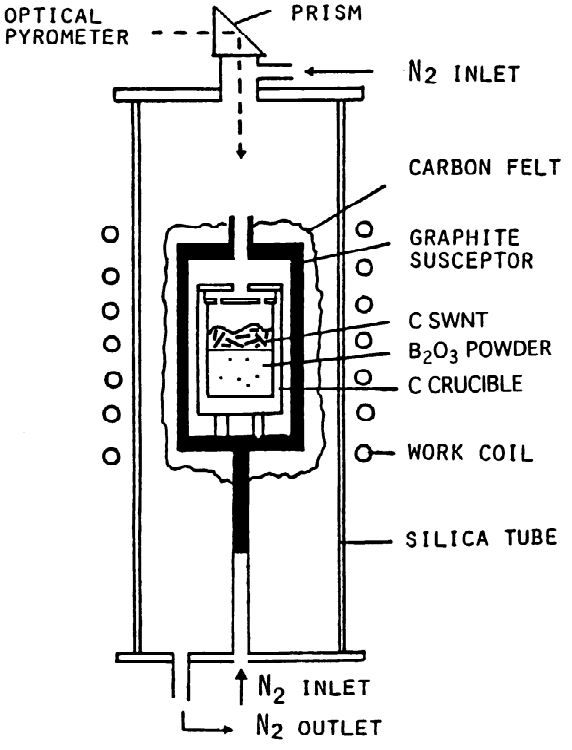

Fig. 1. Experimental set-up for synthesizing B- and N-doped C SWNT bundles.

Upon completing the synthesis the product of the reaction was extracted from the crucible, milled in an agate mortar and mixed with CCl_4. A few drops of the resultant mixture were dripped onto a standard ∅3 mm carbon-coated-cooper grid. High-resolution transmission electron microscopy (HRTEM) was carried out by means of a field emission electron microscope JEM-3000F (JEOL) operating at 300 kV. The microscope had the following characteristics: Spherical aberration coefficient — 1.1 mm; chromatic aberration coefficient — 1.8 mm, point resolution — 0.16 nm; stability of high voltage — 4×10^{-6}; and tilt angle ±30°. HRTEM images were taken at magnification 4×10^5 on a negative film at the vicinity of the optimal defocus value of the microscope, — 56 nm. Parallel detection electron energy loss spectroscopy (Gatan 666) was performed with the aim of measuring B and N contents in the product. Normally, an electron beam focused down to ∅0.5–1.6 nm was placed at different points along and across the SWNT bundles for measuring chemical content variations. Computer simulated SWNT HRTEM images were calculated and displayed using the 'MacTempas' software.

3. Results and discussion

3.1. Effect of synthesis parameters on the B/N contents and yield of doped SWNT bundles

Time/temperature parameters during the syntheses are shown in Table 1. The experimental runs described in the Table may be divided into four main groups, **A**, **B**, **C** and **D**, with respect to the yield of doped SWNT bundles.

Regimes 1 and 2 form group **A**, for which mostly untransformed undoped C SWNT bundles were found. The minority of the resultant bundles contained B, although the overall B-content typically did not exceed 2–4 at%. Normally, the N-doping was not observed (the N-content was probably below the detection limit of the EELS spectrometer).

Group **B**, i.e. Regime 3, was found to be optimal for the B- and N-doped SWNT bundle synthesis. In this case nearly 100% of the C starting SWNT bundles were doped with up to ~10 at% B and up to ~2 at% N. Fig. 2a and b show representative HRTEM images of the B-and N-doped SWNT bundles synthesized under this regime. Typically, resultant SWNTs were stacked in the bundles, although isolated SWNTs were accidentally observed. Numerous EELS spectra taken from the bundles revealed the B/C ratio of ≤0.1 and the N/C ratio of ≤0.02 (Fig. 2c). The diameter of the bundles ranged widely. Thin bundles consisting of just a few individual nanotubes (Fig. 2b) or