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Nanotechnology 27 (2016) 445601 (9pp)

Boron-doped few-walled carbon nanotubes: novel synthesis and properties

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Received 1 May 2016, revised 25 August 2016 Accepted for publication 31 August 2016 Published 26 September 2016



Abstract

Few-walled carbon nanotubes offer a unique marriage of graphitic quality and robustness to inkprocessing; however, doping procedures that may alter the band structure of these few-walled nanotubes are still lacking. This report introduces a novel solution-injected chemical vapor deposition growth process to fabricate the first boron-doped few-walled carbon nanotubes (B-FWNTs) reported in literature, which may have extensive applications in battery devices. A comprehensive characterization of the as-grown B-FWNTs confirms successful boron substitution in the graphitic lattice, and reveals varying growth parameters impact the structural properties of B-FWNT yield. An investigation into the optimal growth purification parameters and ink-making procedures was also conducted. This study introduces the first process technique to successfully grow intrinsically p-doped FWNTs, and provides the first investigation into the impact factors of the growth parameters, purification steps, and ink-making processes on the structural properties of the B-FWNTs and the electrical properties of the resulting spray-coated thin-film electrodes.

S Online supplementary data available from stacks.iop.org/NANO/27/445601/mmedia

Keywords: carbon nanotubes, boron doping, few-walled, ink

(Some figures may appear in colour only in the online journal)

Introduction

The carbon nanotube (CNT) is an intensely studied nanostructure since its discovery in the 1990s by Iijima [1]. Due to a similar intrinsic lattice structure to graphene, carbon nanotubes share many of the beneficial electrical, mechanical, and optical properties of graphene; however, their one-dimensionality enable their use in electrodes as conductive channels that form a percolation network. Coupled with the low-cost and availability of carbon, carbon nanotubes make ideal nanostructures to form conducting networks that may act as charge carriers in batteries or electrodes [2, 3]. In order to achieve stable CNT inks without the use of disruptive and insulating surfactants it is required to attach functional groups to the carbon nanotube sidewalls to separate highly resistive tube bundles and promote a homogenous ink dispersion [10-14]. Surface functionalization through an acid reflux forms structural defects in single walled nanotubes (SWNTs) that digests long tubes into smaller sections thus disrupting the charge transport across the network. Few-walled carbon nanotubes (FWNTs) are multi-walled nanotubes that still exhibit a high aspect ratio and low defect density by possessing a wall number between two and six, yet their electrical properties are not diminished after surface functionalization since the structural integrity of the inner tubes remains intact. FWNTs thus possess a unique morphology that marries the high aspect ratio of SWNTs with the robustness of multi walled nanotubes (MWNTs), and are optimal for many applications such as surfactant-free spray-coated conductive networks [4–9]. Spray-coated surfactant-free solutions of FWNTs are demonstrated to reach as high as $\sim 2100 \text{ S cm}^{-1}$, which is the highest for conductive CNT networks formed from surfactant-free inks [31].

Although ink processing techniques enable highly conductive FWNT networks, intrinsic limitations in the electrical properties of the individual nanotubes may still hinder the overall film conductivity. A common method to lower the resistance of semiconducting sp^2 carbon structures is to

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Figure 1. Images of (a) the powdered Co:Mo:MgO catalyst and (b) the resulting FWNT yield after the CVD growth [31]. (c) The schematic of the solution-injected CVD setup for the growth of B-FWNTs, and (d) the resulting B-FWNT yield after this growth.

p-dope the nanostructures by substituting impurities into the graphitic lattice. This technique is demonstrated on SWNTs and MWNTs with large outer diameters (>20 nm) [15–25]. Since FWNTs are an ideal carbon nanostructure for thin-film electrodes formed from solution-based techniques, it is important to exclusively target FWNTs for substitutional p-doping through new unique growth techniques in order to optimize the bulk electrical properties of the growth yield.

Substitutional doping mechanism

The procedures to substitute boron atoms into the carbon nanotube lattice may be separated into two categories: (1) ingrowth doping methods and (2) post-synthetic doping methods. In-growth methods include a concentration of boron in the carbon source during the synthesis of nanotubes; these methods include arc-discharge, pulsed-laser ablation, and chemical vapor deposition (CVD). Post-synthetic processes substitute boron into the carbon lattice after the carbon nanotubes are grown. In-growth doping methods typically effect all the nanotubes in the bulk yield, whereas postsynthetic procedures are limited to tubes with open vacancies [26]. In order to influence a greater yield of carbon nanotubes, post-synthetic processes are typically conducted at high temperatures with dangerous diborane (B2O3) gas. This separates carbon atoms from the nanotube lattice by forming carbon monoxide, which allows boron to be substituted into the vacant site [27]. In-growth substitutional doping methods are therefore more scalable because they do not require an extra post-growth step with dangerous B₂O₃ to form substitutionally doped CNTs; however, such methods to grow substitutionally doped FWNTs are not reported in literature.

The following study introduces a novel solution-injected CVD growth process to safely synthesize boron-doped FWNTs (B-FWNTs). This CVD process uses an alcohol solution containing boric acid to grow B-FWNTs, which is safer than using combustible gases such as acetylene or methane as the carbon source and a diborane gas post-treatment as the p-doping mechanism. The impact of the solutioninjected CVD growth parameters on the structural properties of the B-FWNTs is explored and the method to purify the growth yield was optimized. Although previous reports indicate that the inclusion of substituted dopants in the graphitic lattice affect the mechanical properties of the CNTs [45-48], the focus of this report is on the impact of substitutional doping on the electrical properties of the FWNTs. The resulting B-FWNTs are therefore processed into inks and spray-coated into functional conductive thin-film electrodes. This study delivers the first B-FWNTs fabricated with a solution-injected CVD process, and the first investigation into the impact factors of the fabrication process on the structural and electrical properties of spray-coated B-FWNT conductive networks.

Results and discussion

A CVD growth method was used to synthesize high yields of FWNTs with a low defect density from a Co:Mo catalyst embedded in a MgO, and is outlined in the supporting materials. This Co:Mo:MgO catalyst and the resulting FWNT yield is depicted in figures 1(a) and (b) respectively. The structural properties are primarily attributed to the composition of the catalyst; therefore, in-growth substitutional doping of boron into the lattice of FWNTs was facilitated with the same powder catalyst as seen in figure 1(a). Ishii *et al* demonstrate a CVD process to grow boron-doped B-FWNTs with a solution of boric acid dissolved in methanol pumped into the furnace as the source solution [28]. Although the carbon source utilized to grow FWNTs is methane, alcohol solutions have been demonstrated as successful sources for



Figure 2. TEM images of the B-FWNTs grown from the solution-injected CVD setup at various magnifications.

FWNT growth [29]. Reports also indicate that the growth yield of CNTs from pure methanol solutions is low compared to mixtures with ethanol [30]. This is due to a greater atomic decomposition of carbon from ethanol as opposed to methanol; however, the amount of carbonaceous impurities is tapered with higher concentrations of methanol in the source solution. The optimal solution based carbon source to grow B-FWNTs thus stems from a mixture of ethanol and methanol hosting a low concentration of boric acid. Figure 1(c) depicts a schematic of the experimental setup for the in-growth substitutionally doped B-FWNTs synthesized in this study; a syringe pump carrying the source solution inserts a needle into the tube furnace suspended over the powdered catalyst. Figure 1(d) depicts a CVD growth yield of the B-FWNTs under the growth conditions described in experimental methods.

The CVD growth yield demonstrates significant nanotube formation with large lengths extending several microns with varying degrees of bundling and curvatures. The morphology and dimensions of the B-FWNTs are depicted in figure 2. It is clear from figure 2(c) that the nanotubes maintain a high aspect ratio with small bundle sizes no more than several nanotubes. The particles intermingling with the nanotubes are residual catalyst particles from the growth yield. Figure 2(c) demonstrates that the nanotubes have very few structural defects such as kinks or stunted growths. Since these nanotubes are grown to possess few morphological defects with a high aspect ratio, it is clear that the CVD growth process fabricates high quality nanotubes from the Co: Mo:MgO catalyst despite a new carbon source and the presence of concentrations of boron in that source. Figures 2(a)and (b) demonstrate that the wall number of the nanotubes fits within the range of FWNTs, demonstrating that the growth process successfully fabricates FWNTs with a source solution that includes boron. The dark outlines in these HRTEM images are the concentric graphitic walls of the CNT. Figure 2(a) displays several nanotubes with wall numbers ranging from 2 to 5 as well as a presence of defective nanotubes, while figure 2(b) displays an isolated B-FWNT with five walls and no visible defects.

In order to confirm that the FWNTs fabricated by this new growth process successfully includes boron in the carbon



Figure 3. EELS point-scan measurements at areas (a) away from the catalyst and (b) near the catalyst as depicted by the inset S-TEM images and the resulting boron atomic percent given in the adjacent tables. (c) An EELS line-scan measurement along a nanotube as depicted by the inset S-TEM image with the resulting boron atomic percent given in the adjacent bar graph.

lattice, electron energy loss spectroscopy (EELS) was conducted on the as-grown CNT sample. Figure 3 displays an energy-loss spectrum of the B-FWNTs as measured by EELS. The ionization edges of boron and carbon are marked on the energy-loss spectrum of the carbon nanotube; the ionization edge of the boron atom is located at 188 eV and the ionization edge of the carbon atom is located at 284 eV, with each representing the excitation of 1s electrons in the K-shell in the hybridized sp² network [32]. The inset scanning-transmitted electron microscopy images in figure 3 marks the scanning site on a nanotube for the EELS measurement at the arrow. The bright white material that the nanotube emanates out from is an agglomeration of catalyst particles. Once the background of the energy-loss spectrum is extracted and subtracted, the cross-section of the energy-loss spectra σ_K and the intensities at the ionization edge $I_{\rm K}$ for each element may be quantified. The number of atoms per unit area that contribute to the K-edge may be quantified as equation (1)

$$N = \frac{I_{\rm K}}{\sigma_{\rm K} I_{\rm T}} \tag{1}$$

with $I_{\rm T}$ representing the total transmitted intensity of the electron beam. The ratio of *N* for each element in the spectrum gives an atomic ratio of the elements in that scanning area. The atomic ratio of boron to carbon derived from the EELS measurements in figure 3 are given by the adjacent tables, and demonstrate the success of the in-growth CVD doping method. The atomic percent of boron in the nanotube was found to be greater at EELS scan points closer to the catalyst agglomeration, as demonstrated in figure 3(b).

Since the source solution in the CVD growth of the B-FWNTs consists of 2.0 atm% boron, it is expected that the

4 methane (undoped)



Figure 4. (a) Raman spectra of Sample 1, Sample 2, and Sample 3 stacked to compare band shifts. (b) The characteristic Raman measurements and details on the samples summarized in the table.

1325.8

1575.1

2619.7

0.0986

850 °C

boron content throughout the nanotube does not exceed 2.0 atm% if the individual boron atoms are individually substituted into the carbon lattice uniformly. EELS measurements on a finite point of a nanotube may register boron content greater than 2.0 atm% due to a coincidence that more boron atoms substituted into the lattice in that scanning area or because the boron atoms arrange themselves into BC₃ nanodomains in the carbon lattice during the nanotube growth. In order to better discern the behavior of boron substitution in the carbon lattice of the nanotubes EELS measurements were taken in a line scan along the length of a CNT extending out of a cluster of catalyst particles. Figure 3(c) illustrates the energy-loss spectrum taken by EELS along a nanotube depicted in the inset STEM image. The 1s $\rightarrow \pi^*$ and 1s $\rightarrow \sigma^*$ transitions are clearly visibly for carbon with the K-edge at 284 eV [33]. The 1s are detectable for boron with the K-edge at 188 eV for some energy-loss spectra. This indicates varying atomic ratios of B/C across the nanotube. The adjacent bar graph in figure 3(c) depicts the relative composition along the line scan of the nanotube, which shows that there is higher boron content in the nanotubes closer to the catalyst. This agrees with previous reports that boron primarily substitutes into the carbon lattice near the tube ends during the growth of CNTs [34]. Atomic percentages of boron near the end of the CNT range above the 2.0 atm% boron content found in the source solution. This suggests that the boron does not evenly substitute into the carbon lattice throughout the nanotube, but concentrates towards the ends of the nanotubes extending out of the catalyst. This behavior may be indirect evidence for the formation of BC₃ domains as opposed to individual atomic substitutions.

The effect of the growth parameters on the structural characteristics of the B-FWNTs was investigated. Figure 4(a)

illustrates the Raman spectra of B-FWNT growths with different combinations of the temperature and content of the source solution. The comparative metrics for these spectra are shifts in the wavelengths of the characteristic peaks (D-band, G-band, and G'-band) reported for undoped FWNTs and differences in the ratio of the D-band and G-band intensities (D/G) [23, 35–39]. These characteristics are summarized for the spectra in the table figure 4(b).

Previous studies demonstrate that p-doping the carbon lattice with boron will lead to shifts in the characteristic peaks of the Raman spectra of the B-FWNT; upshifts in the G-band occur due to alterations to the Fermi energy, and downshifts occur in the D-band and G*-band due to a weaker C-B bond compared to C-C bonds. As we see in figure 4, there is a strong downshift of the D-band of undoped FWNTs by approximately 12.3 cm⁻¹ and a stronger downshift of the D'band by approximately 19.2 cm^{-1} for Sample 1. This infers weaker coupling of B-C bonds included in the carbon lattice due to boron substitution. In addition, there is a dramatic increase in the ratio of the D-band and G-band intensities (D/ G = 0.1511) from that of undoped FWNTs (D/G = 0.0986). This indicates that boron doping of carbon nanotubes disrupts the graphitization during the growth of carbon nanotubes, which is reported in previous studies [23]. The downshift of the G-band is uncharacteristic for a p-doped graphitic lattice; however, reports indicate that shifts in the G-band are insignificant at low boron concentrations substituted into the carbon lattice [40].

Sample 2 demonstrates a downshift in the D-band of undoped FWNTs by approximately 9.7 cm⁻¹ and in the D'band by approximately 24.2 cm^{-1} , which also indicates shifts in the structure of the carbon lattice from undoped FWNTs. The ratio of the D-band and G-band intensities for Sample 2 is D/G = 0.1897, which is also a significant increase than that for undoped FWNTs. The greater D/G ratio for Sample 2 than for Sample 1 suggests that a decrease in the growth temperature of the CVD method fabricates B-FWNTs with a higher defect density. Smaller downshifts from the wavelengths of the D-band and the D'-band in the Raman spectrum of undoped FWNTs occur for Sample 2 than for Sample 1. This suggests that the greater D/G ratio for Sample 2 is not due to higher concentrations of B-C bond formations in the carbon lattice than Sample 1. Thus lowering the temperature during the CVD growth may lead to B-FWNTs with greater morphological defects such as kinks and bends, or more carbonaceous impurities.

Sample 3 demonstrates a downshift in the D-band of undoped FWNTs by approximately 7.6 cm⁻¹ and in the D'band by approximately 4.0 cm^{-1} , which also indicates shifts in the structure of the carbon lattice from undoped FWNTs. The ratio of the D-band and G-band intensities for Sample 3 is D/G = 0.1803, which is also a significant increase than for undoped FWNTs. The D/G ratio for Sample 3 is greater than for Sample 1 but nearly equivalent to Sample 2; however, the downshift of the D-band and D'-band wavelengths from those of the undoped FWNTs is significantly lower in Sample 3 than in Samples 1 and 2. There is also an upshift in the G-band wavelength for Growth 3 from that of undoped



Figure 5. Thermogravimetric analysis of (a) Sample 3 and of (b) Sample 1.

FWNTs by 3.0 cm^{-1} , which is characteristic for a p-doped graphitic lattice. Evidence of boron substitution in Sample 3 may be drawn from the upshift in the G-band, the downshift of the D-band, and downshift of the D'-band from the undoped FWNTs; however, the increase in the D/G ratio from Sample 1 may not be caused from increased boron substitution since the shifts in the wavelengths of the characteristic peaks in Sample 3 from those of the undoped tubes are smaller than the shifts for Sample 1. Therefore, it may be concluded that increasing the methanol content of the source solution forms nanotubes with greater defect density or forms yields with greater quantities of carbonaceous impurities.

Thermal gravimetric analysis of the B-FWNT growth yields was conducted to determine their content and the thermal stability of the doped nanotubes. The blue line in the TGA measurement illustrates a comparative reference point of the nanotube yield thermal stability. Figure 5(a) depicts a TGA of B-FWNT grown at 850 °C with a 3:1 methanol to ethanol source solution. Figure 5(b) depicts the TGA measurement of B-FWNT grown at 850 °C with a 1:1 methanol to ethanol source solution. For each regression the amorphous carbon oxidizes at approximately 300 °C, which agrees well with literature. It is clear by comparing the TGA regressions in figure 5 that Sample 1 has a higher thermal stability than Sample 3. This is due to the larger area under the TGA curve past 500 °C for Sample 1 compared to Sample 3, which demarks a higher oxidation temperature of the doped nanotubes. Since the D/G ratio of Sample 3 is higher than Sample 1, the lower thermal stability of Sample 3 may be attributed to a higher defect density in the nanotubes. This indicates that the B-FWNTs of Sample 1 possess a higher graphitic quality than Sample 3. Another observation is that the carbon content in Sample 1 contains 6.6 wt% amorphous carbon, whereas there is 10.8 wt% amorphous carbon within the total carbon content of Sample 3. These quantities were evaluated by distinguishing the two carbon phases in the mass loss spectra from 200 °C-700 °C and determining the relative mass loss within the total carbon oxidized during the thermal treatment. It may be concluded therefore that the CVD yield in Sample 3 produces less thermally stable nanotubes and higher impurity content than Sample 1.

Although the expected sheet resistance of the spraycoated films was expected to be nominally lower than the undoped FWNT spray-coatings at the same thickness, it was quickly discovered that it was in fact at least an order of magnitude higher. An investigation into the spray-coated film characteristics reveals that a secondary phase exists in the random network that may impede the electronic transport, as seen in the SEM images of the coating surface in figure 6(a). The SEM images of the spray-coating surface clearly display B-FWNTs with a high aspect ratio incorporated in a random network, along with a secondary phase that appears as an amorphous impurity. Energy dispersive spectroscopy does not distinguish any unordinary element from the sample; only carbon, oxygen, and boron are most prevalent in the sample. This secondary phase is most logically supplied during the CVD synthesis of the B-FWNTs, as evidenced by the additional gray powder visible on the surface of the CVD growth yield in figure 1(d). The consistency of this gray phase is much lighter and separates easier than the powder of tangled nanotubes.

After separating gray 'ash' from the CVD growth yield, ATR-FTIR measurements were performed to compare the secondary phase to the bulk phase of the B-FWNT yield. Figure 6(b) presents the FTIR spectrum of the gray 'ash' secondary phase. The wavenumbers of the characteristic peaks may be representative of multiple components, including oxygenated graphitic structures, boron oxide, and boric acid. These conclusions are formed based on evidence of the formation of a white powder on the window of the tube furnace during the CVD growth, which is reported as boron oxide and boric acid in the literature [41]. The characteristic wavelengths in figure 6(b) are representative of bonds reported for boron oxide; a wide peak centered at about 3350 cm^{-1} for stretching of O–H bonds and a sharp asymmetric peak at about 1196 cm^{-1} representative of B–O



Figure 6. (a) An SEM image of the spray-coated B-FWNT network before methanol-washing, (b) ATR-FTIR spectrum of impurity phase (gray ash) in B-FWNT growth yield, (c) ATR-FTIR spectrum of B-FWNT growth yield after oxidation, and (d) SEM image of the spray-coated B-FWNT network after methanol-washing.

deformation. Boron carbide was eliminated as the prominent secondary phase since the broad shoulder around 1050 cm^{-1} characteristic of boron carbide phonons is not present [41, 42]. Another condition that is not met for the formation of prevalent boron carbide impurities during the CVD procedure is a high growth temperature (>1000 °C) [43, 44].

After the B-FWNT yield was oxidized at 500 °C we see additional peaks characteristic of oxygen groups appear in the FTIR spectrum. As illustrated in figure 6(c), a peak emerges in the FTIR spectrum at about 1407 cm⁻¹ representing B-O bond stretching. Furthermore, a sharp peak at 1024 cm^{-1} emerges after the oxidation, which is attributed to B-O-C bond stretching. It is also observable in figure 6(c) that the peak representing O-H bonds flattens after the oxidation with regards to the background baseline while the absorption peak intensity at 1184 cm⁻¹ attributed to B–O bond deformation increases. This illustrates that there is a decrease in amorphous carbon after oxidation, but not a removal of the secondary phase. Although these peaks infer that the secondary phase consists of boron oxide, the additional B-O-C peak muddles the explanation of the exact structural composition from the FTIR spectra.

Since it appears that the secondary phase of the CVD growth yield consists of bonds that attribute to boron oxide,

an additional purification step was instituted to remove it from the B-FWNT yield. After thermally treating the as-grown B-FWNTs, the gray 'ash' was carefully scraped off the primary phase. The primary phase B-FWNTs were then dispersed in methanol and boiled via a heating mantle in order to dissolve any residual boron oxide remaining after scraping off the 'ash'. After the B-FWNTs were boiled in methanol, an ink-making process was conducted to disperse the nanotubes in IPA following an acid reflux. The resulting inks were finally spray-coated with an airbrush on a cleaned glass substrate. Figure 6(d) demonstrates SEM images of the surface of the spray-coatings, which may be compared to figure 6(a) to determine a difference in the composition of the random network. The surface coating depicted in figure 6(d)demonstrates a clear decrease in the amorphous phase material overwhelming present in the SEM images depicted in figure 6(a); however, there is still a distinguishable impurity intermingled with the random network of B-FWNTs. Since the methanol wash is expected to remove any residual boron oxide or boric acid that remain present in the B-FWNT growth yield after a thermal purification, it may be concluded that an additional impurity phase is formed in the CVD synthesis. Since the elemental composition and molecular structure of the B-FWNT sample does not distinguish any

 Sample	Zeta poten- tial (mV)	Thickness $(\times 10^{-5} \text{ cm})$	Sheet resistance ($\Omega \text{ sq}^{-1}$)	Conductivity (S cm ⁻¹)
Thermally treated B-FWNTs	-17.2	2.5–3	>10 K	<5
Thermally treated, HN0 ₃ refluxed B-FWNTs	-29.5	6–7	138	103.5–120.8
Thermally treated, methanol washed, HN0 ₃ refluxed B-FWNTs	-29.5	4–5	116	172.4–215.5

Table 1. Zeta-potential and spray-coated film properties of the inks formed with B-FWNTs at various purification stages.

other unique phases that may be eliminated with additional purification steps, it is proven difficult to efficiently eliminate all the impurities that may exist in the CVD yield.

Although it is clear that the inadequate purification of the B-FWNT yield prevents the formation of highly conductive spray-coatings, improving the ink dispersion through surface functionalization of the nanotube surface is still observed to impact the spray-coating uniformity and thus improve the electrical properties of the nanotube network. A comparison of spray-coated film properties formed from IPA-based inks containing B-FWNTs that either have or have not been refluxed in acid is presented in table 1. It is clear from the comparison of the zeta-potential of the IPA inks and the resulting surface coatings that the inks consisting of B-FWNTs refluxed in HNO₃ (Sample B) possess a higher zeta-potential, which results in a higher spray-coating uniformity. We may conclude that the greater conductivity of the random network in Sample C than Sample B is achieved by better eradicating disruptive impurities from the film. Although the conductivity of the Sample C spray-coating is higher than that for Sample A, it is more than an order of magnitude lower than the conductivity reached by undoped FWNTs. This relatively low conductivity contradicts our initial expectations, but it may be due to a few reasons: (1) the presence of a disruptive impurity not eliminated by the thermal purification and methanol washing steps, (2) the destruction of B-FWNTs in the acid reflux because of greater reactivity due to inherently greater strain from the boron substitution, or (3) higher intrinsic resistance of the B-FWNTs due to a greater density of morphological defects than FWNTs.

Summary

In conclusion, we introduce a new method to fabricate a novel boron-doped few walled carbon nanotube structure via a safe solution injected CVD synthesis method. Initial characterization of the B-FWNTs reveals that the graphitic lattice contains varying amounts of boron, which is reflected in EELS and Raman spectroscopy measurements. An investigation into the effect of the growth parameters on the B-FWNT structure revealed that a higher concentration of methanol in the source solution forms B-FWNTs with a lower thermal stability and a greater concentration of defective carbon. Additional studies on the impurity phases present in the growth yield and purification steps to eliminate them revealed the presence of boron oxide among the B-FWNTs, which was proven to be effectively removed from a methanol wash purification step. The surface functionalization of methanol washed B-FWNTs showed better film uniformity with higher conductivity than for untreated B-FWNTs. This investigation into the growth mechanism, purification process, and the resulting properties of B-FWNTs may stand as the foundation for additional efforts to optimize the conductivity of FWNTs and thus improve the conductivity of spray-coated carbon nanotube networks.

Experimental methods

B-FWNT synthesis

A carrier gas composed of Ar/H_2 is used to ramp the temperature and set the flow rate of the vaporized source during the growth. An exhaust bubbler is attached as a precaution to dilute any acid vapor that may condense away from the furnace. The Co:Mo:MgO catalyst for the CVD growth is synthesized through a combustion method with a ratio of 1:0.5:100, which is outlined in the supplementary materials. The source solution for the CVD growth of the B-FWNTs is prepared by dissolving boric acid in a 1:1 methanol + ethanol mixture so as to contain 2 atm% boron. After the furnace is ramped to 850 °C the source solution is injected into the

furnace via the syringe pump at 20 ml hr^{-1} for 33 min with Ar flowing at 1600 sccm as the carrier gas.

B-FWNT spray-coating process

As mentioned in the previous section, Growth 1 of B-FWNTs was conducted with a CVD growth at a temperature of 850 °C with a 2.0% atm boron solution with a mixed solvent of ethanol/methanol at a ratio of 1:1. To investigate the effect of temperature on the CVD growth process for B-FWNTs, the source solution of 1:1 methanol/ethanol with a 2.0 atm% boron content was introduced to the tube furnace after ramping to 750 °C. Reports on CVD growths of FWNTs also indicate that a higher concentration of methanol in a methanol/ethanol carbon source solution reduces the amount of B-FWNTs was thus conducted with a carbon source solution consisting of a 3:1 methanol/ethanol ratio with a 2.0 atm% boron content.

Since the nanotubes synthesized in each of the growths demonstrated significant degrees of bundling, an ink-making process was utilized to disperse the B-FWNTs in IPA. A thermal purification step to eliminate amorphous carbon from the growth yield without reducing the B-FWNT content was conducted on the pristine nanotube yield at a temperature of 625 °C for 1 h in accordance. This yield was then washed in 100 ml of boiling methanol for 1 h to eliminate the boron oxide. Approximately 30 mg of the purified B-FWNTs were then refluxed in 80 ml of a 10 M HNO₃ solution for approximately 2 h. The refluxed B-FWNTs were then washed with over 500 ml of DI water via a vacuum filtration, and then redispersed in IPA at an approximate concentration of 0.6 mg ml^{-1} . The resulting inks were finally spray-coated with an airbrush (A470M airbrush at 200 kPA of argon) onto 100 mm^2 area on a cleaned glass substrate heated to $120 \text{ }^\circ\text{C}$.

References

- [1] Iijima S 1991 Nature 354 56
- [2] Hu L, Hecht D S and Grüner G 2010 Chem. Rev. 110 5790
- [3] Kim S Y, Hong J, Kavian R, Lee S W, Hyder M N, Shao-Horn Y and Hammond P T 2013 *Energy Environ. Sci.* 6 888
- [4] Kumar N, Jeon I, Sohn G, Jai R, Kumar S and Baek J 2011 ACS Nano 5 2324
- [5] Lee S W, Gallant B M, Lee Y, Yoshida N, Kim D Y, Yamada Y, Noda S, Yamada A and Shao-Horn Y 2012 *Energy Environ. Sci.* 5 5437
- [6] Feng Y, Ju X, Feng W, Zhang H, Cheng Y, Liu J, Fujii A, Ozaki M and Yoshino K 2009 Appl. Phys. Lett. 94 123302
- [7] Zhao B, Zhang L, Liang Y, Qiu H and Yang J 2012 *Appl. Phys.* A **108** 351
- [8] Qian C, Qi H, Gao B, Cheng Y, Qiu Q, Qin L-C, Zhou O and Liu J 2006 J. Nanosci. Nanotechnol. 6 1346
- [9] Di J, Hu D, Chen H, Yong Z, Chen M, Feng Z, Zhu Y and Li Q 2012 ACS Nano 6 5457
- [10] Martinez M et al 2003 Carbon 4 2247
- [11] Bower C, Kleinhammes a, Wu Y and Zhou O 1998 Chem. Phys. Lett. 288 481

- [12] Datsyuk V, Kalyva M, Papagelis K, Parthenios J, Tasis D, Siokou A, Kallitsis I and Galiotis C 2008 Carbon 46 833
- [13] Geng H, Kim K, So K, Lee Y, Chang Y and Lee Y 2007 J. Am. Chem. Soc. 129 7758
- [14] Hersam M C 2008 Nat. Nanotechnol. 3 387
- [15] Cao Q and Rogers J A 2009 Adv. Mater. 21 29
- [16] Reich S, Thomsen C and Maultzsch J 2004 Carbon Nanotubes: Basic Properties and Physical Concepts (New York: Wiley-VCH)
- [17] Wirtz L 2003 AIP Conf. Proc. 685 402
- [18] Yi J-Y and Bernholc J 1993 Phys. Rev. B 47 1708
- [19] Tang Y, Yin L, Yang Y, Bo X, Cao Y, Wang H and Zhang W 2012 ACS Nano 3 1970
- [20] Koretsune T and Saito S 2008 Phys. Rev. B 77 165417
- [21] Fuentes G, Borowiak-Palen E, Knupfer M, Pichler T, Fink J, Wirtz L and Rubio A 2004 Phys. Rev. B 69 245403
- [22] Gai P L, Stephan O, McGuire K, Rao A M, Dresselhaus M S, Dresselhaus G and Colliex C 2004 J. Mater. Chem. 14 669
- [23] McGuire K, Gothard N, Gai P L, Dresselhaus M S, Sumanasekera G and Rao A M 2005 Carbon 43 219
- [24] Czerw R, Chiu P-W, Choi Y-M, Lee D-S, Carroll D, Roth S and Park Y-W 2002 Curr. Appl. Phys. 2 473
- [25] Wei B, Spolenak R, Kohler-Redlich P, Rühle M and Arzt E 1999 Appl. Phys. Lett. 74 3149
- [26] Maiti U N, Lee W J, Lee J M, Oh Y, Kim J Y, Kim J E, Shim J, Han T H and Kim S O 2014 Adv. Mater. 26 40
- [27] Liu X M, Gutiérrez H R and Eklund P C 2010 J. Phys.: Condens. Matter 22 334213
- [28] Ishii S, Nagao M, Watanabe T, Tsuda S, Yamaguchi T and Takano Y 2009 Physica C 469 1002
- [29] Zhang Y, Gregoire J M, van Dover R B and Hart A J 2010 J. Phys. Chem. C 114 6389
- [30] Qi H, Qian C and Liu J 2006 Chem. Mater. 18 5691
- [31] Preston C, Song D, Dai J, Tsinas Z, Bavier J, Cumings J, Ballarotto V and Hu L 2015 Nano Res. 8 2242
- [32] Han W, Bando Y, Kurashima K and Sato T 1998 Chem. Phys. Lett. 299 368
- [33] Redlich P, Loeffler J, Ajayan P M, Bill J, Aldinger F and Riihle M 1996 Chem. Phys. Lett. 260 465
- [34] Hsu W K et al 2000 J. Mater. Chem. 10 1425
- [35] Fischer P 2011 Mater. Sci. Eng. R 72 81
- [36] Piscanec S, Lazzeri M, Robertson J, Ferrari A C and Mauri F 2006 Phys. Rev. B 73 24
- [37] Pisana S, Lazzeri M, Casiraghi C, Novoselov K S, Geim A K, Ferrari A C and Mauri F 2007 Nat. Mater. 6 198
- [38] Ferrari A C 2007 Solid State Commun. 143 47
- [39] Yan J, Zhang Y, Kim P and Pinczuk A 2006 *Phys. Rev. Lett.* 1 1
- [40] Monteiro F H, Larrude D G, Maia da Costa M E H, Terrazos L A, Capaz R B and Freire F L 2012 J. Phys. Chem. C 116 3281
- [41] Borowiak-Palen E, Pichler T, Fuentes G G, Graff A, Kalenczuk R J, Knupfer M and Fink J 2003 Chem. Phys. Lett. 378 516
- [42] Reigada D C and Freire F I Jr 2001 Surf. Coat. Technol. 889 142
- [43] Deshpande S V, Gulari E, Harris S J and Weiner A M 1994 Appl. Phys. Lett. 65 1757
- [44] Lee S, Mazurowski J, Ramseyer G and Dowben P A 1992 J. Appl. Phys. 72 4925
- [45] Cruz-Silva E, Lopez-Urias F, Munoz-Sandoval E, Sumpter B G, Terrones H, Charlier J C, Meunier V and Terrones M 2009 ACS Nano 3 1913
- [46] Ayala P, Arenal R, Rümmeli M, Rubio A and Pichler T 2010 Carbon 48 575
- [47] Fakhrabadi M M S, Allahverdizadeh A, Norouzifard V and Dadashzadeh B 2012 Solid State Commun. 152 1973
- [48] Fakhrabadi M M S, Allahverdizadeh A, Kamkari B and Vahabi M 2013 J. Comput. Theor. Nanosci. 2536