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## Letters to the Editor

# Direct and large scale electric arc discharge synthesis of boron and nitrogen doped single-walled carbon nanotubes and their electronic properties

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### ABSTRACT

Boron and nitrogen co-doped single-walled carbon nanotubes (BN-SWCNTs) were directly synthesized at large scale using an electric arc discharge method. X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and UV–vis–NIR spectroscopy were performed to investigate structure and properties of BN-SWCNTs. These results show that the band gaps of SWCNTs have been tuned greatly with B and N doping.

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Owing to their unique structural and electronic properties, single-walled carbon nanotubes (SWCNTs) have been widely accepted as prime candidates for many applications in nano-electronic devices [1]. However, as-prepared SWCNTs can be either metallic or semiconducting with varying band gaps depending on their helicities and diameters [2]. This presents a serious obstacle to their utilization in nanoelectronic devices, because different types of devices require certain types of SWCNTs. Therefore, the control of the electronic properties of SWCNTs is essential to their applications. Doping of heteroatoms into carbon nanotubes can be an effective way to tune their electronic properties. Thus, boron or/and nitrogen doped carbon nanotubes have attracted much attention because of their tunable band gap which is primarily controlled by their chemical composition rather than their geometry [3].

Since an electric arc discharge method was reported in 1994 [4], several studies and methods have been reported on the synthesis of B and N doped multi-walled carbon nanotubes (MWCNTs) [5,6]. But the direct synthesis of both B and N doped SWCNTs (BN-SWCNTs) was reported only until re-

cently using hot filament chemical vapor deposition (HF-CVD) [3] and laser ablation [7]. It is still a great challenge to synthesize BN-SWCNTs at large scale with certain and tuned band structures. Herein, we report the direct synthesis of B and N doped SWCNTs by an electric arc discharge technique at large scale (up to tens of grams per run) and their tuned electronic properties.

For preparing BN-SWCNTs, CoNiB amorphous alloys were prepared by chemical reduction method [8] as the catalyst and boron source. The consumable anodes were prepared by the CoNiB amorphous alloys with graphite using our previous method [9]. The contents of Co, Ni and B in anodes were 2:2:1.9 at%. The experiment was carried out under a mixed buffer gas with He/N<sub>2</sub> (volume ratio: 9:1) at a total pressure of 530–550 Torr and the arc discharge was created by a current of 100 A with a distance of ~3 mm between the electrodes. Using this process, we can produce BN-SWCNTs at the scale of 10 g/h. For comparison, undoped SWCNTs were prepared under the same conditions using anodes that had Co and Ni at 2:2 at% in pure He gas.

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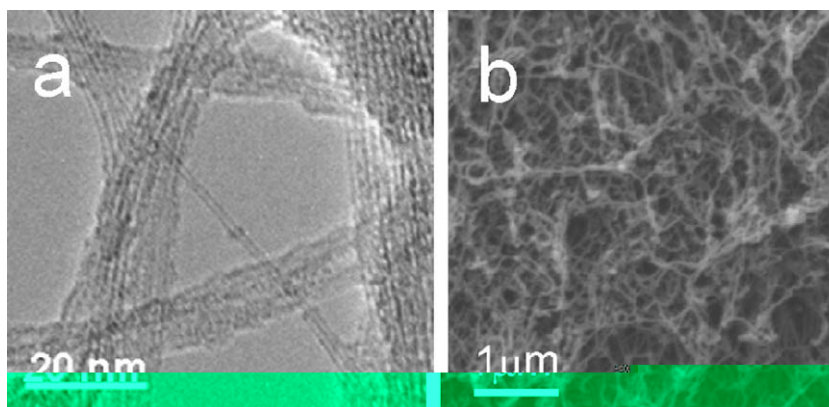


Fig. 1 – (a) TEM and (b) SEM images of as-prepared BN-SWCNTs produced by the electric arc discharge method.

A typical transmission electron microscopy (TEM) image of BN-SWCNTs is shown in Fig. 1a. Most of the tubes were found in bundle form, and occasionally some individual tubes were observed. The diameters of BN-SWCNTs were  $\sim 1.2$ – $1.6$  nm, based on large amounts of TEM images. Fig. 1b shows the scanning electron microscopy (SEM) image of BN-SWCNTs. The product contains high-density nanotubes. Most nanotubes exist in bundles and tangled each other.

X-ray photoelectron spectroscopy (XPS) was used to estimate the contents of boron and nitrogen and study their bonding environments in BN-SWCNTs. The high resolution B 1s and N 1s XPS spectra are shown in Fig. 2. These spectra have been curve-fitted by Voigt lines to detect bonding structures in BN-SWCNTs. The B 1s spectrum of BN-SWCNTs (Fig. 2a) appears broad and has an asymmetric peak profile. The broad band can be deconvoluted into two bands at 190.1 and 192.6 eV, which can be assigned to the B–C and B–O bonding structures, respectively. The N 1s spectrum (Fig. 2b) can be deconvoluted as a band at 399.5 eV, corresponding to the N–C bonding structure [10]. The B and N concentrations in BN-SWCNTs were estimated to be 1.20 and 2.19 at%, respectively. These XPS spectra mainly reflects the bonding structure of BN-SWCNTs bundles at the surface, since the escape depth of photoelectrons in XPS is only about

1–3 nm for carbon materials. To find where the B/N atoms locate, e.g. whether in the impurity such as on the surface amorphous carbon or incorporated into the nanotubes, we have studied the inner atom composition of BN-SWCNT bundles using etching technique. The surface layer was etched away by Ar<sup>+</sup> sputtering for 3 min. The B 1s and N 1s spectra of BN-SWCNTs before and after Ar<sup>+</sup> sputtering are shown in Fig. 3. The XPS profiles of N 1s exhibit similar features before and after Ar<sup>+</sup> etching. But Ar<sup>+</sup> sputter etching reduced the intensity of the peak at 192.6 eV corresponding to B–O bond while increased the intensity of the peak at 190.1 eV corresponding to B–C bond in the B 1s spectrum. This indicates that B atoms have been partly oxidized on surface of the bundles. After Ar<sup>+</sup> sputter etching, the B and N concentrations in BN-SWCNTs were estimated to be 0.97 and 1.86 at%, respectively. These results indicate that B and N atoms are incorporated into the carbon nanotubes.

The most attractive feature of doped SWCNTs is their electronic properties can be tuned by dopants. Theoretical studies have predicted that B and N doping in SWCNTs could create localized impurity states in the energy gaps of nanotubes and the band gaps of doped semiconducting SWCNTs would be decreased by increasing B and N concentrations [11]. Recently, the decreasing of the band gaps in SWCNTs by B dop-

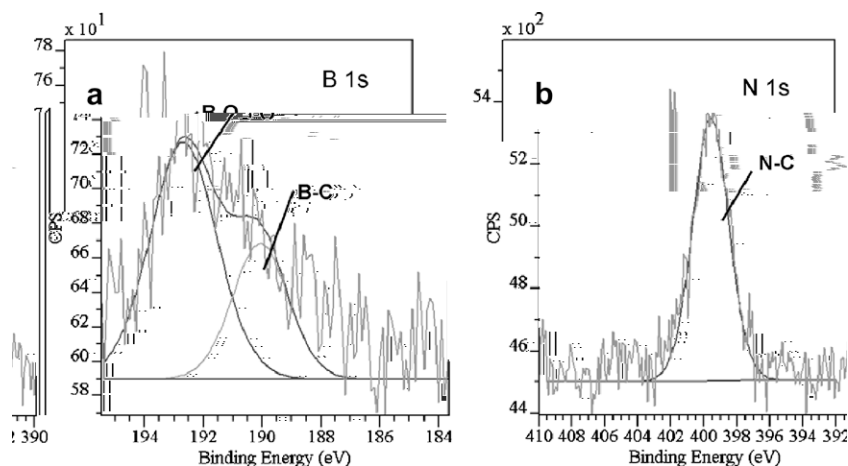
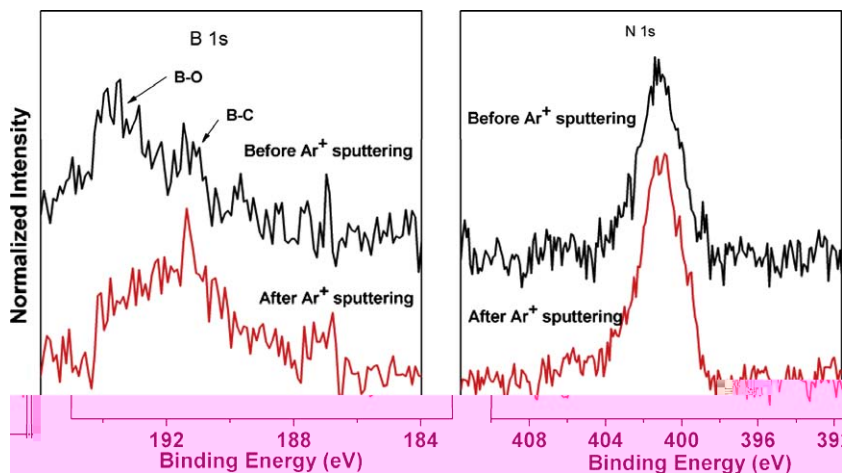
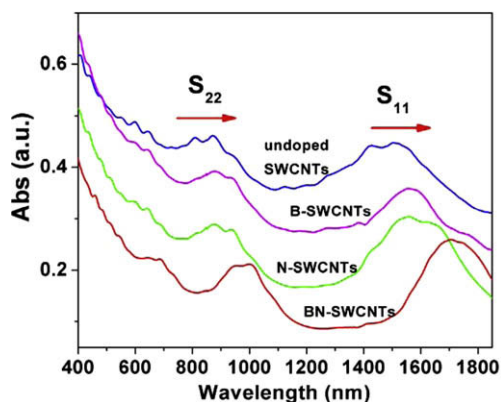


Fig. 2 – High resolution (a) B 1s and (b) N 1s XPS spectra of BN-SWCNTs. All of the high resolution XPS spectra were subtracted with the Shirley background and curve-fitted by Voigt lines.



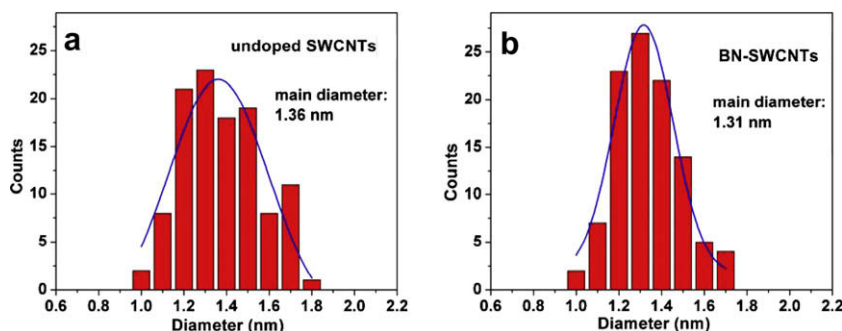
**Fig. 3** – B 1s and N 1s XPS spectra of BN-SWCNTs before (black) and after Ar<sup>+</sup> sputtering (red). The profiles of B–C and N–C bonding inside the bundles are nearly the same as on the surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ing was experimentally demonstrated [12]. Here, UV–vis–NIR absorption was used to explore the band gaps of BN-SWCNTs. Fig. 4 shows the typical absorption spectra of BN-SWCNTs compared to undoped SWCNTs. For the undoped one, the peaks at 1422 and 1507 nm arise from the electronic transitions between the first pair of van Hove singularities (vHs)



**Fig. 4** – UV–vis–NIR absorption spectra of undoped SWCNTs B-SWCNTs, N-SWCNTs and BN-SWCNTs dispersed in 1 wt% sodium dodecyl benzene sulfonate/D<sub>2</sub>O solution.

in semiconducting SWCNTs ( $S_{11}$  band), and the peaks at 810 and 870 nm are assigned to the  $S_{22}$  band. After B and N doping,  $S_{11}$  band shifts significantly to 1706 nm (about 200 nm red shift), and the main peaks of  $S_{22}$  shift to 943 and 1000 nm (about 130 nm red shift). The remarkable red shifts of  $S_{11}$  and  $S_{22}$  indicate that the doping with B and N atoms has significantly changed the band gaps of SWCNTs. For the control experiment, we have prepared B doped SWCNTs (B-SWCNTs) and N doped SWCNTs (N-SWCNTs) by electric arc discharge method (see S1). Similar changes have also been observed for the B or N doped SWCNTs as shown in Fig. 4, through less significant. However, the influence of tube diameters on band gaps should be considered, since the band gaps of semiconducting SWCNTs are inversely proportional to the tube diameters [2]. Diameter distributions of BN-SWCNTs and undoped SWCNTs were performed based on high resolution TEM (HRTEM) images (Fig. 5). These results show that the tubes main diameters decreased after B and N doping, though they exhibit similar diameter distributions, as observed in the Raman spectra (Fig. S1). Smaller diameter should lead to blue shifts of  $S_{11}$  and  $S_{22}$  for normal SWCNTs. But we observed opposite trend (red shifts of  $S_{11}$  and  $S_{22}$ ) for the doped SWCNTs. Therefore, it is believed that the red shifts of  $S_{11}$  and  $S_{22}$  are mainly due to the B and N doping effect on the electronic properties of SWCNTs.



**Fig. 5** – Diameter distributions of (a) undoped SWCNTs and (b) BN-SWCNTs based on HRTEM images. The distributions were fitted by the Gaussian function.

In summary, we have synthesized at large scale both B and N doped SWCNTs using an electric arc discharge method. UV-vis-NIR show the electronic properties, including band gaps of SWCNTs, have been tuned with B and N doping. We expect that this method would offer an efficient way to produce BN-SWCNTs at large scale with tailored band structures. This would make it possible for BN-SWCNTs to practical applications, such as in field-effect transistors, photovoltaic devices, and composite materials in the future.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.02.027.

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# Dechlorination of chlorophenols mediated by carbon nanotubes in the presence of oxygen

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## ABSTRACT

Using chlorophenols as probe compounds, we examined the occurrence of oxidative coupling during carbon nanotube adsorption of phenolic compounds in the presence of oxygen. The oxidative coupling was confirmed by the agreement of the dechlorination stoichiometries of various chlorophenols with the free-radical mechanism of oxidative coupling. The oxidative coupling reaction was first-order with respect to chlorophenols on carbon nanotubes and increased with the increase of pH.

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