Magnetic-field-induced diameter-selective synthesis of single-walled carbon nanotubes†

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Received 18th November 2011, Accepted 18th December 2011
DOI: 10.1039/c2nr11783e

We report a facile and scalable approach to synthesize single-walled carbon nanotubes (SWNTs) with selected diameter distribution by applying a magnetic field perpendicular to the electric field in the arc plasma region. It is found that this magnetic field-induced diameter-selectivity strategy enables the control of the SWNTs with different diameter distributions in different regions, and the diameter-selective efficiency could be enhanced by modifying the direction of magnetic field. Our results indicate that the motions of the catalysts with different particle sizes, positive carbon ions and electrons are significantly influenced by the magnetic field and electromagnetic force, resulting in the different nucleation and growth processes of SWNTs due to the collective interactions between the magnetic field and arc plasma. This approach would enable a viable route towards the synthesis of SWNTs with desired diameter through the tuning of arc parameters in the arc discharge process.

Introduction

The superior electronic and optical properties of single-walled carbon nanotubes (SWNTs) strongly depend on their diameter and chiral angle,†,‡ which are identified as the chiral indices (n, m). All SWNTs are divided into semiconducting and metallic depending on all possible (n, m)s, and the bandgap of semiconducting SWNTs is inversely proportional to the diameter. Therefore, synthesis of the SWNTs with desired chiral angle or diameter distribution is important for the advancement of SWNTs in nanoelectronic applications.†,‡ Based on chemical vapor deposition (CVD) techniques, extensive efforts towards the controllable synthesis of SWNTs with specific diameter distribution or chirality have been made by modifying the catalyst type,§ particle size,* and growth conditions (such as the temperature, carbon source concentration, and gas flow rate).†,‡,§,‖,‡,‡ However, it is still a great challenge to effectively control the diameter distribution during the growth process; and the as-synthesized SWNTs are known to contain some structural defects.

The direct current (DC) arc discharge method is considered to be one of the most efficient techniques for large-scale synthesis of defect-free SWNTs.†,‡,‡ Unfortunately, this method exhibits low tunability and controllability of the SWNT growth process as compared to other SWNT synthetic techniques. However, significant progress in the control of the SWNT growth process has been achieved through applying an axial external magnetic field to the arc plasma.†,‡,‡ Recently, Volotskova et al.† demonstrated that the distribution of SWNT chiralities synthesized by DC arc discharge was affected by the application of an axial magnetic field (0.2–2 kG) to the region of the arc plasma. Although the plasma density and electron temperature have been changed after applying an axial magnetic field, the tunability of chirality-distribution of the SWNTs is quite limited due to the weak Lorentz force on the arc plasma. In this paper, we report a facile and efficient method for diameter-selective synthesis of SWNTs, in which a weak magnetic field (B) perpendicular to the electric field (E) was applied to the arc plasma in the inter-electrode gap. The plasma morphologies were controlled by modifying the direction and strength of the magnetic field, for the first time proving that the SWNTs with different diameter distributions can be selectively obtained in different regions. Moreover, this diameter-selective efficiency can be controlled by changing the strength of the applied magnetic field.

Experimental

The synthesis of SWNTs was performed as described earlier.‡ In all experiments reported in this contribution, the SWNT samples were synthesized with a current of 90 A between the consumable graphite anode with Ni/Y catalyst in a Ni : Y = 4.2 : 1 ratio and the pure graphite cathode under a He buffer gas at a pressure of 50 kPa. SWNT samples were synthesized with and without adding a transverse magnetic field. A permanent magnet with different strengths was used to create a transverse magnetic field perpendicular to the electric field, which was placed outside the arc chamber, the horizontal distance between the magnet and the
discharge gap is about 15 cm. The magnetic field strength in the discharge gap is about 10–30 G (as measured by a Gaussmeter).

To characterize the morphology, diameter distribution and SWNT purity of as-synthesized SWNTs, we employed a combination of scanning electron microscopy (SEM), Raman spectroscopy, UV-vis-NIR, and thermogravimetric analysis (TGA). SEM images were acquired on a Zeiss Ultra55 FE-SEM instrument operating at 5 kV. Raman spectroscopy was characterized using a Bruker Senterra dispersive Raman microscope with laser excitation at 632.8 nm and 785 nm. UV-vis-NIR data were collected between 400 and 1300 nm using a PerkinElmer Lambda 950 UV-vis-NIR spectrophotometer. TGA measurements were performed on a PerkinElmer Pyris 1. Samples were analyzed at a heating rate of 10 °C min$^{-1}$ up to 900 °C in air atmosphere.

Results and discussion

Fig. 1 shows a schematic diagram of magnetic field-assisted arc discharge and a typical photograph of arc plasma after adding a transverse magnetic field. One can see that the morphology of arc plasma can be easily changed by applying a weak transverse magnetic field to the arc plasma. Moreover, the direction of oriented arc plasma shows excellent tunability, which will be easily altered by changing the direction of a transverse magnetic field. The arc plasma will result in selective deposition of SWNTs in a certain region. In addition, it is found that magnetic field-assisted DC arc discharge results in a larger disposition speed of SWNTs in different regions, SEM and TGA were used to evaluate the morphologies of SWNT samples from the front and backside of the oriented arc plasma (Fig. 1b), marked by F-SWNT and B-SWNT, respectively. A SEM image in Fig. 2a shows that the as-synthesized SWNTs in F-SWNT samples have a smooth and clean surface, only a few impurity particles were attached. While a large amount of impurity particles are observed in the B-SWNT sample (Fig. 2b) and the SWNTs are covered by numerous amorphous carbon, suggesting that the purity of SWNT products can be controlled by applying a transverse magnetic field to the arc plasma. Thermogravimetric analysis was carried out in air atmosphere to evaluate the purity of the as-synthesized SWNT samples with/without the magnetic field. Three weight losses in all SWNT samples are clearly observed from Fig. 2c due to the combustion of different carbon species. After burning, the contents of the residuals are different from each other, indicating that the motions of catalysts are controlled by both the magnetic field and drag force of the oriented arc plasma after adding a transverse magnetic field. DTG curves in Fig. 2d show three peaks at 378, 510, and 640 °C, corresponding to the oxidizations of amorphous carbon, SWNTs, and graphite nanoparticles, respectively. The peak areas in DTG curves are related to the content of different carbon species in SWNT samples. Compared with SWNTs synthesized without the magnetic field, the purities of SWNTs in F-SWNT and B-SWNT samples are improved, and the contents of amorphous carbon and graphite nanoparticles are lowered. Importantly, the purity differences of SWNTs between F-SWNT and B-SWNT samples suggest that the purity of as-synthesized SWNTs can be improved by applying a transverse magnetic field to the arc plasma.

To characterize the effect of magnetic field on the diameter distribution of SWNTs after adding a transverse magnetic field, Raman spectroscopy was performed using 633 nm and 785 nm as excitation wavelengths. The radial breathing mode (RBM) (Fig. 3) in Raman spectra depends strongly upon the diameter of SWNTs, and has been widely used to determine the diameter of SWNTs.$^{18}$ One can see clearly that the density of strong RBM peak (Fig. 3a) at 144 cm$^{-1}$ (1.72 nm) is significantly reduced after applying a magnetic field, indicating that the applied magnetic field will result in the increase of small SWNTs, which is consistent with Volotskova et al.$^{17}$ Comparing Raman spectra of B-SWNT samples with RBM peaks at 145 cm$^{-1}$ (1.71 nm) and 161 cm$^{-1}$ (1.52 nm), low-frequency Raman spectra of F-SWNT samples in Fig. 3a consist of four RBM peaks at 145 cm$^{-1}$ (1.71 nm), 162.5 cm$^{-1}$ (1.51 nm), 176 cm$^{-1}$ (1.38 nm) and
187 cm$^{-1}$ (1.29 nm), suggesting that the SWNTs with different diameter distributions are selectively deposited in different regions by applying a transverse magnetic field to the arc plasma. The differences in the diameter distribution of SWNTs between F-SWNT and B-SWNT samples are attributed to the differences in nanoparticle sizes of the catalysts captured by the magnetic field in the arc plasma region. Low-frequency Raman spectra (Fig. 3b) with excitation wavelength 785 nm are used to verify the separation of SWNTs with different diameter distributions after adding the magnetic field. One can see that there are two RBM peaks at 151.5 cm$^{-1}$ (1.63 nm) and 163 cm$^{-1}$ (1.50 nm) in F-SWNT samples, which are different from those at 150.5 cm$^{-1}$ (1.64 nm) and 160.5 cm$^{-1}$ (1.53 nm) in B-SWNT samples, providing further supports for magnetic-field-induced diameter selectivity.

To further investigate the effect of magnetic field on the diameter distribution of SWNTs in different regions, we synthesized different SWNT samples through changing the direction of magnetic fields. RBM spectra (b, d and f) of the as-synthesized SWNTs in different regions using 633 nm as an excitation wavelength. RBM peaks were normalized to the maximum peaks.

Fig. 3 Schematic diagram of arc plasma morphologies (a, c and e) after changing the direction of magnetic fields. RBM spectra (b, d and f) of the as-synthesized SWNTs in different regions using 633 nm as an excitation wavelength. RBM peaks were normalized to the maximum peaks.

To further investigate the effect of magnetic field on the diameter distribution of SWNTs in different regions, we synthesized different SWNT samples through changing the direction of the transverse magnetic field. According to the orientations of arc plasma induced by the transverse magnetic field, the directions of the transverse magnetic field are marked by X, $-X$ and Y, respectively. Four SWNT samples were collected from the front, back, right and left side of the oriented arc plasma (see Fig. S1†), marked by F-SWNT, B-SWNT, R-SWNT, and L-SWNT, respectively. The magnetic field strengths in four regions are different and labelled in the ESI (Fig. S2†). Fig. 4 shows the schematic diagram of the arc morphologies and RBM spectra of the as-synthesized SWNTs collected in different regions using 633 nm as excitation wavelength. After applying a X magnetic field (Fig. 4a), the SWNTs with different diameter distributions are selectively deposited into different regions (Fig. 4b). Except for RBM peaks at about 161 cm$^{-1}$ (1.52 nm), RBM peaks about 145 cm$^{-1}$ (1.71 nm) have different intensities, indicating that the differences in the growth process of the SWNTs with about 1.71 nm are generated after applying a transverse X magnetic field due to different magnetic field strengths and arc plasma densities in four regions. Fig. 4d shows RBM spectra of the as-synthesized SWNTs collected in different regions after applying a $-X$ magnetic field, similar differences in the diameter distribution of SWNTs in four regions are also clearly observed. Except for RBM peaks at about 162 cm$^{-1}$ (1.51 nm), the new RBM peak at 174.5 cm$^{-1}$ (1.39 nm) in R-SWNT samples suggests that the SWNTs with smaller diameters are selectively deposited in these regions. Large blue-shifts for RBM peaks in L-SWNT samples show that the diameters of the SWNTs in L-SWNT samples are larger than those in other regions. To investigate the effect of the direction of magnetic field on the diameter-selectivity of SWNTs, a Y magnetic field was applied to the arc plasma, shown in Fig. 4e. Remarkable differences in RBM peaks (Fig. 4f) between F-SWNT and B-SWNT samples are observed, indicating that the diameter distribution of SWNTs can be tailored by controlling the direction of magnetic field. The intensities of RBM peaks at about 144 cm$^{-1}$ (1.72 nm) also exhibit differences between R-SWNT and L-SWNT samples, which are ascribed to different magnetic field strengths. The RBM spectra (Fig. S3†) with 785 nm excitation are also performed to verify the effect of magnetic field on the diameter distribution of SWNTs in different regions. Different RBM peaks and peak intensities can also be observed, namely, the SWNTs with different diameter distributions are selectively deposited into different regions, providing further supports for magnetic field-induced diameter selectivity.

Fig. 4 Schematic diagram of arc plasma morphologies (a, c and e) after changing the direction of magnetic fields. RBM spectra (b, d and f) of the as-synthesized SWNTs in different regions using 633 nm as an excitation wavelength. RBM peaks were normalized to the maximum peaks.

UV-vis-NIR absorption spectra are used to evaluate the semiconducting/metallic (S/M) ratio of the SWNTs in the as-synthesized products. Fig. 5 represents the UV-vis-NIR absorption spectra of SDS-dispersed SWNTs synthesized with X magnetic field. The bands of $S_{22}$ (800–1200 nm) and $S_{33}$ (400–550) correspond to the first and second one-dimensional van Hove singularities, and the $M_{11}$ (550–800 nm) band corresponds to the first-order transition of metallic SWNTs. The broad bands in absorption spectra indicate that the samples still contain SWNT bundles. The S/M ratios of SWNTs are evaluated through measuring the peak areas of $S_{22}$ and $M_{11}$ bands (Table S1†). The results show different S/M ratios of SWNTs in four regions, which further support a magnetic field induced selective synthesis of the SWNTs during DC arc discharge.
The position-dependent diameter distribution of SWNTs may render some information on the diameter-selectivity mechanism. The aforementioned results (Fig. 4) indicate that the SWNTs with different diameter distributions can be obtained from four different regions and selectively deposited into certain regions by changing the direction of magnetic field. One can conclude that this selective synthesis of SWNTs with different diameter distributions is closely related to the changes of plasma parameters and particle motions of catalyst Ni in the magnetic field.\textsuperscript{17,22} Previous researchers\textsuperscript{17,22} demonstrated that plasma density and electron temperature in the centre of the arc plasma are easily tailored by applying an axial magnetic field to the arc discharge. It means that the SWNT–plasma interactions and the ratio between ions and neutral density will be changed, which will influence the SWNTs growth process.\textsuperscript{14,23} In our experiments, the arc morphology has been altered significantly after applying a magnetic field perpendicular to the electric field, indicating that the density distributions and motions of carbon ions and electrons in the arc plasma are altered by the Lorentz force, as shown in Fig. 6. The motions of the charged carbon species and the size distribution of catalysts in the non-uniform magnetic field (Fig. S2\textsuperscript{†}) will be altered and differentiated in different directions due to different motions (e.g., velocity and direction) in the arc plasma,\textsuperscript{23} leading to different SWNT growth rates. The SWNTs with different diameter distributions may be formed and removed from the arc plasma due to the different nucleation process and catalyst Ni with different sizes in a magnetic field.\textsuperscript{17} Therefore, we conclude that the collective interactions aforementioned between the magnetic field and arc plasma would alter the nucleation process and growth process of SWNTs. The as-synthesized SWNTs with different diameter distributions could be selectively deposited into different regions due to their variable motions (e.g., velocity and direction) in the transverse magnetic field.

**Conclusions**

We demonstrated a facile and scalable method to selectively synthesize SWNTs with different diameter distributions by applying a magnetic field perpendicular to the electric field in the arc plasma region. This magnetic field-induced diameter-selectivity strategy enables the control of the SWNTs with different diameter distributions in different regions, and the diameter-selective efficiency can be enhanced by changing the direction of magnetic fields. Our findings support that the motions of the catalysts with different particle sizes in the oriented arc plasma are altered by a transverse magnetic field, leading to SWNTs with different diameter distributions. The density distributions and motions of carbon ions and electrons are also significantly altered by the Lorentz force, leading to the different growth process of SWNTs due to the collective interactions between the magnetic field and arc plasma. We believe that this approach would enable a viable route toward the synthesis of SWNTs with desired diameter through tuning the arc parameters during arc discharge.

**Acknowledgements**

We thank the support from the U-M/SJTU Collaborative Research Program in Renewable Energy Science and Technology. Financial supports from the National Natural Science Foundation of China (no. 6106002 and 50730008), Shanghai Science and Technology Grant (no. 1052nm02000) are acknowledged.

**Notes and references**

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