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Narrow-chirality distributed single-walled carbon nanotube synthesis by remote plasma enhanced ethanol deposition on cobalt incorporated MCM-41 catalyst

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Abstract

We demonstrated the synthesis of single-walled carbon nanotubes (SWCNTs) with narrow chiral distribution on cobalt incorporated MCM-41 catalyst using ethanol as carbon feedstock by remote plasma enhanced chemical vapor deposition. The use of remote plasma enables the decomposition of the nontoxic ethanol to occur away from the site of SWCNT growth. This allows separate manipulation of carbon radical generation and SWCNT growth. A series of syntheses were carried out at plasma power from 0 to 250 W and growth temperature from 625 to 875 °C. Results have revealed that the plasma power and growth temperature affect carbon radical generation and recombination, as well as the reduction and nucleation of cobalt species. In addition, the remote ethanol plasma etching does not damage the grown SWCNTs. The chirality of resulting SWCNTs shows minor changes under different plasma power. On the other hand, the diameter of SWCNTs can be adjusted (from 0.7 to 1 nm) by changing the growth temperature. At the optimum condition of 200 W plasma power and 775 °C growth temperature, (7,5) and (8,4) nanotubes account for more than 50% of all semiconducting nanotube species. These results demonstrate the potential of utilizing plasma process in chiral selective growth of SWCNTs.

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1. Introduction

Electronic and optical properties of single-walled carbon nanotubes (SWCNTs) depend on their chirality, which can be specified by a chiral index (n,m) . [1] SWCNTs with uniform (n,m) structures are essential for many uses in the field of electronics and medicinal applications. [1, 2] As such, intensive efforts have been dedicated to improving their chirality control, [3-8] including designing chiral selective catalysts [9-19] and optimizing growth conditions. [20-22] In the commonly used SWCNT synthesis method, *i.e.* thermal chemical vapor deposition (T-CVD), carbon feedstocks, such as hydrocarbon, carbon monoxide or volatile organic solvents, adsorb on small catalytic particles, and are decomposed at high temperature ($\sim 700 - 1100\text{ }^{\circ}\text{C}$) to generate atomic carbon species. Then, these carbon species organize themselves into nanotubes in the presence of small catalytic particles. However, the T-CVD has yet to achieve optimized SWCNT chirality control, because it is difficult to control precisely the decomposition of carbon feedstocks, nucleation of catalytic particles and the interaction between growing carbon structures and catalysts at the same time.

The plasma process plays an important role in the development of microelectronic devices. Plasma based SWCNT synthesis methods are attractive due to the possibility of achieving better control, as well as integrating SWCNT synthesis with electronic device fabrication. A few recent studies have discussed the potentials and underlying physical processes of plasma based methods for chirality-controlled SWCNT synthesis, including preparation of well-defined catalysts, selective nucleation etching and reacting tubes after growth. [23-25] A microplasma-based process has been used to prepare size- and compositionally controlled metal nanoparticles for SWCNT growth. [10] Plasma enhanced CVD (PE-CVD) can promote the decomposition of carbon feedstocks at a much lower temperature ($\sim 350-800\text{ }^{\circ}\text{C}$) compared with T-CVD. [26] Early PE-CVD studies usually produced multi-walled carbon nanotubes (MWCNTs) or carbon fibers, [27, 28] as the direct plasma etching damages small diameter SWCNTs.

However, with the optimization of PE-CVD growth parameters, it can lead to the formation of SWCNTs [29-32] and even SWCNTs with narrow chiral distribution.[33] Remote PE-CVD (RPE-CVD) is a method which places the plasma source away from the site of SWCNT growth. Due to this reason, damages or interferences by plasma toward SWCNT growth can be minimized.[34] Methane and water RPE-CVD have been used to grow SWCNTs.[29, 31, 32] It has also been shown that RPE-CVD can selectively etch metallic SWCNTs.[34] Our theoretical study has suggested that single carbon atoms may cause chirality changes in growing carbon caps, while C₂ dimers lead to the continuous growth of SWCNTs without chirality changes.[35] Another simulation study suggests that SWCNT chirality may also change during the restructuring process of carbon caps by incorporating asymmetric defects.[36] This defect healing process is affected by the continuous addition of new carbon atoms, which may be controlled by PE-CVD.[37, 38] As such, RPE-CVD serves as a potential tool to generate suitable carbon radicals from carbon feedbacks. Thus, it is useful to explore the prospective of RPE-CVD in chiral selective growth of SWCNTs.

Co incorporated MCM-41 catalyst (Co-MCM-41) was used because of its excellent performance in producing SWCNTs with narrow (n,m) distribution.[39] It produces (7,5) enriched SWCNTs at a high temperature (800–850 °C) and carbon monoxide pressure (6 bar) in T-CVD.[40, 41] For potential integration of SWCNT growth with electronic device fabrication, it is desirable to lower the growth temperature and pressure, and replace the toxic carbon monoxide with a nontoxic carbon feedstock. Ethanol has been widely used to grow high purity SWCNTs in T-CVD while hydroxyl radicals from thermally decomposed ethanol are known to facilitate the removal of amorphous carbon.[42] MWCNTs have also been successfully synthesized using ethanol PE-CVD.[43, 44] In this work, we have studied the synthesis of SWCNTs on Co-MCM-41 catalyst using ethanol RPE-CVD. It combined the benefits from three aspects: (1) RPE-CVD ensures a lower SWCNT growth temperature by generating carbon

radicals away from SWCNT growth locations, (2) Co–MCM-41 catalyst has good (n,m) selectivity control, and (3) ethanol is able to synthesize high purity SWCNT as a nontoxic carbon feedback. Two key growth parameters which influence the quality of SWCNTs, *i.e.* plasma power and growth temperature, were also systematically studied.

2. Experimental

2.1 Synthesis system

The RPE–CVD system is shown in Fig. 1. A customized remote plasma kit manufactured by CEVP Ltd, UK was used to generate remote plasma at the entrance of a tube furnace. Inductively coupled plasma (ICP) was generated by water cooled copper inductive coils surrounding a 2-inch quartz tube. The ICP coil and the quartz tube were placed in a stainless steel sealed chamber with ceramic and aluminum thermal insulation for radio frequency (RF) electromagnetic shielding and safe operation. The RF coil was connected to a 13.56 MHz RF power supply through matching network. Water cooled stainless compression seals were used to couple the remote plasma kit with the quartz tube. Carbon feedstocks and carrier gases were injected through an axis symmetrical diffuser at one end of the chamber inlet. A boat to host catalysts was placed in the quartz tube at the center of the tube furnace, which was 21 cm away from the ICP coil. A thermocouple was attached to the upper surface of the catalyst boat to monitor the temperature of catalysts. No significant variation was detected in the measured temperature by using this method or inserting the thermocouple directly into catalysts. A vacuum pump was fixed at the other end of the quartz tube to remove gases from the chamber. A needle valve was installed to control the reaction pressure. Various operation parameters, such as temperature, gas flow rate, pressure, and plasma power, can be tuned to facilitate the synthesis of SWCNTs.

Fig. 1 - A schematic drawing of the remote plasma enhanced CVD system.

2.2 SWCNT synthesis

The Co-MCM-41 catalyst with 1 wt% Co was prepared according to the procedure described in our previous work.[39] The catalyst was calcined in air at 500 °C, and the resulting catalysts satisfy the following quality control criteria: (1) surface area determined by nitrogen adsorption-desorption isotherms is larger than 1000 m²/g, (2) full width at half-maximum of the pore size distribution curve is less than 0.2 nm, (3) temperature programmed reduction (TPR) profiles of Co-MCM-41 catalysts show one major reduction peak centered above 800 °C, and (4) features associated with Co₃O₄ and CoO below 500 °C are absent in TPR profiles.[45] In a typical SWCNT synthesis, 80 mg of catalysts was loaded in the catalyst boat. Catalysts were reduced under 80 sccm of atmospheric pressure H₂ (99.99%, Soxal) from room temperature to 500 °C at a ramping rate of 10 °C/min. After reduction, H₂ were quickly purged by Ar (99.99%, Soxal). The catalyst temperature was further increased to the specific SWCNT synthesis temperature. At the same time, the reactor was evacuated by a vacuum pump to 0.1 mbar. Subsequently, the plasma kit was turned on. During SWCNT synthesis, ethanol evaporated from a reservoir at 2 mbar went through the plasma zone before entering the quartz tube. SWCNT growth was carried out for 30 min. Eventually, the reactor was cooled to room temperature under Ar flow. The experiments were repeated for at least three times for each set of synthesis parameters to minimize system errors.

2.3 SWCNT characterization

SWCNT characterization in this study was focused on the purity and (n,m) distribution. Scanning electron microscope (SEM), Raman spectroscopy, ultraviolet–visible–near-infrared (UV–vis–NIR) absorption spectroscopy and thermogravimetric analysis (TGA) were used to evaluate the purity of SWCNTs. The intensity ratio between the SWCNT Raman disorder band (D-band) and the graphitic band (G-band) provides an indication of SWCNT purity. UV–vis–NIR absorption spectroscopy can also be used to determine the purity of SWCNT samples by the ratio of AA(S)/AA(T),[46] where AA(S) is the area of the S_{22} resonant adsorption peaks of SWCNTs after their baseline subtraction, and AA(T) is the total area under their absorption spectrum. By deconvoluting TGA weight loss profiles through derivative thermogravimetric (DTG) analysis, the weight fraction of different carbonaceous materials is determined. Further, UV–vis–NIR absorption spectroscopy and photoluminescence (PL) spectroscopy were used to analyze the (n,m) distribution of SWCNTs.

After SWCNT growth, as-synthesized carbon deposits were directly examined by a field emission SEM (JSM-6700, JEOL). Their Raman spectra were collected on a Renishaw Ramanscope with a 633 nm laser. Aqueous nanotube suspensions were prepared by dispersing 10 mg of as-synthesized carbon deposits in 10 mL of 2 wt% sodium dodecylbenzene sulfonate (99%, Sigma) in D₂O solution. Tip sonication (20 W, VCX-130, SONICS) was applied to facilitate the debundling of nanotubes. After 1 hour sonication in an ice water bath, the dispersion was centrifuged at 80,000 g force for 1 hour (CP-80, Hitachi) to remove catalyst supports, metal particles and other impurities. 60 % of the resulting clear supernatants were extracted for spectroscopic characterization. UV–vis–NIR absorption spectra were collected on a Varian Cary 5000 spectrometer, and the purity indices were extracted between 540 and 770 nm. PL contour plots were obtained on a Jobin Yvon Nanolog-3 fluorospectrometer equipped with an InGaAs detector and a 350 W xenon lamp as excitation source. The as-synthesized carbon deposits

were also refluxed in 2 M NaOH solution to remove the silica MCM-41 support for TGA on a PerkinElmer Diamond thermal analyzer. The sample was first heated to 200 °C, and held for 10 min under airflow (200 sccm) to remove moisture. Then, the temperature was increased from 200 to 1000 °C at a 10 °C /min rate. The weight loss of the sample was monitored and recorded as a function of the temperature. The same procedure was repeated after the sample was cooled to room temperature to obtain the second weight–temperature curve for baseline correction.

3. Results and discussion

3.1 Effect of plasma power

The key purpose of introducing remote plasma in SWCNT synthesis is to assist the decomposition of carbon feedstocks, which depends on the plasma power.[27] Thus, the effect of plasma power is first studied. The temperature in the reactor was fixed at 775 °C, and the power of the remote plasma source was changed from 0 to 250 W. Fig. 2 show the SEM images of as-synthesized carbon deposits. Nanotube bundles are observed on all samples in Fig. 2a to 2c. Raman spectroscopy analysis was carried out on as-synthesized solid samples, and their spectra are shown in Fig. 3. Several typical SWCNT Raman features can be identified, including radial breathing mode (RBM) peaks (100~400 cm^{-1}), the D band (~1300 cm^{-1}), the split G band (~1550 cm^{-1} and ~1590 cm^{-1}) and the 2D band (~2620 cm^{-1}). The intense RBM peaks and weak D band peaks suggest that high purity SWCNTs are produced. The ratio between D band and G band peaks (see the insert of Fig. 3) was used to evaluate the purity of SWCNTs. The Raman D/G ratio first decreases with an increase in plasma power up to 200 W, and subsequently increases when the plasma power is further increased to 250 W. The UV–vis–NIR absorption spectra of SWCNTs and their purity indices were shown in Fig. 4. SWCNTs are successfully synthesized under all conditions as evident from the sharp S_{11} and S_{22} transition peaks of different (n,m) species. The major

(n,m) species are small diameter (6,5), (7,5), (7,6) and (8,4) nanotubes. Underneath the resonant transition peaks, there is a broad background, depending on carbonaceous impurities, sidewall functionalization of nanotubes, spectral congestion, nanotube aggregation and metallic nanotubes.[47] As all SWCNT dispersions were prepared using the same procedure, we used the ratio of resonant to background absorptions to estimate their purity. As shown in Fig. 4b, the purity index increases with the rise of the plasma power until it reaches 200 W, and then decreases rapidly.

Fig. 2. SEM images of SWCNTs synthesized on Co-MCM-41 catalyst at different conditions: (a) 775 °C, 0 W; (b) 775 °C, 200 W; (c) 775 °C, 250 W; (d) 625 °C, 200 W; (e) 675 °C, 200 W and (f) 875 °C, 200 W.

Fig. 3 – Raman spectra of SWCNTs synthesized at different remote plasma powers. The insert shows the correlation between plasma power and the D band to G band peak ratios. Raman spectra were shifted in y-axis for better comparison.

Fig. 4 - (a) UV–vis–NIR absorption spectra of SWCNTs synthesized at different remote plasma powers. Spectra are shifted in y-axis for better comparison. (b) Calculated purity indices of SWCNTs from their absorption spectra (without shifting spectra).

Fig. 5. Thermogravimetric analysis and derivative thermogravimetric analysis of SWCNTs synthesized under 0, 200 and 250 W remote plasma.

The growth of SWCNTs without plasma can be attributed to the direct thermal decomposition of ethanol on the catalyst at 775 °C. However, the low absorption purity index and high Raman D/G ratio suggests that large amount of carbonaceous impurities are produced without the activation of plasma. With the increase of plasma power, more ions or radicals are generated, leading to more SWCNT growth. Thus, the absorption purity index increases, while the D/G ratio decreases. When the plasma power exceeds beyond 200 W, the decreased purity index and higher D/G ratio suggests two possibilities: (1) SWCNTs are damaged by ion etching under intense plasma and/or (2) more carbonaceous impurities are produced because of the abundant carbon radicals.[29, 48] TGA measurements were conducted on SWCNTs synthesized under 0, 200 and 250 W remote plasma to better understand the synthesis process. As shown in Fig. 5, amorphous/defective carbon has oxidation temperature below 400 °C. The sharp peaks centered at 530~540 °C are from SWCNTs. Other peaks at higher temperature could be assigned to MWCNTs (600~700 °C) and graphitic impurities (>850 °C). The position of the SWCNT oxidation peak can be used to qualitatively determine the defective level of SWCNTs because defective SWCNTs would have a lower oxidation temperature. There is minor variation on oxidation temperature in Fig. 5 at 535, 540 and 541 °C, suggesting that the defect density of the SWCNTs is similar. DTG curves in Fig. 5 were deconvoluted to determine the weight fractions of different carbon species, and the results were listed in Table 1. The amorphous/defective carbon fraction increases from 40.5 to 53.2 wt%, SWCNT fraction decreases from 59.5 wt% at a plasma power of 200 W to less than 37.6 wt% at 250 W. MWCNTs and graphite account for 9.2 wt% at 250 W. Based on these results, we propose that under intense remote plasma (250 W), SWCNTs are not damaged by ion etching. The large amount of carbon radicals results in the formation of amorphous carbon, while MWCNTs and graphite are produced because of the formation of large metal particles. In our experiments, the distance between remote plasma source and catalysts was fixed at 21 cm. A previous

simulation study of a similar RPE-CVD system has showed that the ion density/energy at this distance would decrease to a negligible level.[49] We have also explored varying this distance, and found that if the catalysts were placed less than 10 cm to the plasma source, the SWCNTs were damaged under the intense plasma. Besides, the shift of SWCNT oxidation peaks in TGA can be observed. In another words, when the plasma source is placed far enough from catalysts, the direct etching of SWCNTs by ions can be minimized. However, abundant carbon radicals are available, which would quickly saturate Co particles, leading to the formation of more amorphous/defective carbon. Furthermore, more hydrogen containing radicals would also be present under the intense remote plasma, thus Co species in MCM-41 could be reduced and nucleate into larger Co particles. These large Co particles together with the abundant carbon radicals would facilitate the formation of MWCNTs and graphite.

Table 1. Carbon composition of SWCNT samples obtained at different remote plasma power.

plasma power, W	weight fraction, wt%			
	amorphous/defective carbon	SWCNTs	MWCNTs	graphite
0	47.8	52.2	-	-
200	40.5	59.5	-	-
250	53.2	37.6	4.2	5.0

Fig. 6. PL contour plots as a function of excitation and emission wavelength from SWCNTs synthesized under different remote plasma powers at 775 °C. Major chiral nanotubes identified in PL are marked with their (n,m) indexes.

Absorption spectra in Fig. 4 show that the (n,m) distribution is almost the same under different plasma powers. PL spectroscopy was used to substantiate this result. PL contour plots of SWCNTs synthesized under different remote plasma powers are shown in Fig. 6. (8,3), (6,5), (7,5), (7,6) and (8,4) nanotubes are the major species. No significant (n,m) distribution changes are observed. Previous study reported that small diameter SWCNTs are vulnerable to plasma etching.[34] In contrast, the PL intensities of small diameter (6,5) and (8,3) nanotubes in Fig. 6 slightly increase with the increase in plasma power. Besides, previous studies also showed that longer growth time in PE-CVD would damage SWCNTs and thus the growth time is usually limited to 1 min. Conversely, our growth time is 30 min,

and the D/G ratio of resulting SWCNTs is comparable to the best values reported in previous studies.[32, 50] These results are consistent with TGA results, suggesting that the remote ethanol plasma is mild and does not result in direct damage of the SWCNTs. On the other hand, the minimum change in chiral selectivity under different plasma power suggest that the catalyst used may play a more important role in (n,m) selectivity other than carbon radicals at the growth sites.

3.2 Effect of synthesis temperature

Fig. 7 – Raman spectra of SWCNTs synthesized at different growth temperature under 200 W remote plasma. The insert show the correlation between growth temperature and the D band to G band peak ratios. Raman spectra were shifted in y-axis for better comparison.

Fig. 8 - (a) UV–vis–NIR absorption spectra of SWCNTs synthesized at different growth temperature with 200 W remote plasma. Spectra are shifted in y-axis for better comparison. (b) Calculated purity indices of SWCNTs from their absorption spectra (without shifting spectra). (c) An enlarged view of S_{11} absorption spectra of SWCNTs synthesized at different temperature.

Next, the remote plasma power was fixed at 200 W, while the synthesis temperature (measured at the catalyst boat) was varied from 625 to 875 °C. SEM images (Fig. 2d to 2f) show that few SWCNTs exist on the catalyst at growth temperature of 625 or 875 °C. Their Raman spectra and the D/G ratios are shown in Fig. 7. RBM peaks in Fig. 7 are weak when the growth temperature is below 675 or at 875 °C. The changes in D/G ratios suggest that growth temperature around 750 °C results in minimum formation of amorphous carbon. Fig. 8 shows the UV–vis–NIR absorption spectra and calculated purity indices of dispersed SWCNTs. Similar to the Raman results, the weak resonant absorption peaks in Fig. 8a suggest that few SWCNTs were synthesized when growth temperature is at 625 or 875 °C. Fig. 8b indicates that the purity index is low at 625 °C, and increases with growth temperature, reaching a maximum at around

750 °C. Then, it drops when growth temperature further increases. In our previous study, high purity SWCNTs can be obtained from the Co–MCM-41 catalyst at a growth temperature as high as 900 °C under 6 bar of CO without plasma. It is surprising that the SWCNT formation is strongly affected by slight changes in growth temperature, considering many carbon radicals should be available under the 200 W plasma power.

We further examined the chirality distribution of SWCNTs. More results at growth temperature of 750 and 800 °C are included. The S_{22} absorption spectra in Fig. 8c shows that the major (n,m) species produced at 725 °C are (6,5) nanotubes, while (7,5) and (8,4) nanotubes dominate at 775 °C. This change is better illustrated by PL contour plots shown in Fig. 9. The (6,4) and (7,3) nanotubes with smaller diameter than (6,5) can be observed in SWCNTs synthesized at 675 and 725 °C. When the growth temperature is further increased to higher than 750 °C, these small diameter SWCNTs disappear. Larger diameter (> 0.8 nm) (7,5) and (8,4) become dominant. The PL efficiency of SWCNTs depends on their (n,m) species, defect density, aggregation and length.[51] Since the dispersing procedure is the same for all SWCNT samples, we simply used the PL intensity of individual (n,m) species to estimate their relative abundance. It was calculated by dividing the intensity of individual (n,m) species with the sum of intensities of all observed (n,m) semiconducting species. The results are listed in Table S1 to S6 in the supplementary data. The relative abundance of a few major (n,m) species is listed in Table 2, confirming the observations from the PL contour plots. At 775 °C, (7,5) and (8,4) nanotubes account for more than 50% of all semiconducting species. The formation of larger diameter SWCNTs suggests that larger Co particles are formed at higher growth temperature.

Fig. 9. PL contour plots as a function of excitation and emission wavelength from SWCNTs synthesized at different temperatures with the remote plasma at 200 W. Major chiral nanotubes identified in PL are marked with their (n,m) indices.

Table 2. Relative abundance of (n,m) species estimated by their PL peak intensity

(n,m)	d_t , nm	Synthesis temperature, °C					
		675	725	750	775	800	825
(7,3)	0.70	18.9	12.6	5.5	-	-	-
(6,5)	0.76	24.9	25.8	24.0	13.3	10.4	6.4
(7,5)	0.83	10.7	14.9	20.8	30.1	26.6	24.6
(8,4)	0.84	9.5	10.6	17.0	20.2	21.7	23.4
(7,6)	0.90	5.7	6.2	7.9	11.1	13.4	16.1

Cobalt in fresh Co-MCM-41 is a mixture of Co^{2+} and Co^{3+} in tetrahedral and distorted tetrahedral coordinations with a pseudo-octahedral environment with high stability.[41] In previous studies,[52-54] it was found that hydrogen reduction of Co-MCM-41 at 500 °C produce Co^{1+} intermediate species in the MCM-41 silica framework. These Co intermediate species would form Co carbonyl-like compounds with high mobility when the catalyst is exposed to CO at 750 °C. The fast migration and formation of metallic clusters at 750 °C enables the dissociation of CO and growth of SWCNTs. The control of Co particle sizes in Co-MCM-41 enable SWCNT diameter control. The size of Co clusters resulting from Co-MCM-41 can be varied by adjusting pH of synthesis condition, pore size of MCM-41 template, catalyst calcination condition, Co loading, reaction temperature, H_2 reduction condition, and pressure of CO.[40, 41, 55-58] Thermal decomposition of ethanol at 775 °C generates hydrogen containing radicals, which can reduce Co, resulting in the growth of SWCNTs without plasma as shown in Fig. 2 and 3. RPE-CVD can significantly increase the generation of carbon, hydrogen, and other radicals. Since the plasma power is fixed at 200 W, it is likely that the similar density of radicals is generated. We propose that the diverse growth behaviors observed at different growth temperatures can be understood from three aspects. Firstly, hydrogen containing radicals might reduce more Co with the increase of growth temperature. Below 650 °C, less metallic Co particles would be available for SWCNT growth compared with higher growth temperature. Secondly, reduced metallic Co would nucleate faster at a higher growth temperature, resulting in large metal particles, which are less selective for SWCNTs. Lastly, different growth temperatures may also influence the recombination of radicals. At lower growth temperatures, more radicals would recombine. Thus, less active carbon species are available for SWCNT growth.

The current results also suggest a high possibility of isolating the different processes of carbon feedback decomposition, catalyst particle nucleation, and SWCNT growth. For example, remote plasma could be used to generate suitable combination of radicals (*i.e.* C atoms and C_2 dimers), catalyst

particles with controlled size and composition can be generated through microplasma-based process, and then SWCNTs are synthesized at suitable temperature windows. Thus, the individual processes can be separately optimized, which may be an efficient way to achieve better chirality control in SWCNT growth. Moreover, in a few recent studies, sorted SWCNTs [59] or synthesized organic carbon nanorings [60] have been used as templates to grow structurally uniform SWCNTs. Those “cloning” methods usually have poor efficacy in nanotube length extension. Remote plasma is promising to be used to supply suitable carbon radicals for efficient nanotube extension.

4. Conclusion

We have studied the growth of SWCNTs on Co–MCM-41 catalyst using ethanol RPE–CVD. Remote plasma assists the decomposition of ethanol and generates active carbon species which are favorable for SWCNT synthesis without etching grown nanotubes. The plasma power and growth temperature affect radical generation and recombination, as well as the reduction and nucleation of catalytic metal species. At the optimum condition of 200 W plasma power and 775 °C growth temperature, (7,5) and (8,4) nanotubes account for more than 50% of all semiconducting nanotube species. These studies show the potential of utilizing plasma process to achieve chiral selective growth of SWCNTs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at online link.

Supplementary data

Narrow-chirality distributed single-walled carbon nanotube synthesis by remote plasma enhanced ethanol deposition on cobalt incorporated MCM-41 catalyst

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Table S1. Abundance evaluation of chiral species in the nanotube sample obtained at 675 °C.

(n,m) index	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	Intensity	Abundance, %
(6,4)	0.692	23.4	866.811	578	546.451	5.40
(6,5)	0.757	27	972.715	568	2523.64	24.94
(7,3)	0.706	17	991.334	508	1913.35	18.91
(7,5)	0.829	24.5	1016.64	642	1085.71	10.73
(7,6)	0.895	27.46	1117.43	644	575.587	5.69
(8,3)	0.782	15.3	945.784	664	1067.82	10.55
(8,4)	0.84	19.11	1106.66	578	965.034	9.54
(8,6)	0.966	25.28	1162.44	716	169.472	1.67
(8,7)	1.032	27.8	1265.15	728	77.179	0.76
(9,1)	0.757	5.2	905.303	690	267.971	2.65
(9,4)	0.916	17.48	1101.02	720	327.902	3.24
(9,5)	0.976	20.6	1241.84	672	133.222	1.32
(10,2)	0.884	8.95	1053.23	738	326.12	3.22
(10,3)	0.936	12.7	1245.9	628	141.028	1.39

Table S2. Abundance evaluation of chiral species in the nanotube sample obtained at 725 °C.

(n,m) index	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	Intensity	Abundance, %
(6,4)	0.692	23.4	866.811	582	365.917	3.69
(6,5)	0.757	27	974.268	568	2613.82	26.37
(7,3)	0.706	17	991.851	508	1272.7	12.84
(7,5)	0.829	24.5	1018.7	644	1504.14	15.17
(7,6)	0.895	27.46	1117.43	646	627.278	6.33
(8,3)	0.782	15.3	946.302	666	1072.51	10.82
(8,4)	0.84	19.11	1108.2	586	1073.76	8.81
(8,6)	0.966	25.28	1164.48	718	191.374	1.93
(8,7)	1.032	27.8	1264.14	728	97.9406	0.99
(9,1)	0.757	5.2	906.343	692	297.421	3.00
(9,4)	0.916	17.48	1101.02	722	355.933	3.59
(9,5)	0.976	20.6	1245.9	672	143.826	1.45
(10,2)	0.884	8.95	1051.69	738	341.948	3.45
(10,3)	0.936	12.7	1250.97	632	155.091	1.56

Table S3. Abundance evaluation of chiral species in the nanotube sample obtained at 750 °C.

(n,m) index	d_t , nm	θ , °	E_{11} , nm	E_{22} , nm	Intensity	Abundance, %
(6,4)	0.692	23.4	N/A	N/A	N/A	N/A
(6,5)	0.757	27	973.233	568	5155.3	24.00
(7,3)	0.706	17	991.851	508	1172.7	5.46
(7,5)	0.829	24.5	1018.7	644	4474.2	20.83
(7,6)	0.895	27.46	1115.38	644	1692.9	7.88
(8,3)	0.782	15.3	945.784	664	2631.8	12.25
(8,4)	0.84	19.11	1108.2	588	3652.4	17.01

(8,6)	0.966	25.28	1172.65	718	413.1	1.92
(8,7)	1.032	27.8	1266.17	728	251.8	1.17
(9,1)	0.757	5.2	N/A	N/A	N/A	N/A
(9,4)	0.916	17.48	1105.12	720	741.1	3.45
(9,5)	0.976	20.6	1244.88	672	290.1	1.35
(10,2)	0.884	8.95	1049.63	734	709.8	3.31
(10,3)	0.936	12.7	1251.98	632	290.647	1.35

Table S4. Abundance evaluation of chiral species in the nanotube sample obtained at 775 °C.

(n,m) index	d_t , nm	θ , °	E ₁₁ , nm	E ₂₂ , nm	Intensity	Abundance, %
(6,4)	0.692	23.4	N/A	N/A	N/A	N/A
(6,5)	0.757	27	974.785	568	1067.8	12.35
(7,3)	0.706	17	N/A	N/A	N/A	N/A
(7,5)	0.829	24.5	1019.74	644	2422.6	26.44
(7,6)	0.895	27.46	1118.45	644	895.8	14.77
(8,3)	0.782	15.3	947.339	664	743.2	2.70
(8,4)	0.84	19.11	1109.23	588	1628.9	27.44
(8,6)	0.966	25.28	1172.65	718	141.4	2.24
(8,7)	1.032	27.8	1267.18	728	62.1	1.60
(9,1)	0.757	5.2	N/A	N/A	N/A	N/A
(9,4)	0.916	17.48	1105.12	718	422.8	4.68
(9,5)	0.976	20.6	1247.93	672	108.8	3.01
(10,2)	0.884	8.95	1051.69	734	432.6	1.41
(10,3)	0.936	12.7	1256.04	632	121.08	3.35

Table S5. Abundance evaluation of chiral species in the nanotube sample obtained at 800 °C.

(n,m) index	d_t , nm	θ , °	E ₁₁ , nm	E ₂₂ , nm	Intensity	Abundance, %
(6,4)	0.692	23.4	N/A	N/A	N/A	N/A

(6,5)	0.757	27	971.68	568	728.1	9.20
(7,3)	0.706	17	N/A	N/A	N/A	N/A
(7,5)	0.829	24.5	1018.7	644	1860.9	22.19
(7,6)	0.895	27.46	1117.43	646	935.3	16.85
(8,3)	0.782	15.3	946.302	666	492.1	1.96
(8,4)	0.84	19.11	1109.23	588	1517.7	27.93
(8,6)	0.966	25.28	1172.65	716	191.3	3.30
(8,7)	1.032	27.8	1263.13	726	92.7	2.62
(9,1)	0.757	5.2	N/A	N/A	N/A	N/A
(9,4)	0.916	17.48	1105.12	722	474.4	5.74
(9,5)	0.976	20.6	1244.88	674	139.3	4.21
(10,2)	0.884	8.95	1051.69	734	418.3	1.49
(10,3)	0.936	12.7	1250.97	634	149.557	4.52

Table S6. Abundance evaluation of chiral species in the nanotube sample obtained at 825 °C.

(n,m) index	d_t , nm	θ , °	E ₁₁ , nm	E ₂₂ , nm	Intensity	Abundance, %
(6,4)	0.692	23.4	N/A	N/A	N/A	N/A
(6,5)	0.757	27	970.645	566	374.0	5.33
(7,3)	0.706	17	N/A	N/A	N/A	N/A
(7,5)	0.829	24.5	1018.7	642	1446.7	19.46
(7,6)	0.895	27.46	1119.48	644	947.4	19.25
(8,3)	0.782	15.3	945.784	662	297.2	1.33
(8,4)	0.84	19.11	1109.23	586	1378.3	28.61
(8,6)	0.966	25.28	1173.67	714	211.6	4.12
(8,7)	1.032	27.8	1266.17	728	87.0	2.77
(9,1)	0.757	5.2	N/A	N/A	N/A	N/A
(9,4)	0.916	17.48	1104.1	720	469.1	6.40
(9,5)	0.976	20.6	1247.93	670	171.4	5.85

(10,2)	0.884	8.95	1050.66	734	334.2	1.34
(10,3)	0.936	12.7	1249.95	632	162.36	5.54