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Synthesis and optical characterization of carbon nanotube arrays

Md. Mahfuzur Rahman[a,*], Hammad Younes[a], George Ni[b], TieJun Zhang[a], Amal Al Ghaferi[a,**]

[a] Institute Centre for Energy (iEnergy), Mechanical and Materials Engineering Department, Masdar Institute of Science and Technology (MIST), P.O. Box 54224, Abu Dhabi, United Arab Emirates
[b] Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139, United States

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ABSTRACT

Catalyst annealing time and growth pressure play a crucial role in the chiral selective and high-efficiency growth of single-walled carbon nanotubes (SWCNTs) during low pressure chemical vapor deposition (LPCVD). We achieved a high growth rates for SWCNTs and a change the chiral distribution towards metallic (n, m) increasing the catalyst annealing time in hydrogen. A strong correlation is revealed between the catalyst annealing time at lower growth pressures and the shape of the G band, which indicates the metallic or semiconducting nature of the SWCNT and predict the chirality distribution. Under a 15 min annealing time and 10 mbar of growth pressure, the bottom of the G band is broadened with a sharp G^- peak, and the G-band exhibited asymmetrical Breit–Wigner–Fano (BWF) shape. In addition, the growth of SWCNTs with smaller diameters and rich in metallic character is confirmed by the shift of the G-band to a smaller Raman frequency. Homogeneity and vertical alignment of as-grown SWCNT arrays are optically studied using UV/vis/NIR Spectrophotometer. Wavelength-independent and low reflectance resulted from the growth of uniform arrays of SWCNTs. Because of their tunable electronic and optical properties, selective growth of SWCNTs promises great application potential, particularly in electronics and solar industries.

1. Introduction

Carbon nanotubes (CNTs) have attracted increasing research interest because of the tunability of their optical, electrical and mechanical properties. Depending on the diameter, length, type, and alignment, CNTs show a variety of exciting applications. For example, vertically aligned carbon nanotubes VA-CNTs have blackbody absorption and emission properties because of the low volume ratio of CNTs to air, and the consequently low refractive index [1–3]. This reduction in the index of refraction leads to very high and wavelength-independent absorptance and emittance. These optical properties are promising in solar thermal absorbers for novel nanophotonic energy conversion devices [4] and other solar thermoelectric plants, where the receiver performance is dominated by the solar absorptance. In addition to the excellent optical properties, VA-CNTs have distinct advantages because of their high-temperature stability in vacuum, and thus may be used in conjunction with evacuated glass tubes [4].

Significant research efforts have been devoted to chiral-selective synthesis of SWCNTs. Catalytic chemical vapor deposition is so far most promising technique for growing SWCNTs in terms of scalability and chiral-selectivity. However, chiral-selective growth of SWCNTs is still considered a poorly understood process. All CVD parameters such as temperature, gas flow, pressure, and catalyst species, influence the chiral distribution of the produced SWCNTs [5,6]. Many studies have focused on understanding the factors that lead to the chiral-selective growth of SWCNTs [7–10], however, much work is still needed to understand the parameters that affect chirality during synthesis. Homochiral SWCNTs have potential applications in magnetic nanofluids [11–14], high performance transparent conductive films [15], absorbers in solar thermo-photovoltaic energy conversion [3,4], and solar cell active layers [16].

Catalyst type and pretreatments are critical for controlling the resultant SWCNT diameter and chirality distributions [9,17,18]. SWCNTs are grown from catalysts are deposited on substrates. The pre-annealing time of as-deposited catalysts like Fe films plays a

* Corresponding author. Fax: +971 28109901.
** Corresponding author.
E-mail addresses: mrahman@masdar.ac.ae, mahfuz.ipe@gmail.com (M. M. Rahman), aalghaferi@masdar.ac.ae (A. Al Ghaferi).

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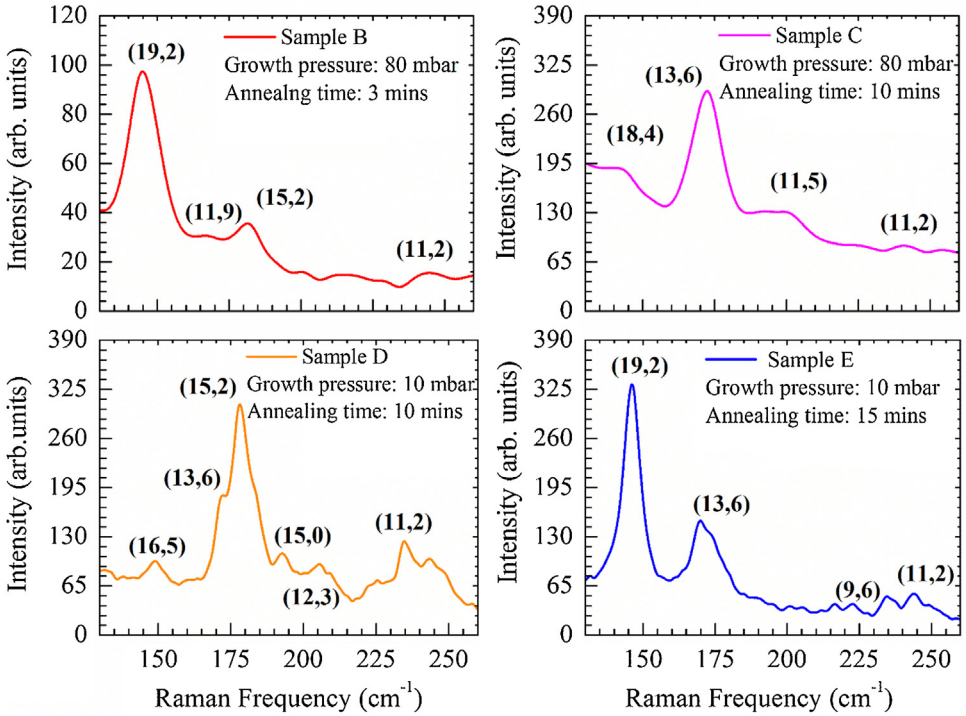

Fig. 1. Micro-Raman spectra of SWCNTs. The RBM regions at excitation wavelength (531.78 nm) for SWCNTs samples grown by tuning catalyst annealing time and growth pressure.

vital role in affecting the density and the growth rate of the SWCNTs. Annealing the catalyst in presence of hydrogen de-wets the deposited Fe film, and forms nano-droplets of Fe on the substrate, which act as SWCNT growth sites [19]. In addition, the annealing time affects the size and number density of the Fe nano-droplets, affecting the diameter and density of the resultant SWCNT array [19].

Resonance Raman spectroscopy is a powerful technique for CNT characterization and can identify the radial breathing mode (RBM) with the frequencies ω_{RBM} between 120 cm^{-1} and 350 cm^{-1} for SWCNTs with diameters in the range of $0.7 \langle d \langle 2$ nm, and the G-band modes appearing in Raman spectra at a frequency range of 1500–1600 cm^{-1} [20]. The presence of the RBM confirms the existence of nanotubes. Once the RBM peaks are identified in a Raman spectra, a chirality index (n, m) can be assigned by using the experimental Kataura plot [7,21,22]. These chiral indices (n, m) are used to predict the electronic properties of a SWCNT. For semiconducting SWCNT species, $(n - m)\, mod\, 3 = 1 or 2$ and for metallic species

Table 1
Summary of results for the relative chirality abundance of SWCNTs. Experimental ω_{RBM} at 2.33 eV and calculated diameter range d_1 ($A = 227$, $B = 0$) and d_2 (using assigned chirality index) together with electronic property (M: metallic; S: semiconducting).

	ω_{RBM}	$d_1 = \frac{227}{\omega_{RBM}}$	n	m	$(n-m)$ mod 3	M or S	$d_2 = 0.142\sqrt{3(n^2+nm+m^2)}/\pi$	$\frac{d_1-d_2}{d_1} \times 100\%$
Sample B	144.8	1.5677	19	2	2	S	1.5724	−0.30
	168	1.3512	11	9	2	S	1.3589	−0.57
	181.9	1.2479	15	2	1	S	1.2606	−1.01
	243.5	0.9322	11	2	0	M	0.9497	−1.87
Sample C	140.5	1.6157	18	4	2	S	1.5899	1.59
	172.7	1.3144	13	6	1	S	1.3177	−0.25
	201	1.1294	11	5	0	M	1.1105	1.67
	241	0.9419	11	2	0	M	0.9497	−0.83
Sample D	149.2	1.5214	16	5	2	S	1.4882	2.18
	172	1.3198	13	6	1	S	1.3177	0.16
	178.4	1.2724	15	2	1	S	1.2606	0.93
	192.8	1.1774	15	0	0	M	1.1749	0.21
	205.4	1.1052	12	3	0	M	1.0768	2.56
	234.4	0.9684	11	2	0	M	0.9497	1.94
	243.1	0.9338	11	2	0	M	0.9497	−1.70
Sample E	146	1.5548	19	2	2	S	1.5724	−1.13
	169.93	1.3358	13	6	1	S	1.3177	1.36
	216.6	1.0480	9	6	0	M	1.0243	2.27
	223	1.0179	9	6	0	M	1.0243	−0.62
	234.5	0.9680	11	2	0	M	0.9497	1.89
	244.4	0.9288	11	2	0	M	0.9497	−2.25