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Dendrimer-assisted controlled growth of carbon nanotubes for enhanced thermal interface conductance

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Abstract

Multi-walled carbon nanotubes (MWCNTs) with systematically varied diameter distributions and defect densities were reproducibly grown from a modified catalyst structure templated in an amine-terminated fourth-generation poly(amidoamine) (PAMAM) dendrimer by microwave plasma-enhanced chemical vapor deposition. Thermal interface resistances of the vertically oriented MWCNT arrays as determined by a photoacoustic technique reveal a strong correlation with the quality as assessed by Raman spectroscopy. This study contributes not only to the development of an active catalyst via a wet chemical route for structure-controlled MWCNT growth, but also to the development of efficient and low-cost MWCNT-based thermal interface materials with thermal interface resistances $\leqslant 10\ \mathrm{mm^2\ K\ W^{-1}}$.

1. Introduction

The extraordinary properties of carbon nanotubes (CNTs) have sparked interest in their potential application in nanoelectronics, electronics packaging, sensors and energy storage. In particular, CNTs possess very high intrinsic thermal conductivity, which has made them attractive for heat transfer applications [1–5]. For several applications, including flat panel displays and heat transfer applications, arrays of vertically oriented high-quality CNTs with large, uniform coverage, controlled diameter and quality are required. Multiwalled carbon nanotubes (MWCNTs) of such dimensions have been reproducibly grown by plasma-enhanced CVD (PECVD) on substrates with suitable transition metal catalysts (Co, Ni, and Fe) [6]. Prior studies have shown the efficacy of such MWCNT arrays for use as thermal interfaces [3, 4, 7, 8] and as enhanced surfaces for pool boiling [9]. In these studies, variations of the catalyst characteristics were minimal, as the ultimate morphology of film-type catalysts is relatively difficult to control. However, the use of catalyst nanoparticles offer the flexibility required to vary the catalyst structure, and ultimately the structural properties of MWCNTs.

Here, we consider in detail the effects of the catalyst structure used to create MWCNT arrays and its influence on the diameter, quality and thermal interface resistance. Using modified Fe_2O_3 nanoparticles derived from a dendrimer ‘nanotemplate’, vertically oriented MWCNT arrays of variable diameter distributions and quality were grown with high reproducibility. The concentration of Fe used for complexation with the dendrimer and the calcination temperature of the dendrimer-templated nanocomposites are key parameters that have been used to modify the catalyst structure. Owing to its high precision, the photoacoustic (PA) technique provides a reliable approach to characterize the thermal interface performance of the MWCNT arrays [4].

Catalyst nanoparticles produced by wet chemical routes have shown high selectivity and reproducibility for CNT growth by PECVD over a wide temperature range [6], including low temperatures as demonstrated recently [10, 11]. This approach also offers substantial economic advantages as the catalyst solution is stable over several months and the problem of catalyst contamination is highly reduced,

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ensuring high reproducibility of CNT growth. Fe_2O_3 nanoparticles were prepared via an interdendritic templating mechanism involving Fe^{3+} ions and an amine-terminated fourth-generation poly(amidoamine) (PAMAM) dendrimer (hereinafter referred to as G4-NH_2). The dendrimer 'nanotemplate' efficiently delivers nearly monodispersed transition metal nanoparticles to substrates [12]; the resultant Fe_2O_3 nanoparticles obtained after calcination have been used for the growth of high-quality single-walled carbon nanotubes (SWNTs) via both thermal CVD [13] and PECVD [14].

2. Experimental details

The G4-NH_2 dendrimer having an ethylene diamine core, supplied as a 10% methanol solution from Aldrich, was used as a carrier to deliver isolated Fe_2O_3 nanoparticles to a Ti (30 nm)-coated SiO_2/Si substrate. The catalyst solution was prepared by mixing separate 20 ml solutions of the G4-NH_2 dendrimer and $FeCl_3 \cdot 6H_2O$, with G4-NH_2:Fe mole ratios corresponding to 1:16 and 1:46. The synthesis procedure was adapted from a recipe provided by Fahlman and co-workers [15]. The catalyst was transferred to the Ti/SiO_2/Si substrate by dip coating for 10 s, and calcined at different temperatures (250, 550, 700, and 900 °C) for 10 min resulting in the formation of exposed monolayer of Fe_2O_3 nanoparticles. The mole ratio of Fe:G4-NH_2 and the temperature of calcination are the parameters that are varied here to control the mean diameter and the quality of MWCNTs. The catalyst solutions with G4-NH_2:Fe mole ratios corresponding 1:16 and 1:46 are hereafter referred to as 1Fe@den and 3Fe@den, respectively.

Arrays of vertically oriented MWCNTs with dense and uniform coverage on the substrate were grown from the Fe_2O_3 nanoparticles by PECVD at 900 °C. A detailed description of the microwave PECVD system has been reported previously [16]. Briefly, the Ti/SiO_2/Si-supported catalyst was placed on a 2 inch diameter Mo puck in the PECVD chamber and was evacuated to a pressure of 0.5 Torr using an external mechanical pump, and then purged with N_2 for 5 min. The catalyst was annealed in an N_2 ambient to enhance the stabilization of the Fe_2O_3 nanoparticles, as demonstrated in a recent study [14]. Induction substrate heating supplied by a 3.5 kW RF source acting on a graphite susceptor upon which the Mo puck rested was applied to heat the chamber to the reaction temperature (RT). At RT, the chamber was evacuated and pressurized to 10 Torr with H_2 flow of 50 SCCM (SCCM denotes cubic centimeter per minute at STP). The H_2 plasma was ignited using a power of 200 W, and 10 SCCM of CH_4 (Praxair, ultrahigh purity) was introduced into the chamber under these conditions for 20 min. The morphology, microstructure and quality of the 'as-grown' MWCNTs were studied by FESEM (Hitachi S-4800) and Raman spectroscopy. A PA technique was used to characterize the thermal performance of the MWCNT interfaces, and a detailed experimental set-up of the technique is described in [4]. Briefly, in the PA technique, a sinusoidally modulated fiber laser is used to periodically heat the surface of the MWCNT interface samples. The heated area of the sample's surface is surrounded by a sealed acoustic chamber; thus, a periodic pressure signal is produced, as measured by a microphone housed in the chamber wall. The measured pressure signal is used in conjunction with the model of [4] to determine thermal properties—in this study the thermal interface resistance. The time-resolved characteristic of the PA technique facilitates a precision necessary to identify small changes in thermal interface resistance (~1 mm^2 K W^{-1}) [4], thus distinguishing different MWCNT array morphologies in terms of thermal interface resistance.

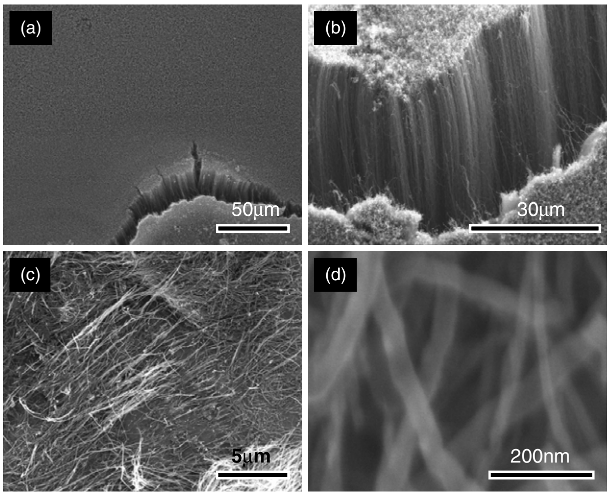

Figure 1. FESEM images of MWCNTs grown from 1Fe@den catalysts calcined at 550 °C. (a) low-resolution image showing the large and uniform coverage of MWCNTs; (b) vertical orientation of the MWCNTs; (c) the substrate after scratching; and (d) high-resolution image of MWCNTs.

3. Results and discussion

Figure 1 shows representative FESEM images of MWCNTs grown from 1Fe@den calcined at 550 °C, while figure 2 shows images of MWCNTs grown from 3Fe@den calcined at 250, 550, 700 and 900 °C. The spatial coverage of MWCNTs for all the samples as determined by ImageJ [17] was roughly the same, in the range of 65–70%. Little secondary growth of smaller-diameter MWCNTs was observed. The control of CNT diameter and quality are critical for most CNT-based applications. Also, for heat transfer applications, CNTs are required to be well anchored to the substrate. MWCNTs grown from 1Fe@den and 3Fe@den catalysts meet this criterion as demonstrated by the simple test we carried out to determine the adhesion of the MWCNTs to the substrate. A representative FESEM image of the MWCNT sample after scratching is shown in figure 1(c). The fragments of MWCNTs present after scratching are still strongly bonded to the substrate, suggesting that the MWCNTs are well anchored to the substrate.

Raman spectroscopic measurements recorded on a Renishaw Raman imaging microscope equipped with a 785 nm (1.58 eV) diode laser, reveal two strong peaks at 1312 cm^{-1} (D-band) and 1600 cm^{-1} (G-band), which are characteristic CNT vibration modes. The D-band represents the degree of defects or amorphous carbon, while the G-band represents the tangential stretching mode of highly ordered sp2 graphite. The integrated intensity of the D-band relative to the G-band (I_D/I_G) has been used to evaluate the quality of MWCNTs. The ratio is also affected by the change in CNT

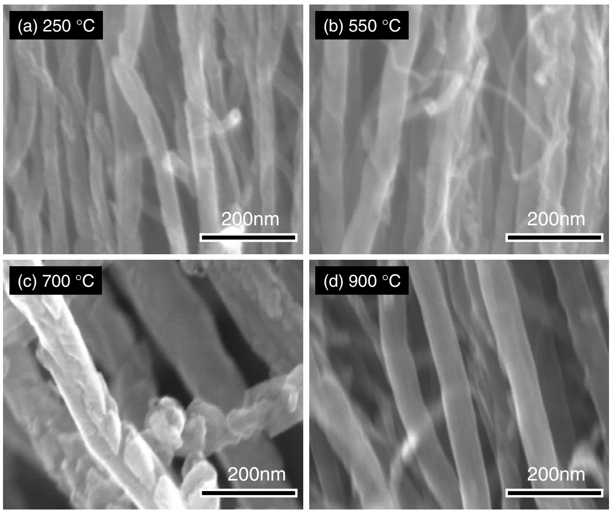

Figure 2. FESEM images of MWCNTs of different diameter distributions grown from 3Fe@den catalysts calcined at (a) 250 °C, (b) 550 °C, (c) 700 °C, and (d) 900 °C.

selectivity (i.e. single-wall or multiwall), which is insignificant in the present case because all the samples were MWCNTs. Therefore, amorphous carbon content and the number of defect sites on the MWCNT walls are expected to be the main contributors to the change in I_D/I_G ratio. The I_D/I_G ratios of MWCNTs grown from the respective catalysts are presented in table 1. The Raman spectrum for each sample (not shown) was an average of four spectra acquired randomly from the sample. The results reveal a clear difference in the quality of MWCNTs grown from 1Fe@den and 3Fe@den catalysts. MWCNTs grown from 1Fe@den catalysts exhibit I_D/I_G ratios in the range of 1.1–1.2, which is substantially lower than that observed for MWCNTs grown from 3Fe@den catalysts with I_D/I_G ratios in the range of 1.4–1.7. This indicates that MWCNTs grown from the 3Fe@den catalysts possess more defects or amorphous carbon.

This work demonstrates a reliable method for varying the diameter range of MWCNTs grown from Fe_2O_3 nanoparticles. The catalysts (1Fe@den and 3Fe@den), calcination temperatures, and the corresponding diameter distribution, I_D/I_G ratio, and thermal resistance of MWCNTs are summarized in table 1. The diameter distribution of MWCNTs was obtained from a random statistical count of 130 nanotubes imaged by high-resolution FESEM, and the histograms of MWCNT diameters grown from 1FXD@den and 3FXD@den catalysts are presented in figures 3 and 4, respectively. At low Fe concentration (1Fe@den), the average diameters of MWCNTs decreases slightly as the calcination temperature increases; at higher calcination temperatures (700 and 900 °C), the average diameter remains roughly unchanged (15–40 nm); a high-resolution image is shown in figure 1(d). The calcination of 3Fe@den at different temperatures allows the variation of MWCNTs diameters distributions within the 20–90 nm range. The calcination of 3Fe@den catalyst at 250, 550, 700 and 900 °C resulted in the growth of MWCNTs with corresponding diameter distributions of 28.85 ± 12.42, 35.43 ± 10.89, 70.34 ± 16.47, and 51.34 ± 15.02 nm (±, standard deviation), respectively (figures 2(a)–(d)).

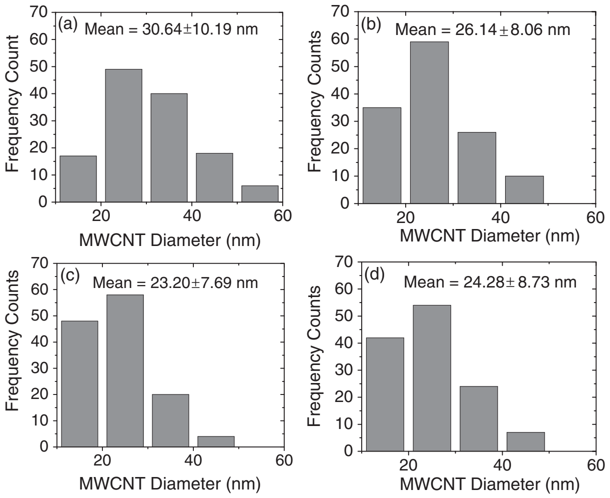

Figure 3. Histograms of MWCNT diameters grown from 1FXD@den catalysts calcined at (a) 250 °C, (b) 550 °C, (c) 700 °C, and (d) 900 °C.

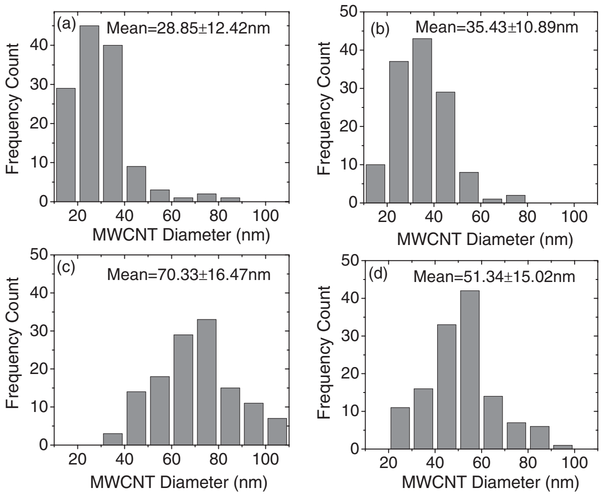

Figure 4. Histograms of MWCNT diameters grown from 3FXD@den catalysts calcined at (a) 250 °C, (b) 550 °C, (c) 700 °C, and (d) 900 °C.

As shown in table 1, the average diameters and diameter distributions of MWCNTs grown from 3Fe@den calcined at 900 °C are lower than MWCNTs grown from the same catalyst calcined at 700 °C. This result is likely the effect of a decrease in the size of the Fe_2O_3 nanoparticles upon calcination at temperatures higher than 700 °C and is consistent with the work of Ago *et al* [18]. The calcination process plays two key roles: (i) removal of the dendrimer template resulting in the formation of exposed Fe_2O_3 nanoparticles, and (ii) the determination of the size and the grain structure of Fe_2O_3 nanoparticles to enable variation of the MWCNT diameter. The latter role becomes more dominant at higher Fe concentration, as observed for 3Fe@den catalysts.

The MWCNT thermal interface is created by placing a piece of Ag foil (25 μm thick) atop a MWCNT-covered Si wafer. The room temperature thermal interface resistances of the Si–MWCNT–Ag are presented in table 1. The resistance measurements are performed at two interface pressures that

Table 1. Summary of the effect of the calcination temperature of 1Fe@den and 3Fe@den catalysts on the diameter distribution, I_D/I_G ratio, and thermal resistance of MWCNTs.

Catalyst G4-NH_2:Fe molar ratio	Calcination temperature (°C)	Diameter distribution (nm)	I_D/I_G ratio Std. error = ±0.1	Thermal resistance (mm^2 K W^{-1}) Std. error = ±0.5 mm^2 K W^{-1} 10 psi	30 psi
1:16 (1Fe@den)	250	30.61 ± 10.96	1.10	16	12
1:16 (1Fe@den)	550	26.14 ± 8.06	1.15	15	13
1:16 (1Fe@den)	700	23.20 ± 7.69	1.14	18	16
1:16 (1Fe@den)	900	24.28 ± 8.73	1.18	14	13
1:46 (3Fe@den)	250	28.85 ± 12.42	1.51	11	8
1:46 (3Fe@den)	550	35.43 ± 10.89	1.63	14	10
1:46 (3Fe@den)	700	70.34 ± 16.47	1.68	11	9
1:46 (3Fe@den)	900	51.34 ± 15.02	1.44	14	13

are representative of those commonly used to mate a heat sink to a microprocessor. The thermal resistance values reported here are comparable to those reported for MWCNT interfaces grown from film catalysts [3, 4]. Interestingly, MWCNTs grown from the 3Fe@den catalysts, which possessed more defects and impurities, achieved lower thermal interface resistances ($\leqslant 10$ mm^2 K W^{-1}) except for samples calcined at 900 °C. In general, differences in the quality of the MWCNTs resulted in the largest differences in thermal interface performance, and the apparent effects of diameter and small variations in spatial density were not distinguishable. The MWCNT quality-dependent thermal performance is clearly identified for samples calcined at 250 °C. Here, the diameter ranges are similar, yet the more defective MWCNTs grown from the 3Fe@den catalysts achieve thermal interface resistances that are approximately 33% lower than those of the higher-quality MWCNTs grown from the 1Fe@den catalysts.

The thermal resistances of well adhered, one-sided CNT array interfaces such as the Si–MWCNT–Ag interfaces of this study are dominated by the resistance at the free CNT tips interface [4]. Thus, we postulate that the lower-quality MWCNTs are more mechanically conformable due to a defect-induced Young's modulus reduction for individual tubes [19] that lowers the effective bulk modulus of the MWCNT array. As a result, the real contact area at the free CNT tips interface increases to improve thermal interface conductance. Recently, Zhang *et al* [20] showed that the effective bulk modulus of carbon nanofiber arrays decreases as the number of defect sites and impurities increases, and their observations are consistent with the postulate stated above.

4. Conclusions

In summary, the diameter distribution and quality of MWCNTs have been successfully varied using Fe_2O_3 nanoparticles derived on a dendrimer 'nanotemplate'. The concentration of Fe in the catalyst solution and the calcination temperature of the Fe@den nanocomposites are key parameters that enable the modification of the catalyst structure, resulting in variation of the MWCNT structure. The effects of the foregoing factors on the MWCNT structure are more significant at higher Fe concentration. PA measurements reveal enhanced thermal interface performance of MWCNTs grown from 3Fe@den catalysts ($\leqslant 10$ mm^2 K W^{-1} for 3Fe@den catalysts calcined at 250, 550, and 700 °C), and they suggest that real interfacial contact area may be increased by the additional conformability provided by MWCNT arrays with an increased number of defects. It is clear from our study that there seem to be an inverse relationship between the thermal interface resistance and the quality or the number of defect sites on the walls of the MWCNTs.

Acknowledgments

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