High-Density Growth of Single-Wall Carbon Nanotubes on Silicon by Fabrication of Nanosized Catalyst Thin Films

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A simple method for the synthesis of metal oxide thin films through gel solutions of inorganic metal salts using poly(ethylene glycol) was developed. The technique was then applied to fabricate nanoscale MgO-supported catalysts for the surface CVD growth of single-wall carbon nanotubes (SWNTs.) The results showed that the catalytic films greatly promoted the growth of SWNTs of high quality, density, and uniformity. The bundle sizes, growth density, and orientation of the resulting SWNTs could be controlled to some extent by choosing the type of catalyst and by suitable modification of the reaction parameters.

Introduction

Carbon nanotubes are novel materials which may be utilized in many fields.[1–3] However, their wider application is currently limited by the inability to control their synthesis to the desired requirements, including yield efficiency, degree of purity, uniformity of dimensions, and so forth. Carbon nanotubes can be synthesized in bulk but may also be grown directly on surfaces.[4] The direct growth of nanotubes on surfaces offers a number of potential advantages in field emission[5,6] and the fabrication of microelectronic devices.[7,8] For these reasons, a great deal of work has been carried out in this area over the past 3 years.[9–13] Carbon nanotube films, especially patterned or aligned, can now be generated by special treatment of catalytic films[14–17] or via porous templating techniques.[18–20] However, most of this work

has been confined to the synthesis of multiwalled carbon nanotube (MWNT) films. The growth conditions for single-walled carbon nanotubes (SWNT) seem more exacting and are dependent upon the suitable preparation of the catalysts. As SWNTs generally have a higher degree of structural perfection and better electronic behavior than MWNTs, growth of SWNT films on surfaces will be thus more useful for practical application and fundamental research.[1,4,21]

Compared with arc discharge and laser ablation methods, the chemical vapor deposition (CVD) method seems more effective for the controllable synthesis of SWNTs.[4] As the growth mechanism of SWNTs in the CVD process generally involves the dissociation of hydrocarbon molecules into carbon atoms, dissolution and saturation of these atoms within the metal catalyst, and further precipitation into tubular carbon deposits, this growth process is inevitably affected by the type of hydrocarbon source, the furnace temperature, the type and particle size of the catalyst, and any interactions between the supporting material and the catalyst.[4] Recent studies by our group[22] and others[23,24] have revealed that MgO, especially a porous MgO material, is a good candidate support material for the scalable growth of SWNTs. In the present study, we describe a simple method to synthesize MgO-supported catalytic nanofilms on Si substrates. The resulting catalytic surface was found to be extremely effective for the direct methane CVD growth of SWNT films with high quality and density at low cost.

Experimental Section

Preparation of Catalytic Films and Powders. Supporting MgO nanofilms suitable for the surface synthesis of carbon

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nanotubes on silicon substrates were prepared by using a simple gelling method. Magnesium nitrite (0.15 g) and poly-(ethylene glycol) (PEG) (MW = 8000; 0.1 g)) were sonicated in 4 mL of absolute alcohol until the solution appeared clear. The resulting gel solution of Mg salt was then coated onto Si (111) wafers at 3500 rpm using a spin-coating technique. To ensure that the gel solution covered the silicon substrate uniformly, Si (111) wafers were first thoroughly cleaned with "piranha" solution (98% H_2SO_4:30% H_2O_2 = 4:1, v/v) followed by ethanol and finally water. Magnesium oxide thin films were then formed on silicon wafers by heating the gel-covered substrates at 600 °C in air for 1 h. For the preparation of catalytic films, 5−50% (weight ratio, relative to the weight of Mg salt) of Fe, Co, or Ni nitrate was added to the gel solution of Mg salt. The catalytic films were then prepared using the same procedure as that described above for the MgO films.

In comparison, the MgO-supported catalyst material used for bulk synthesis of carbon nanotubes was also prepared in this work. It was made by impregnating MgO powder material, which was obtained by thermal decomposition of alkaline magnesium carbonate at 400 °C in Fe nitrate solution;[22] the weight ratio at 10% ($W_{Fe(NO_3)_2}$:W_{MgO}) was determined for optimal growth of SWNTs.

Growth of Carbon Nanotubes. For surface growth of SWNTs, a piece of catalyst-covered Si wafer was placed in a quartz boat and inserted into a tubular furnace. The furnace was heated to 800 °C in an Ar atmosphere with a flow rate of 300 mL/min and was then purged with methane at 100 mL/min for 30 min. After the reaction, the methane was turned off, leaving the Ar supply on, until the Si wafer had cooled to room temperature. For bulk synthesis of SWNTs, about 1 g of catalyst powder was placed into an alumina boat within a quartz tube. The sample was then heated in the furnace using the same reaction conditions as described above. The as-prepared SWNT products required further purification in concentrated hydrochloric acid to remove catalyst and support impurities from the carbon deposits.

Characterization of Nanotube Products. The carbon nanotubes produced by using the methods described above were characterized by using SEM, TEM, and micro-Raman spectroscopy. SEM was carried out at 25 kV with a Hitachi H-800 field-emission microscope. TEM was performed at 200 kV by using a JEOL JEM 2010 microscope. Micro-Raman experiments were done with a Renishaw system 1000 in an ambient atmosphere and at room temperature. Raman spectra were then recorded using a 50-mW He−Ne laser operating at 632.8 nm and a CCD detector.

Results and Discussion

Preparation of Nanosized Catalystic Thin Films. Some attempts have been previously made to prepare Fe, Co, or Ni oxide films as catalysts for carbon nanotube growth, but in general these only have been suitable for the growth of MWNT films.[16,17] As for the growth of SWNT films, it should be achieved with special synthetic strategies, such as preparing well-dispersed nanosized Mo−Fe particles on a surface[25] and nanosized alumina-supported Fe particles[26−28] and using ferritin protein to fabricate discrete catalyst particles for SWNT growth.[29] It seemed that suitably controlling the size and dispersion of catalyst particles would be critical for the successful surface synthesis of SWNTs. In this study, we aimed to fabricate a nanosized MgO
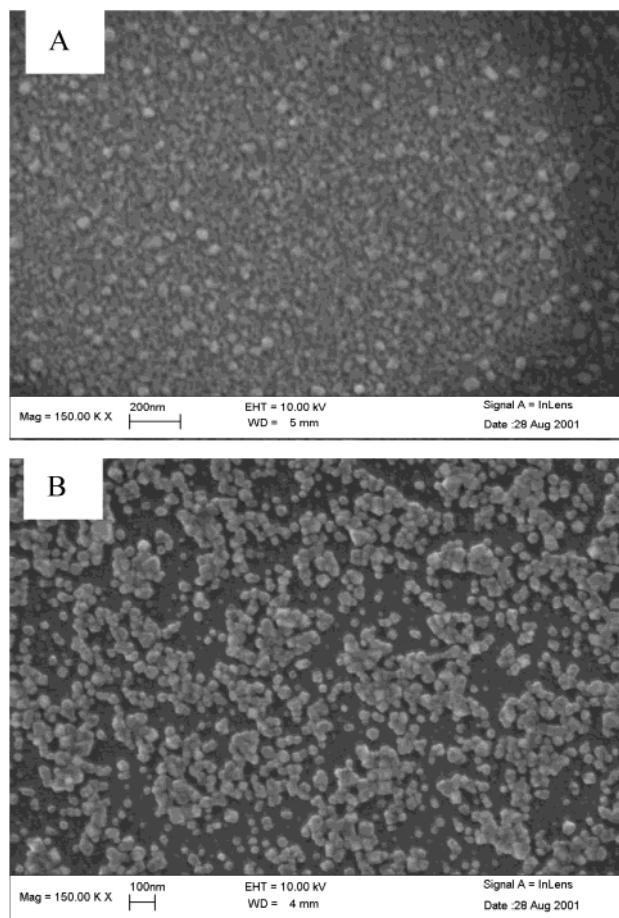

Figure 1. SEM images of MgO (A) and MgO-supported Fe catalyst (B) thin films prepared by a gelling method.

thin film as a supporting layer to prepare well-dispersed catalysts for SWNT growth on a surface.

MgO thin films can be synthesized by using several methods, including laser pulse ablation,[30] electron beam evaporation,[31] chemical vapor deposition,[32] and sol−gel methods with magnesium acetylacetonate as a precursor.[33] In this work, we have established an alternative simple method for preparing MgO thin films through gelling of an alcohol solution containing magnesium salts with PEG. Uniform and dense MgO thin films can be formed through a stable and well-dispersed gel solution of magnesium nitrate alcoholic solutions with the addition of PEG. Moreover, suitable control of the concentration of PEG in the Mg salt solution was responsible for the final quality of the MgO film. Figure 1A shows a typical SEM image of the resulting MgO film made from magnesium nitrite gel solution. The MgO film was dense with particle sizes distributed in the range from 20 to 50 nm. Elemental analysis from EDXS analysis of SEM and XPS data demonstrated the formation of MgO after heating the coating on Si above 600 °C. It is worth mentioning that this method was also efficient for the synthesis of other kinds of metal

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oxide films, such as Fe oxide, Co oxide, Ni oxide, and so forth. The thickness of the resulting film prepared by coating with two layers of gel solution was about 100 nm, as determined by TEM.

Following the successful synthesis of MgO nanofilms, 5−50% Fe nitrate was introduced into the Mg gel solution and catalytic films were synthesized by using the same procedure. As shown in Figure 1B, the supported catalyst particles in such thin films were also in the same size range as that which appeared in the MgO thin film. No aggregation or fusion of the catalytic particles was observed, even when the films were heated at high temperature for more than 5 h. However, under the same methane CVD conditions, SWNTs grown on such nanosized catalytic thin films were quite distinct from those arising from MgO-supported catalytic powders as described below.

Growth of SWNTs over MgO-Supported Catalytic Powders. MgO is an efficient supporting material for the synthesis of SWNTs.[22−24] Our previous work indicated that the yield of SWNTs formed over MgO-supported catalytic powders was dependent upon the loading of Fe salts.[22] However, even at the highest impregnating concentrations of Fe salts (50%), the yield of SWNTs on the catalytic powders was <25%. A higher loading amount of Fe salts in the supported catalysts may also give rise to the formation of more carbon impurities. For this reason, MgO-supported catalytic powders were loaded with 10% Fe salts to have the high-purity growth of SWNTs. The corresponding yield was therefore only around 10%. Given the presence of numerous contaminants arising from both the catalyst and support mixtures, treatment with concentrated HCl was carried out before SEM and TEM characterization of nanotube deposits. Figure 2 shows SEM and HRTEM images of purified SWNTs grown on catalytic powders; TEM characterization revealed that the carbon nanotubes were indeed single-walled, and the quality of SWNTs was high as the walls of tubes were clean, were whole, and had fewer defects. SEM characterization indicated that the carbon nanotubes were formed in bundles, and the bundle sizes were not quite uniform in such tubular products.

Promoted Growth of SWNTs over Nanosized Catalyst Films. Figure 3 shows the SEM images of the as-grown carbon nanotubes over a MgO-supported catalyst thin film without any further purification steps. In contrast to the results obtained by using the catalytic powders, the growth densities of surface-grown SWNTs decreased with increasing Fe salts concentrations in the nanosized catalytic thin films. In the range from 10 to 50%, the lower the Fe catalyst concentration, the higher the growth density of SWNTs on silicon. In our study, we found that the sizes of the catalytic particles formed on the surface also varied with the concentration of Fe salt added to the gel solution. Higher concentrations of Fe salt favored the formation of catalytic particles of smaller size; however, this did not favor the high-density growth of SWNTs. A concentration of 10% Fe salt added to the gel solution was finally determined to be optimum for high-density surface growth of SWNTs.

The observations from SEM (Figure 3) were in close agreement with the results from Raman spectroscopy (see Figure 4), providing further evidence that the
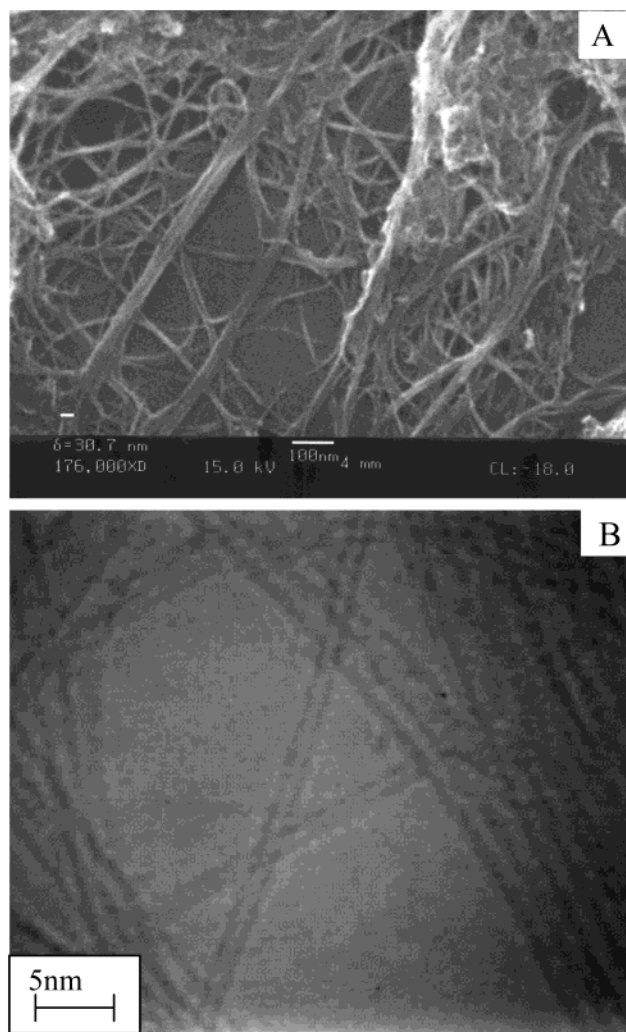

Figure 2. SEM (A) and TEM (B) images of purified SWNTs grown over MgO-supported Fe catalyst powder.

ropelike carbon deposits were made of SWNTs. This was evidenced by the characteristic RBM (radial breath mode) frequencies of SWNTs centered around 200 cm^{-1}, which could be clearly observed. On the basis of the equation ν (cm^{-1}) = 223.75/d(nm),[34] the predominant diameter of SWNTs grown on the catalytic nanofilms was estimated to be about 1.15 nm. SEM images of the SWNT film revealed an average diameter of the ropelike structures to be about 15 nm, implying that surface-grown SWNTs also preferred to exist in bundles. With increasing Fe salt in the catalytic films, the density of surface-grown SWNTs was low, and the corresponding intensities of RBM, G-line, and D-line frequencies in their Raman spectra became unclear and weak.

The number of coating layers used was also found to affect the quality of SWNTs growth as the catalytic particle density on the surface could be manipulated by varying the number of coatings of the gel solution. Under the preparation conditions used here, the optimal growth of SWNTs could be achieved using two or three coating layers. The use of more layers, however, might give rise to agglomeration and slot formation in the films with correspondingly poor growth of SWNTs.

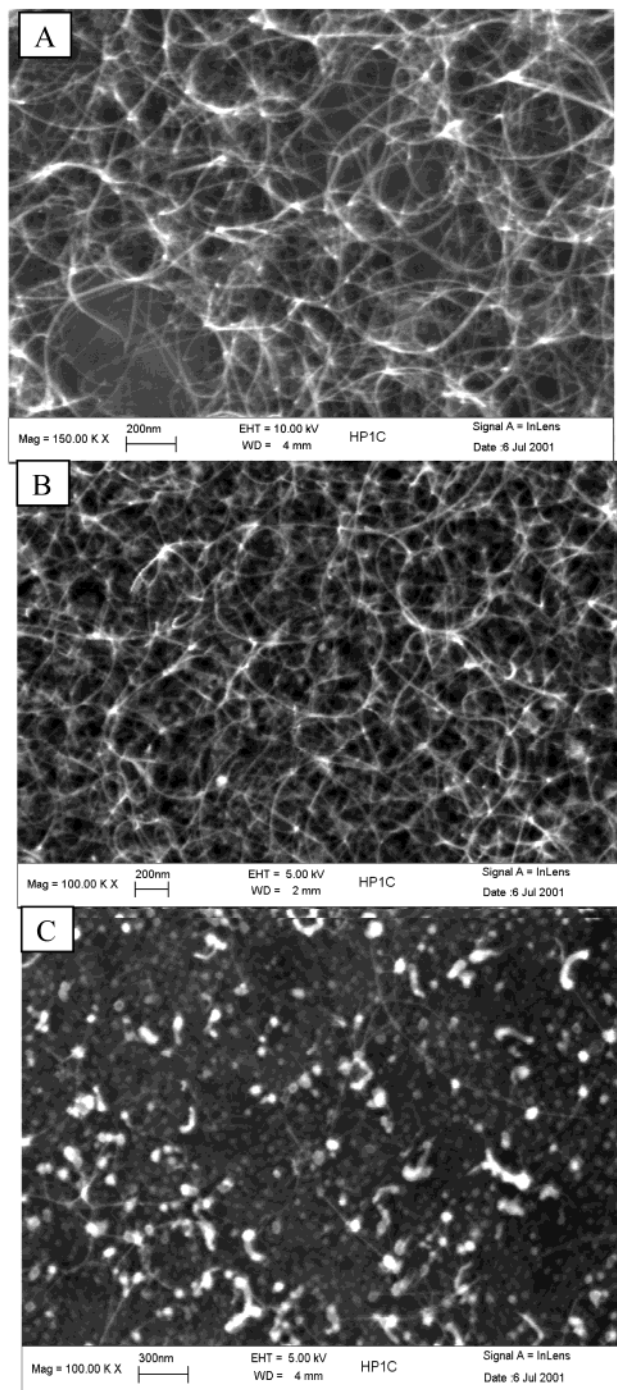(34) Bandow, S.; Asaka, S.; Saito, Y.; Rao, A. M. *Phys. Rev. Lett.* **1998**, *80* (17), 3779.

Figure 3. SEM images of SWNTs grown on Fe catalyst films loaded with different amounts of Fe salts: A, 10%; B, 25%; C, 50%.

Figure 4. Raman spectra of as-grown SWNTs film on MgO films with different catalyst loadings.

Compared to the bulk growth of SWNTs on MgO-supported catalytic powder, remarkable differences in the purity, density, and uniformity of products were found during the growth of SWNTs on the silicon surface. The yield of SWNTs gained in bulk growth over catalyst powders was often around 10%; SEM imaging of as-prepared SWNTs cannot be obtained clearly if the carbon deposit was not purified in acid solutions and dispersed thoroughly in advance. While the growth of SWNTs on nanosized catalyst films was greatly improved, clear SEM images of SWNT films could be obtained directly without any further treatment, showing much higher density, purity, and uniformity.
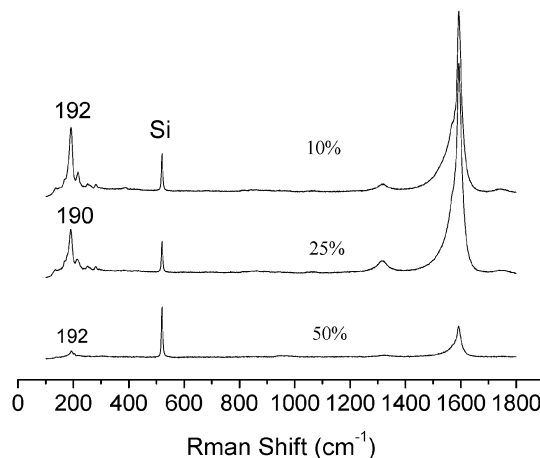
It is generally held that the ideal catalytic material for SWNT synthesis should possess a strong interaction between the metal and support and have a high surface area. Strong metal−support interactions may facilitate high metal dispersion and thus generate a high density of catalytic sites. In addition, it may also prevent the catalytic particles from aggregating and forming unwanted large particles, which are associated with the formation of amorphous carbon or defective multiwalled tube structures. A large density of catalytic sites would ensure efficient contact with carbon atoms formed by the decomposition of the original carbon source and their rapid diffusion into metal particles. The apparent improvements in the surface growth of SWNTs demonstrated in the present study may be mainly attributed to the formation of MgO nanofilms, as nanosized MgO particles would provide a suitably large surface area, and MgO itself has been shown to be a good material to prepare well-dispersed supported catalysts. This can be seen in Figure 1B, where the catalytic particles were dispersed well on the substrate even after treatment at 800 °C, with no indication of obvious particle aggregation. Compared with the previous work using supported catalyst powders and mesoporous templates, or patterning the catalyst with microlithographic techniques to synthesize carbon nanotubes on a surface,[18−20] the utilization of nanosized supported materials can undoubtedly result in more reaction sites and higher catalytic activity, and therefore higher growth density and yield of tube products.

However, as the catalysts prepared by our procedure are, in fact, a kind of Mg composite compound, when a small amount of Fe salt is added during the formation of nanosized MgO thin film, the Fe species may be well-separated by distribution as defects in the MgO lattice. On the other hand, when excess Fe salts are added, some Fe species may not be efficiently dispersed, as there are insufficient defect sites within the MgO lattice. Aggregation of Fe particles would therefore inhibit the formation of SWNTs, which may be the main reason a lower density of SWNTs was observed on the surfaces of catalytic nanofilms that contained larger amounts of Fe salts.

Besides Fe catalyst films, Ni and Co catalyst films fabricated in this way were also effective for high-density growth of SWNTs. It was worth mentioning here
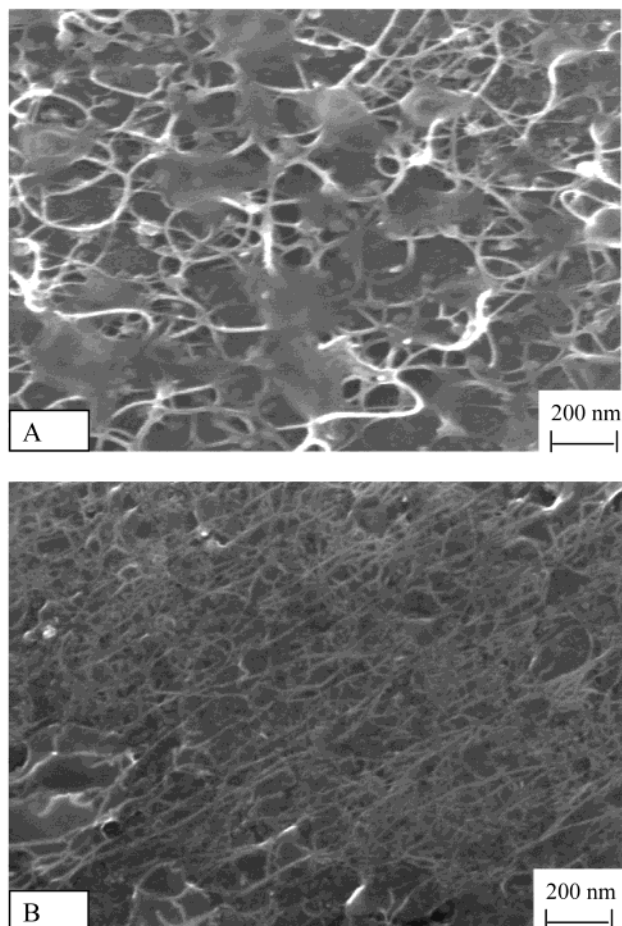
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Figure 5. SEM images of as-grown SWNTs on Co (A) and Ni (B) catalyst films.

that the oxide particles formed in these two kinds of films were even smaller and more uniform. SWNTs grown on such films also exhibited different textural structures from the situation on Fe catalyst film. Large bundles of SWNTs were facilitated on the Co catalyst film while oriented and threadlike SWNTs were grown on the Ni film (shown in Figure 5).

Conclusions

In summary, a simple method for the synthesis of metal oxide thin films through solutions of inorganic metal salts has been demonstrated to achieve a uniform distribution of nanoscale MgO-supported catalysts for the CVD surface growth of SWNTs. Fe, Co, and Ni catalysts were all shown to be well dispersed on a Si substrate, and their particle sizes and surface distribution density could be easily controlled by varying the salt concentration in the gel solution, the heating temperature, and the number of coatings of the gel solution. Catalytic films fabricated in this way were found to be suitable for the effective growth of SWNTs of high quality, density, and uniformity. It was also shown that the type of catalyst used would affect the bundle sizes, growth density, and orientation of as-grown SWNTs. With use of this method, SWNT films could be readily prepared on the surfaces of many different substrates. In this respect it provides a potentially useful tool for the future development and application of nanotechnology and nanofabrication by means of SWNTs.