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A Supercritical Fluid Method for Growing Carbon Nanotubes

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Carbon nanotubes have attracted considerable attention due to their unique mechanical, chemical, thermal and electrical properties,[1,2] and have been demonstrated to have application in microelectronics, hydrogen storage, as reinforcement materials and in catalysis.[3-7] Several different production methods, such as arc-discharge, laser ablation and chemical vapour deposition (CVD) [8-10] have been used to synthesize nanometer-sized carbon materials. However, the yield, structure and properties of carbon nanotubes are strongly dependent on the preparation method and reaction conditions employed.[11-13] Recently, efforts have been made to develop supercritical fluid (SCF) techniques for synthesising nanomaterials including nanowires, nanorods and mesoporous carbons.[14-16] In particular, Korgel et al [17] have pioneered the growth of multi-walled carbon nanotubes (MCNTs) in supercritical toluene and highlighted the potential benefits of using SCFs for growing carbon nanostructures. In comparison to vapor-phase synthetic methods, SCF approaches have the potential for a much higher throughput of product, partly due to the ability to use much higher precursor concentrations and in some cases have a better dispersibility of catalysts, and all in a continuous homogeneous synthetic process. However, the yield of carbon nanotubes obtained by these researchers was low; the selectivity of carbon nanotubes relative to the total carbonaceous material produced was approximately 2 % based on TEM observations. Thus to obtain high purity samples of SCF grown carbon nanotubes, complex post-treatment processes would be required.

In this communication, we report for the first time a continuous-flow SCF method for growing carbon nanotubes with high selectivity, up to 80 % of the carbonaceous materials formed was MCNTs, and in high yield, up to 100 % compared to the amount of catalyst used. In our experiments supercritical carbon monoxide (sc-CO) was used as the carbon source for generating carbon nanotubes. Carbon monoxide was chosen as the carbon source as it has been successfully used as a gaseous reactant, at relatively low pressures, to generate high quality carbon nanotubes at low yields (less than 8 %). [18,19] The structural properties of the carbon nanotubes produced from sc-CO were characterised by scanning and transmission electron microscopy (SEM and TEM), thermal gravimetric analysis (TGA) and Raman spectroscopy. The field emission properties from individual nanotubes grown by the SCF process were also investigated

and compared to carbon nanotubes grown by CVD. Details of the catalyst preparation and the SCF growth process and field emission measurements are presented in the experimental section.

Figure 1 shows typical SEM images of carbon nanotubes synthesized from sc-CO at 750 ^{o}C and 5.17 MPa. From the SEM images a large number of aggregated carbon nanotubes are observed protruding from the surface of catalyst (figure 1a). The length of many of the nanotubes produced is greater than 10 μm. The magnified SEM image, figure 1b, shows that some of the catalyst particles are attached to the as-synthesised nanotubes. From SEM observation and from TGA data the yield of carbon nanotubes produced using the SCF method was high; typically 100 % compared to the weight of the supported catalyst.

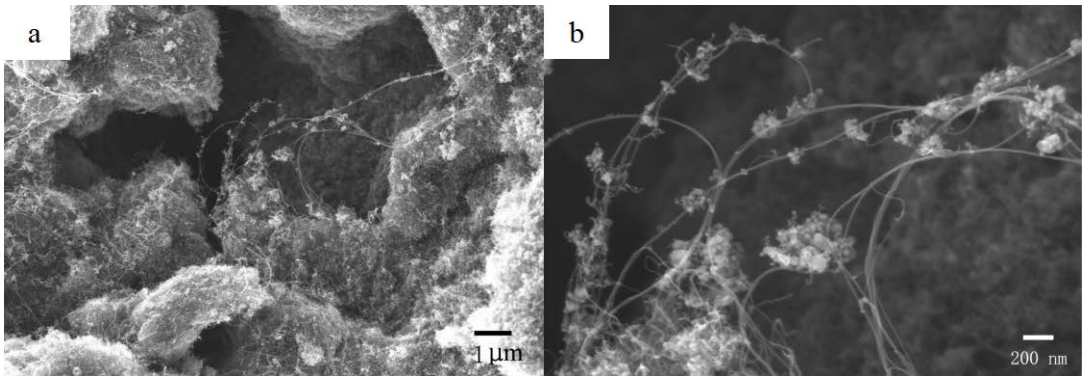

Figure 1. SEM images of carbon nanotubes prepared using a continuous flow SCF deposition reactor, using Co-Mo/MgO as a catalyst and sc-CO as the carbon source at a temperature of 750 ^{o}C and pressure of 5.17 MPa.

A TEM image of carbon nanotubes synthesized at the same conditions is shown in figure 2a. MCNTs are produced under these conditions with a mean diameter of 20 nm. After treatment of the carbon/catalyst samples from the SCF reactor with nitric acid, to remove the catalyst particles, amorphous carbon etc., approximately 80 % of the carbon left was MCNTs, according to TEM observation. Therefore, the selectivity of the SCF process

for forming MCNTs under these experimental conditions is extremely high, particularly in relation to other SCF processes but also compared to CVD growth of MCNTs when using CO as a carbon source.[20,21]

The effect of pressure on the morphology of the carbon nanotubes was also investigated. A pressure of 5.17 MPa was found to be optimal for carbon nanotube synthesis. At higher pressures distorted nanotubes are prepared as observed in figures 2 b and 2c. In particular, distorted carbon nanotubes, with rough surfaces are generated at a pressure of 10.34 MPa (figure 2c). This change in the morphology of the nanotubes at higher pressures is possibly due to the discord between the high decomposition rate of CO and the growth rate of CNT formation on the active centre of the Co catalyst under SCF condition.

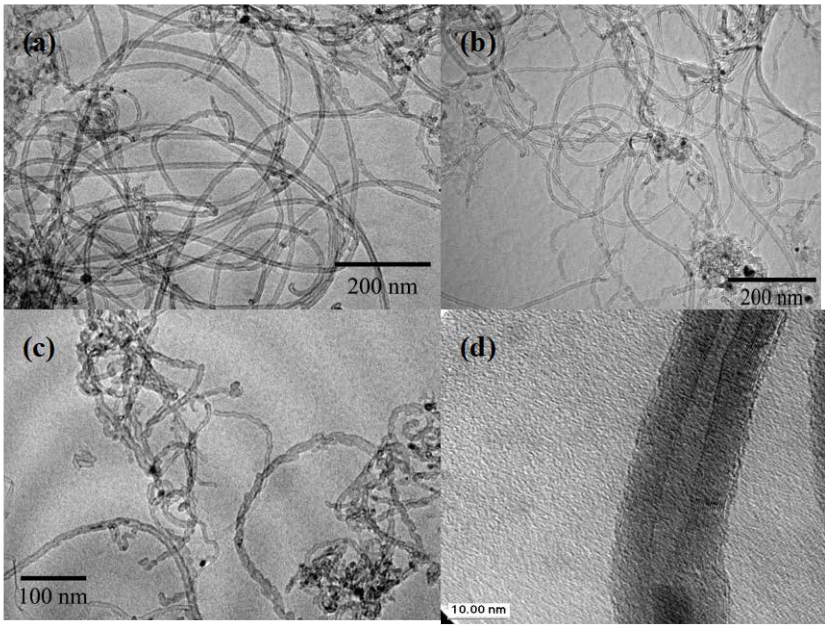

Figure 2. TEM images of MCNTs prepared using SCF deposition over a Co/Mo/MgO catalyst at a temperature of 750 ^{o}C and sc-CO pressure of: (a) 5.17 MPa, (b) 6.89 MPa and (c)10.34 MPa. A high resolution TEM of (a) is shown in image (d).

Raman data of SCF grown MCNTs prepared at a temperature of 750 ^{o}C and pressure of 5.17 MPa show that the nanotubes exhibit a Raman-active E_{2g} mode at 1590 cm^{-1}, which

is characteristic of graphitic sheets, as shown in figure 3. This sharp well defined G-band confirms the presence of sp^2 carbon-type structures present within the tube wall. The appearance of a Raman signal at 1320 cm^{-1} indicates a certain degree of disorder in the MCNTs. There are multiple causes for the disordered nature of the nanotube structures, which includes the destruction of the nanotube walls during treatment with HNO_3, as well as the inability of the Co catalyst to completely convert non-organised carbon to graphitic structures at the low temperature of 750 ^oC. It should be noted that the highest operating temperature of the SCF reactor was 750 ^oC. At a higher temperature, such as 900 ^oC, well graphitised MCNTs should be achievable.

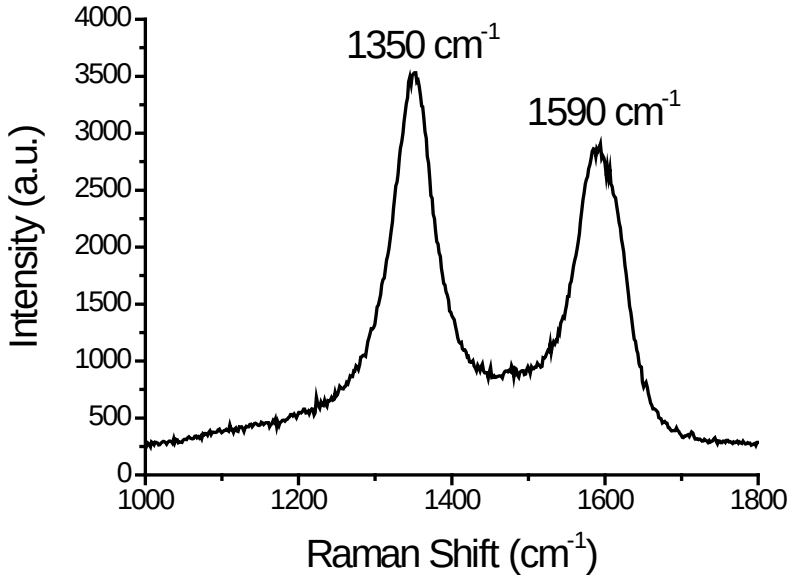

Figure 3. Raman spectrum of SCF grown MCNTs prepared at a temperature of 750 ^oC and a pressure of 5.17 MPa.

The field emission properties of the individual MCNTs, grown at 750 ^oC and 5.17 MPa, were characterized using a combined scanning probe microscopy - transmission electron microscopy (SPM-TEM) technique.[22,23] MCNTs grown by CVD and SCF methods in our laboratory were investigated under identical conditions. Figure 4a shows a TEM image of an individual MCNT grown by SCF method investigated during the field emission measurements. The nanotube has a length of 5.5 μm and a diameter of approximately 20 nm; the distance between nanotube and the electrode is 1 μm. The

corresponding field emission current, depending on local field, is shown in figure 4b. Field emission current for CVD grown nanotubes is shown for comparison. Emission initiates at local fields of 2.5 – 5.0 V/nm and 1.5 – 4.0 V/nm for SCF and CVD grown CNTs respectively (see figure 4b). SCF grown nanotubes exibit slightly higher saturation currents in comparison to the CVD grown nanotubes (from 0.15 to 2 μA for SCF and 0.01 to 0.5 μA for CVD grown nanotubes). Field emission I(V) curves fit well to the Fowler-Nordheim field emission model (figure 4b) for both SCF and CVD grown nanotubes. A work function equal to 5.1 eV, obtained from the literature [24-26], was used to fit the model in both samples.

SCF grown nanotubes also exhibited a slightly better failure-stability in comparison to CVD grown nanotubes. Emission failure of the SCF grown nanotubes occurred at currents between 0.45 and 3.5 μA (local fields between 3.5 and 8 V/nm) whereas in the CVD grown nanotubes breaking occured at currents between 0.1 – 1 μA (local fields 3.0 – 4.6 V/nm). It should be mention that field emission parameters for our SCF produced nanotubes, grown at the low temperature of 750 ºC, are within the range of parameters obtained for CVD produced carbon nanotubes, grown at temperatures between 900-1000 ºC, measured by different groups.[24, 25]

In summary, a SCF deposition technique employing sc-CO has been shown to be an efficient method for the large-scale production of MCNTs. The high concentration of sc-CO used in the reactor results in a remarkably high yield of nanotubes. The diameters of the MCNTs synthesised ranged from 10 to 20 nm, with lengths of several tens of micrometres. The SCF grown nanotubes also exhibited field emission characteristics similar to CVD grown MWNTs. These results suggest that SCF-grown nanotubes are potential nanomaterials for the large-scale fabrication of CNT-based devices.

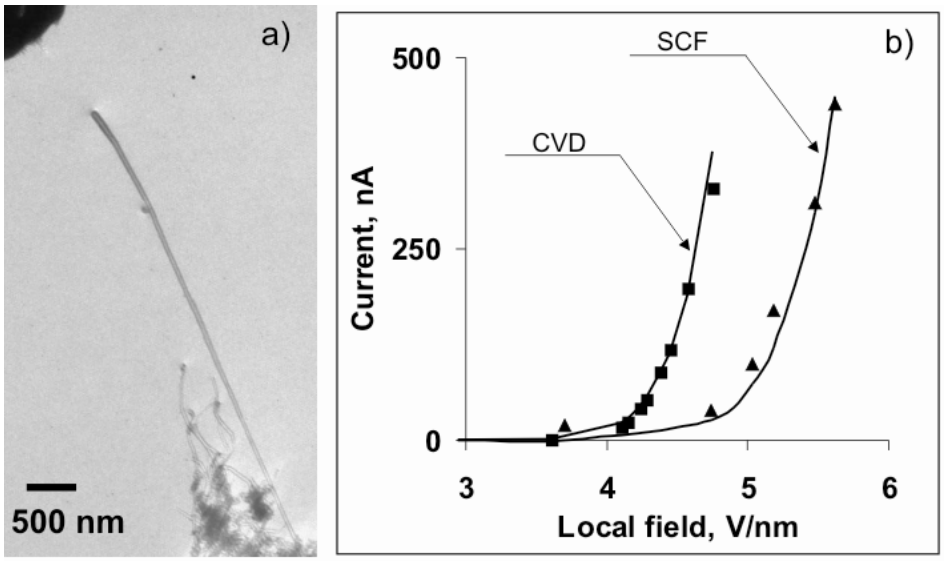

Figure 4. (a) A typical TEM image of a SCF-grown nanotube used for field emission measurements (length = 5.5 μm and radius ≈ 10 nm); (b)field emission current of the SCF grown MWNT (triangles), field emission current of a MWNT grown by CVD method (rectangles) and fitting using the Nordheim-Fowler fit (line) as function of local field..

Experimental

A MgO supported 3 wt.% Co and 4 wt.% Mo catalyst was prepared by an impregnation method: an aqueous solution of $Co(NO_3)_2$ and $(NH_4)Mo_6O_{24}$ were mixed with the MgO support, followed by sonication for 30 minutes and drying. The dried precursor powder was sintered at 450 ºC for 6 hr. In a typical SCF deposition experiment, a quartz boat containing 0.5 g Co/MgO catalyst was placed in the centre of a high pressure reactor (Inconel 625 GR2- Snap-tite, Inc.). The catalyst was then heated in a reducing atmosphere of H_2/Ar (V/V=20/180 ml min^{-1}) at a flow rate of 200 ml min^{-1} for 30 min. CO was first added to a 450 ml stainless steel reservoir as the carbon source. The gas was maintained above the critical temperature and pressure of CO (T_c = -140.4 °C, P_c = 3.49 MPa) at 40 °C in a temperature controlled water bath. A flow through system was established by connecting the inlet and outlet valves of the carbon source reservoir, which

included a piston, to a 260-ml ISCO syringe pump (Lincoln, NE) and the reaction vessel respectively. A back pressure regulator maintained the system at constant pressure and controlled the flow rate of CO through the system. The reaction time was set to 1 hr. When the experiment had finished, the reactor was cooled down to room temperature under an Ar flow, and the powder was treated with 6M HNO_3.

Scanning electron microscopy (SEM) was conducted on a LEO 530 scanning microscope. Transmission electron microscopy (TEM) was performed on a JEOL 2000FX operating at 200 kV and High-resolution TEM images were recorded with a high-resolution TEM (JEM 2010 operating at 200 kV). Raman spectra were recorded on a Renishaw 1000 Raman system in an ambient atmosphere using a 5 mW He-Ne laser (λ = 514.5 nm) and a CCD detector. Thermal gravimetric analysis (TGA) of the carbon sample was performed at a heating rate of 10 ºC min^{-1} up to 900 ºC in air flow of 75 ml min^{-1}.

Individual carbon nanotubes were characterized using scanning tunneling microscope compatible with a transmission electron microscope Philips TEM-301 operating at 80 kV (vacuum in the chamber around 10^{-2} Pa), equipped with Keen View II CCD camera for image acquisition. Nanotubes were bonded onto macroscopic gold tip (gold wire diameter 0.25mm) with conductive epoxy for support. The gold tip was then fixed onto a piezoelectric scanner inside TEM holder. The opposite tip was used as an electrode.

The field emission I(V) characteristics were analyzed using the Fowler–Nordheim (F–N) field-emission theory. The Fowler–Nordheim equation can be written as shown below:

$$I = A\frac{1.5\times10^{-6}}{\phi}\left(\frac{V}{d}\right)^2 \gamma^2 \exp\left(\frac{10.4}{\sqrt{\phi}}\right)\exp\left(\frac{-6.44\times10^{9}\phi^{1.5}d}{\gamma V}\right)$$

Where A is the emitting area, Φ is the working function, γ is the geometric field enhancement factor and is defined as $(0.87L/r + 4.5)$ where L is nanotube length and r – is nanotube radius, and $F = V/d$, where V is the applied voltage; and d the inter-electrode distance.

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