

# Growth of Carbon Nano-Structures in Ceramic Materials

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## ABSTRACT

Tailored pore size mesoporous silica, incorporating different concentrations of transition metal-based catalysts, has been used as platforms for the growth of carbon nanotubes by the chemical vapor deposition method. Thermogravimetric analysis alongside EDX/SEM was employed to characterize the samples prior to CNT growth. The CNTs produced were characterized using Raman Spectroscopy and HI RES SEM. Raman spectroscopy showed good quality highly graphitic CNTs whose diameters matched the corresponding pores of the matrices. The density of the CNTs was found to be high for higher metal concentrations for the same pore diameters. Fe and Co were found to be better catalysts for growth of CNTs than Ni.

**Keywords:** mesoporous silica, carbon nanotubes, chemical vapor deposition, scanning electron microscopy, electron diffraction X-ray

## 1 INTRODUCTION

Since their discovery in 1991 by Iijima [1], carbon nanotubes have attracted attention research from all fields of science. Their fascinating structural, physical and chemical properties are the backbone to curiosity-driven research with an aim for commercially viable applications. By incorporating carbon nanotubes into appropriate matrices, the resulting composites are expected to have enhanced mechanical, thermal and electrical properties. Recent reports list transparent conducting, low weight structures, antistatic and electromagnetic shielding as realistic applications of carbon nanotube composites [2]. Ceramic matrix materials are tough, addition of high thermal conductivity CNTs will reduce operating temperatures as well as enhance thermal shock resistance [3, 4]. Mesoporous silica has been shown to be an effective host for well regularized carbon nanotubes[5], more so without sintering of catalytic metals [6].

In this study, we aim to grow CNTs within the pore system of mesoporous silica. This gives a very homogeneous distribution of reinforcing agent as well as a

very uniform material with isotropic properties. By growing the CNTs within the pore system, reinforcement pull out and nanotube size dependent strength problems are avoided. The principal aim is to provide ceramic materials with increased thermal conductivity and mechanical strength for envisaged use as thermally conductive substrates for microprocessor die mountings, coatings in the electronics industry and possibly packaging. Catalytic chemical vapor deposition is used for the growth of nanotube due to the following known superior advantages over other conventional methods: carbon nanotube control by adjustment of growth temperature, pressure, carrier gas type and flow rate [2,7], easy scale-up and directed placement, nanotube alignment and electronic component construction [8].

## 2 EXPERIMENTAL

### 2.1 Mesoporous Silica Samples

The tailored pore size mesoporous silica samples, incorporating different concentrations of transition metal-based catalysts of Fe, Co and Ni were produced by the Dimensional Solids Group at the University College Cork, which has made considerable progress in the area of mesoporous solid synthesis as described in [9-17]. Both the in-situ addition of transition metal-based phthalocyanine and the post-synthesis method of formation of metal oxide nanoparticles within the mesoporous silica pores by degrading the appropriate transition metal carbonyl in super critical CO<sub>2</sub>, were used for filling the pores with the metal catalysts. Any excess metal on the surface of the samples was successfully removed by stirring in concentrated nitric acid.

### 2.2 CNT Growth

Carbon nanotubes were grown by the catalytic chemical vapor deposition method using a home built CCVD system [18-20]. The pressure of the system was reduced to 10<sup>-2</sup> mbar and its furnace temperature raised to 800°C. Argon carrier gas was flushed at 0.500 sccm allowing the system to reach equilibrium for 15 minutes. A steady 0.050 sccm

flow of the acetylene carbon feedstock was then maintained for an hour over the transition metal-filled sample in a ceramic boat loaded into the CCVD system's furnace. The sample was removed from the furnace for characterization only after cooling to room temperature.

### 2.3 Characterization

Prior to CCVD growth of CNTs, the target ceramic samples were imaged using a scanning electron microscope (SEM) operated in the variable pressure mode at 10 Pa. Compositional and surface analysis were performed using a PGT Spirit Energy Dispersive X-ray (EDX) Analysis. The heat response of the catalyst loaded samples in air were obtained using a Perkin Elmer Pyris 1 TGA thermo gravimetric analyzer by initially maintaining the sample temperature at 30°C for one minute and subsequently heating up to 950°C at 10°C per minute with 5580 points between runs.

High resolution SEM imaging of the CNTs was carried out using a Hitachi S-4300 Field Emission Scanning Electron Microscope operating in high vacuum mode at 20 kV. It was necessary to coat the CNTs with a 10 - 15nm gold film due to the high SEM potential being used, so bringing charge build up to a minimum. A Jobin Yvon Raman System with a HeNe 20 mW laser polarized 500:1 at a wavelength of 632.817 nm was also employed to characterize the CNTs. Each spectrum was averaged over ten accumulations with intensity variations between 10% and 100% adjusting the exposure times for optimization of noise reduction.

## 3 RESULTS AND DISCUSSION

### 3.1 Thermo gravimetric Analysis

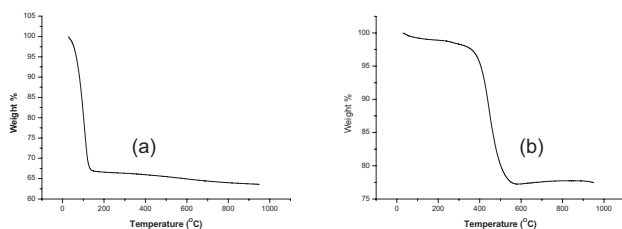


Figure 1: Sample heat responses of catalyst filling methods.

Figure 1. shows the heat responses of the metal filled mesoporous samples when heated in air to 950°C. Figure 1 (a) is from iron based phythalocyanine and shows a 35 % loss of weight at 100°C, largely attributed to water and the remainder very slow loss over higher temperatures is attributed to organic substances. All other phythalocyanine based samples were consistent with this pattern. Figure 1 (b) represents the heat response of dicobalt octacarbonyl in mesoporous silica of 3.3 nm pore diameter, with very large

losses at 500°C. All other supercritical fluid based samples showed the same pattern with major weight losses occurring between 450°C and 600°C. Since the CCVD was being initially done at 800°C, initial growth was preferred on the phythalocyanine samples which showed more stability at that temperature.

### 3.2 Compositional and surface analysis

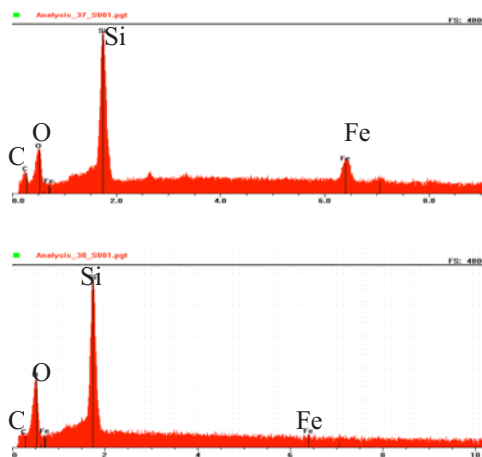


Figure 2: EDX compositional and surface analysis for FePc sample before and after stirring in concentrated nitric acid.

EDX confirmed the existence of respective metal catalysts in the mesoporous samples. EDX/SEM studies done on each sample before and after stirring in concentrated nitric acid confirmed successful removal of excess metal catalysts from the surface. As shown in figure 2, the metal peak was present before stirring and absent thereafter.

### 3.3 HR SEM

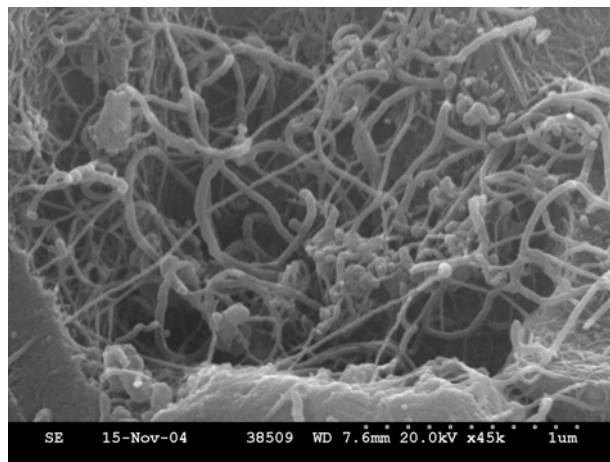


Figure 3: HI RES SEM image of CNTs prepared on uncleaned Fe filled mesoporous silica.

Each of the samples was observed to change color to opaque black after CCVD. This color is commonly associated with the presence of carbon and is expected when CNT growth has taken place.

Figure 3 shows the HI RES SEM images of the CNTs grown from uncleaned FePc samples of 0.5 g loading and 3.3 nm pore diameter. The growth was non-aligned, mostly in clusters and “spaghetti” like. The CNTs grown had different diameters ranging from 20 – 90 nm, so suggesting growth was not strictly from the pores as these diameters were not comparable to surfactant pore diameters. This pattern was typical of all uncleaned samples.

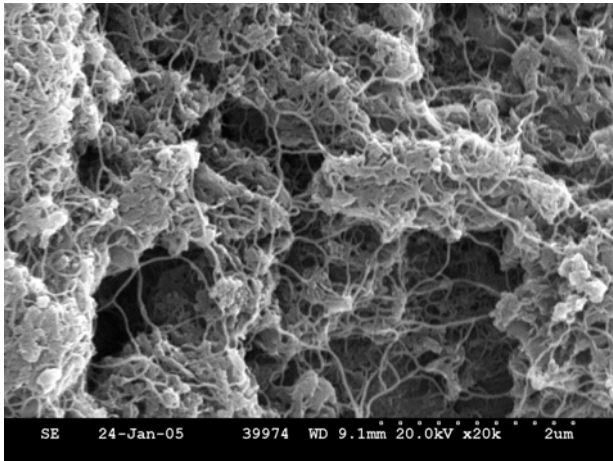


Figure 4: HI RES SEM image of CNTs prepared on cleaned Co filled mesoporous silica.

The HI RES SEM images from the mesoporous samples stirred in concentrated nitric acid have very close to uniform diameters for each sample, as shown in figure 4 for 0.1 g loaded CoPc in 5.0 nm pore diameter mesoporous silica. The diameter measurements from the HI RES SEM images are compared with the surfactant pore diameters in Table 1. The diameters of the CNTs closely compare with the surfactant pore, suggesting possible growth from the pores.

Table 1: CNT diameter measurements

METAL PRECURSOR	METAL WEIGHT (g)	PORE DIAMETER (nm)	CNT DIAMETER (nm)
FePc	0.5	5.0	9 ± 4
FePc	1.0	3.3	10 ± 3
CoPc	0.1	5.0	13 ± 5
CoPc	1.0	5.0	15 ± 7
CoPc	1.0	7.0	8 ± 3
NiPc	0.5	3.3	9 ± 3
NiPc	0.5	5.0	11 ± 3

Figure 5 shows some nanotubes growing out of or into the wall the sample and hence possibly growing from

within the pores. Thus growth from within the pores has been achieved but is at the stage of a non-uniform distribution.

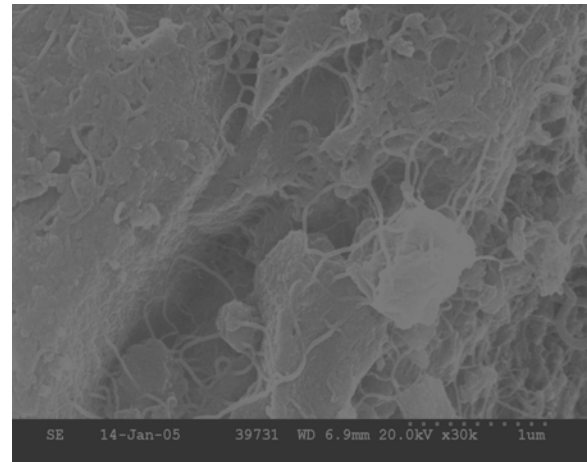


Figure 5: CNTs growing from the pores on FePc sample

The discrepancies in diameters between the CNTs and their corresponding mesoporous sample pore diameters is attributed to thermal expansion due to the high CCVD temperatures. The non - uniform thickness of the 10 – 15 nm gold coating, to prevent charging up of the samples during HI RES SEM, also makes a small contribution to the differences in diameter. HI RES TEM would give near accurate diameter estimations.

From the HI RES SEM images, Fe and Co were found to be better catalysts for CNT growth by CCVD compared to Ni at the same concentration loadings. This was consistent with previous studies [21]. The densities of the CNTs increased with increased catalyst concentration for the same catalyst and sample pore diameter.

### 3.4 Raman Spectroscopy

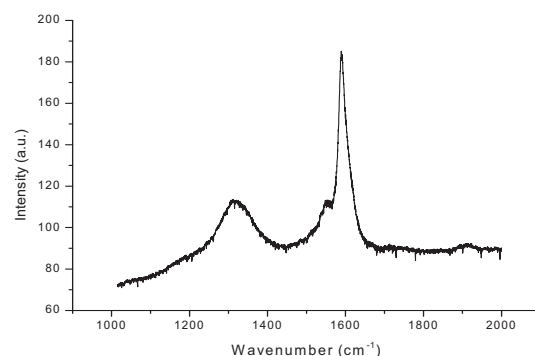


Figure 6: Raman Spectrum for FePc loaded mesoporous silica.

Raman spectral examination of all samples before the CCVD run showed no significant signal. After CCVD, all samples where CNTs had grown successfully showed the

two distinct peaks at  $(1320 \pm 20 \text{ cm}^{-1})$  and  $(1600 \pm 10 \text{ cm}^{-1})$ , corresponding to the D mode for disorder induced and the G mode for graphite respectively [22]. The narrow and high G band shows that good quality and highly graphitized CNTs were grown.

All spectra for which CNT growth had occurred were characteristic of the two bands. As shown in figure 6, some spectra indicated the shoulder close to the G band typical of single walled nanotubes, suggesting the possibility of their growth if conditions were to be suitably changed. The range of the D and G bands obtained in this experiment fits well with results from elsewhere where acetylene feedstock was used for CCVD growth of CNTs [23-25].

## 4 CONCLUSIONS

CNTs were successfully synthesized by CCVD on transition metal filled mesoporous silica. The growth was randomly oriented, spaghetti like and the diameters of the CNTs closely matched the pore size of the respective surfactants, suggesting possible growth from the pores. Raman Spectroscopy confirmed good quality, low defect highly graphitized CNTs.

Of the catalysts used, Fe and Co produced better quality and larger densities of CNTs than Ni.

## 5 ACKNOWLEDGEMENTS

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## REFERENCES

- [1] S. Iijima, "Helical microtubes of graphitic carbon," *Nature*, 354,56,1991
- [2] J. Robertson, "Realistic applications of CNTs", *Materials Today*, 46, October 2004
- [3] W. A. Curtin and B. W. Sheldon, "CNT – reinforced ceramics and metals", *Materials Today*, 44, November 2004
- [4] E. T. Thostenson et al. *Composites Science and Technology*, 61, 1899 – 1912, 2001
- [5] E. Munoz, D. Coutinho, R. F. Reidy, A. Zakhidov, W. Zhou and K. J. Balkus Jr, *Microporous and Mesoporous Materials*, 67, 61-65, 2004
- [6] Y. Mukarami, S. Yamakita, T. Okubo and S. Maruyana, *Chemical Physics Letters*, 375, 393-398, 2003
- [7] J. Li, W. Lei, X. Zhang, B. Wang and L. Ba, *Solid-State Electronics*, 48, 2147-2151, 2004
- [8] J. Zhu, M. Yudasaka and S. Iijima, *Chemical Physics Letters*, 380, 496-502, 2003
- [9] K. M. Ryan, N. R. B. Coleman, D. M. Lyons, J. D. Holmes, T. R. Spalding, M. A. Morris et al., *Langmuir*, 12, 4996, 200
- [10] K. M. Ryan, D. M. Lyons and M. A. Morris, *J Mat. Chem.*, 12, 1207, 2002
- [11] S. O'Brien, S. E. Lawrence, T. R. Spalding and M. A. Morris, *J. Appl. Cat.*, 97, 45, 1998
- [12] M. A. Morris, J. D. Holmes, T. R. Spalding, K. M. Ryan, E. Brennan and T. Russell, *Irish Scientist, Yearbook*, 2002
- [13] J. D. Holmes, T. R. Spalding, K. M. Ryan, D. Lyons, T. A. Crowley and M. A. Morris, 'The use of templated mesoporous materials as templates for the development of ordered arrangements of nanowires and nanorods of electrically important materials' in *Surface Science and Catalysis, Nanoporous Materials III*, A. Sayari and M. Jaroniec (Eds.), Elsevier, Amsterdam, 141, 337, 2002
- [14] N. R. Coleman, M. A. Morris, T. R. Spalding and J. D. Holmes, *J. Am. Chem. Soc.*, 123, 187, 2001
- [15] N. R. Coleman, J. D. Holmes, T. R. Spalding and M. A. Morris, *Chem. Phys. Letts.*, 343, 1, 2001
- [16] N. R. Coleman, N. O'Sullivan, K. M. Ryan, J. D. Holmes, T. R. Spalding and M. A. Morris, *J. Am. Chem. Soc.*, 123, 7010, 2001
- [17] J. D. Holmes and M. A. Morris, *Irish Scientist, Yearbook*, 2001
- [18] E. Munoz, A. B. Dalton AB, W. J. Blau et al, *Chem. Phys. Letts.*, 359, 397, 2002
- [19] R. Murphy, J. N. Coleman, M. Cadek, B. McCarthy, M. Bent, A. Drury, R. C. Barklie and W. J. Blau, *J. Phys. Chem. B*, 16, 187, 2002
- [20] B. Carthy, J. N. Coleman, R. Czerw, A. B. Dalton, H. J. Byrne, D. Tekleab, P. Iyer, P. M. Ajayan, W. J. Blau and D. L. Carroll, *Nanotechnology*, 12, 187, 2001
- [21] K. Hernadi, Z. Konya, A. Siska, J. Kiss, A. Oszko, J. B. Nagy and I. Kirisci, *Materials Chemistry and Physics*, 77, 536-541, 2002
- [22] Z. Zhang et al., *Materials Science and Engineering B*, 116, 363-368, 2005.
- [23] G. L. Hornyak, A. C. Dillon, P. A. Parilla, J. J. Schneider, N. Czap, K. M. Jones, F. S. Fasoon, A. Mason and M. J. Heben, *Nanostructured Materials*, 12, 83-88, 1999
- [24] Z. H. Yuan, H. Huang, L. Liu and S. S. Fan, *Chemical Physics Letters*, 345, 39-43, 2001
- [25] X. Y. Zhang, L. D. Zhang, M. J. Zheng, G. H. Li and L. X. Zhao, *Journal of Crystal Growth*, 223, 306-310, 2001