Supported Catalytic Growth of SWCNTs using the CVD Method

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Abstract. The growth of carbon nanotubes (CNTs) from supported metal catalysts using the CVD method with CH4 as the carbon feedstock was investigated using SEM and TEM. Studies include the influence of the substrate structure, the metal catalyst content and other experimental parameters on the nature of the CNTs produced using calcined aluminium nitrate and delta-alumina nanoparticles (~13nm). The iron catalyst precursors are ferric sulphate and also iron oxide nanoparticles. Using an aberration corrected STEM and a FEGTEM BF imaging has been used to identify symmetries of tubes produced, as well as a TEM-STM tip to measure I-V curves of SWCNTs. It appears the optimum iron precursor and catalyst support for production of SWCNTs is either ferric sulphate or iron oxide nanoparticles supported on delta-alumina nanoparticles.

1. Introduction

Since their discovery by Iijima [1] in 1991, nanotubes have generated a great deal of interest as a result of their unique structural, electronic and mechanical properties. The catalytic chemical vapour deposition (CVD) method has been employed to grow nanotubes as it is simpler than other methods and this process is easier to scale up to an industrial scale. When growing nanotubes by the CVD method, the size and type of the catalyst and support used as well as the synthesis temperature, are the most critical variables with the most effective catalysts being transition metals, their oxides and their mixtures. The nanotubes produced are strongly dependent on the substrate used to disperse and support the catalyst particles. Therefore, the interactions of the substrate with the catalyst also need to be understood. In order to increase the yield of carbon nanotubes (CNTs) produced, the surface area of the substrate needs to be as high as possible and as a result nanoporous aerogels are increasingly being investigated as aerogels are known to have high surface areas, high porosity and very low densities [2].

Presented in this paper are investigations of the structure of the substrate, the metal catalyst content and other experimental parameters on the formation of CNTs. The effects of the surface morphology and crystal structure are being investigated by using various alumina-based supports such as calcined aluminium nitrate and delta-alumina nanoparticles (~13nm in diameter).
2. Experimental Method

2.1. Catalyst Preparation and CNT Growth

The starting materials for alumina/Fe catalysts were $\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$. 0.1M aluminium nitrate was dissolved in 70ml of a ferric sulphate solution saturated in ethanol. This solution was then either dried normally or supercritically dried at 7.5MPa and 260°C for 30 minutes to produce a sample A1 or an aerogel respectively. Using the A1 method, the wt% of Fe was investigated from 5wt% Fe to 40wt% Fe at a synthesis temperature of 880°C, and for 17wt% Fe, the synthesis temperatures were studied from 820°C to 940°C. For the aerogel, the synthesis temperatures ranged from 880°C to 970°C. A nanoparticle substrate was also investigated by supporting ferric sulphate on delta-alumina nanoparticles with an approximately 20wt% Fe concentration (sample B1).

The Fe precursor was changed to iron oxide (nominally magnetite) nanoparticles and supported on calcined aluminium nitrate and delta-alumina nanoparticles. The CNT synthesis temperature used was 880°C.

The catalyst was heated under nitrogen to synthesis temperatures and held at the final temperature for 30 minutes under a methane atmosphere and the CNTs were produced by direct pyrolysis of methane.

2.3. Characterisation

The morphology and microstructure of the catalysts and CNTs were characterised using LEO 1530 FEGSEM, Philips CM200 FEGTEM operated at 200kV and fitted with a Gatan GIF 200 Imaging filter, and a TEM-STM holder from Nanofactory. Gas adsorption studies were carried out using a Quantachrome Autosorb 1 with N$_2$ as the adsorbate.

3. Results and Discussion

3.1. Supports

From TEM investigations, A1 was found to produce better quality and higher yield multi-walled carbon nanotubes (MWCNTs) and bundles of single wall carbon nanotubes (SWCNTs), at lower temperatures, than the aerogel catalyst. For A1, the lowest synthesis temperature at which SWCNTs were observed was 860°C in small quantities as determined by transmission electron microscopy (TEM), and as the synthesis temperature was increased to 880°C, the CNT yield increased dramatically while for further increases in synthesis temperature little significant increase/decrease in yield is observed. For the aerogel, the yield and quality of the CNTs was observed to increase with temperature. For A1, TEM results show the presence of bundles of SWCNTs for all the Fe contents except 5wt% Fe; no CNTs have been observed in this sample. As can be seen from the TEM image in Figure 1, bundles of SWCNTs were produced using a wide range of Fe concentrations. It was expected that at very high concentrations, MWCNTs will be produced due to the agglomeration of Fe to produce larger particles that would result in the formation of more MWCNTs rather than SWCNTs. However, there are still a large amount of SWCNTs present at the higher concentrations as well large carbon onion structures. Figure 2a shows the diameter distribution of SWCNTs produced (determined by TEM) did not vary as the Fe nanoparticle diameter (not shown) increased as might be expected. Figure 2b shows the SWCNT as synthesis temperature is altered. The SWCNT size distribution remains the same although the Fe size slightly increases (not shown).

Gas adsorption shows the presence of pores before methane is introduced with diameters of mostly ~35nm and after carbon has been removed (by combustion) larger pores are also observed between 50-60nm for 17wt% Fe and larger for higher Fe concentrations. For substrates containing larger pores, slightly larger catalyst particles are observed. The aerogel contained a large number of pores between 3-18nm in diameter and a significant amount between 30nm and 200nm.

For B1, larger quantities of CNTs were formed as determined from SEM, consisting of bundles of MWCNTs containing mostly 2 walls as well as some SWCNTs, for which size distributions are given in Figure 3. The pores size distribution before methane is introduced and after carbon is removed, is
relatively unchanged as would be expected from nanoparticles, with the ‘pores’ actually being the spaces between the nanoparticles. Preliminary XRD studies show the presence of a γ-alumina support being present for A1 and B1. Iron oxide nanoparticles nominally magnetite (Fe₃O₄) supported on delta-alumina produced large quantities of SWCNTs also. However, no CNTs were observed when the nanoparticles were supported on calcined aluminium nitrate.

Figure 1. TEM images of SWCNTs produced for a) 17wt% Fe and b) 35wt% Fe.

Figure 2. Graphs showing the size distributions of SWCNTs for a) changing wt% Fe and b) the changing synthesis temperature.

Figure 3. Graph showing the size distributions of SWCNTs and Fe catalyst particles with 20wt% Fe supported on delta-alumina nanoparticles.

Figure 4. SuperSTEM bright field image showing (100) fringes which reveal the chirality of a double-walled tube.
Using BF imaging in an aberration corrected STEM (Figure 4) has allowed the imaging of the chirality of CNTs and this technique is being used to identify the symmetries of tubes produced. The DWCNT in Figure 4 was identified as a metallic tube.

3.2. Nanotube Morphology

Good quality MWCNTs and bundles of SWCNTs are produced from A1 series from 880ºC to 940ºC. However, for the aerogel no CNTs were observed at 880ºC, although graphitic layer formation was observed. CNTs were first observed at 940ºC with the yield increasing with temperature. Since the only difference between samples is the catalyst, it is clear that the catalyst preparation conditions affect the Fe-catalyst significantly.

B1 (with non-porous surfaces) produced more MWCNTs (mostly double wall) for the same Fe concentration as in A1. The SWCNTs produced were mostly between 1-2nm in diameter with the Fe particles having a much larger distribution.

3.3. Nanotube Properties

It has been possible to investigate the electronic properties of CNT bundles in a purified sample of A1, using an STM-Tip mounted on a TEM holder and manipulated inside a FEGTEM.

![TEM image of STM-tip (on left) in contact with a bundle of tubes (~10nm bundle diameter), and b) the I-V curve obtained from bundle in a).](image)

Figure 5. a) TEM image of STM-tip (on left) in contact with a bundle of tubes (~10nm bundle diameter), and b) the I-V curve obtained from bundle in a).

Figure 5b shows an I-V curve for a bundle of CNTs in Figure 5a. The I-V relationship is approximately linear indicating metallic behaviour with a resistivity of approximately 100µΩm. Although not presented here, I-V curves showing semi-conducting behaviour were also obtained.

4. Conclusions and Future Work

SWCNTs have been produced using Fe catalyst supported on alumina. The substrate surface morphology has had a large affect on the production of CNTs. Calcined aluminium nitrate has produced few tubes but mostly SWCNTs whereas the nanoparticle support produced a higher yield, mostly MWCNTs. The iron oxide nanoparticles were found to produce large quantities of CNTs also. However, no CNTs were observed when the nanoparticles were supported on aluminium nitrate. The I-V curves of SWCNTs measured using a TEM-STM holder indicated the presence of both metallic and semi-conducting tubes.

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References

[1] Iijima S, Nature, 354, pp56, 1991
[2] Husing N, Schubert U, Angew. Chem. Int. Ed. 37, pp22, 1998