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Growth of Carbon Nanotubes from Supported Metal Catalysts

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The growth of carbon nanotubes (CNTs) from supported metal catalysts is under investigation using the chemical vapour deposition (CVD) method with CH_4 as the carbon feedstock. Studies include the influence of the structure of the substrate, the metal catalyst content and other experimental parameters on the nature of the CNTs produced. The effects of the surface morphology are being investigated using various alumina-based supports such as calcined aluminium nitrate, delta-alumina nanoparticles (~13nm) and calcined gibbsite ($Al(OH)_3$). The gibbsite was calcined under a nitrogen atmosphere for 1hr at 450°C, 600°C, 700°C, 800°C and 990°C. The iron catalyst precursors are ferric sulphate and iron oxide (nominally magnetite) nanoparticles. The starting materials were mixed in appropriate amounts in ethanol and dried normally. In one case, the aluminium nitrate and ferric sulphate were supercritically dried at 7.5MPa and 260°C, for 30 minutes to produce an aerogel.

The CNTs were prepared by direct pyrolysis of flowing methane over the catalyst, for 30 minutes at temperatures ranging from 820°C to 970°C in 20°C increments. The catalyst was heated from room temperature to 800°C over 1hr, and then heated to the required final temperature in 30mins, under a N_2 atmosphere and held at the final temperature for 30 minutes under a methane atmosphere to grow the CNTs.

From TEM investigations, aluminium nitrate and ferric sulphate (catalyst A1) was found to produce better quality and higher yield multi-walled carbon nanotubes and bundles of SWCNTs, at lower temperatures, than the aerogel catalyst. For A1, very little difference was observed between the samples prepared at different synthesis temperatures, whereas for the aerogel, the yield and quality of the CNTs was observed to increase with temperature. Preliminary 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 Fig 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, from TEM observations, there are still a large amount of SWCNTs present at the higher concentrations. Also, the diameter distribution of the SWCNTs produced did not vary as the Fe nanoparticle diameter increased as was expected. Using BF imaging in an aberration corrected STEM (SuperSTEM - see Fig 2) has allowed the imaging of the chirality of CNTs and this technique is being used to understand the link between chirality and catalyst crystal structure.

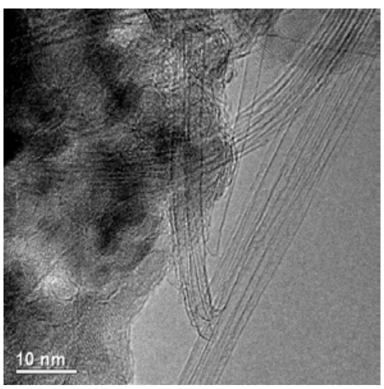
When using the delta-alumina nanoparticles as a substrate and ferric sulphate as catalyst precursor, larger amount of CNTs were formed consisting of bundles of MWCNTs containing mostly 2 walls as well as SWCNTs. Surface area analysis and further TEM analysis of the support medium and the catalyst is underway. Iron oxide nanoparticles supported on delta-alumina produced large quantities of SWCNTs also. However, no CNTs were observed when the nanoparticles were supported on aluminium nitrate.

Further surface effects were investigated using calcined gibbsite. The surface area of the substrate was highest for calcination at 450°C (G450) and decreased to the lowest value for G990. However, SWCNTs were only detected for G600, G700 and G800 and not at G450. As the gibbsite is calcined, the crystal structure is also evolving and it appears the substrate crystal structure has a greater influence on the products formed than just the substrate surface area.

At the present time, we believe the optimum iron precursor and catalyst support for the CVD production of SWCNTs is either ferric sulphate or iron oxide nanoparticles supported on delta-alumina nanoparticles.

References

1. Aslam Z et al, Inst. Phys. Conf. Ser. No 179: Section 11, 471-474, 2003
2. This research was supported by an EPSRC sponsorship.

a) 

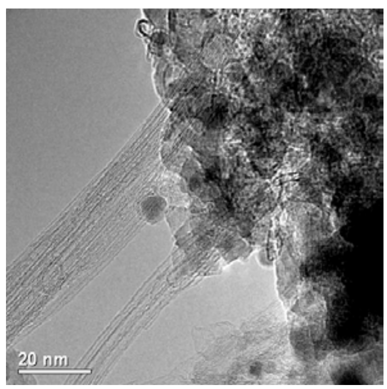
b) 

Fig 1. TEM images showing CNTs produced for sample containing a) 20wt% Fe and b) 30wt%Fe.

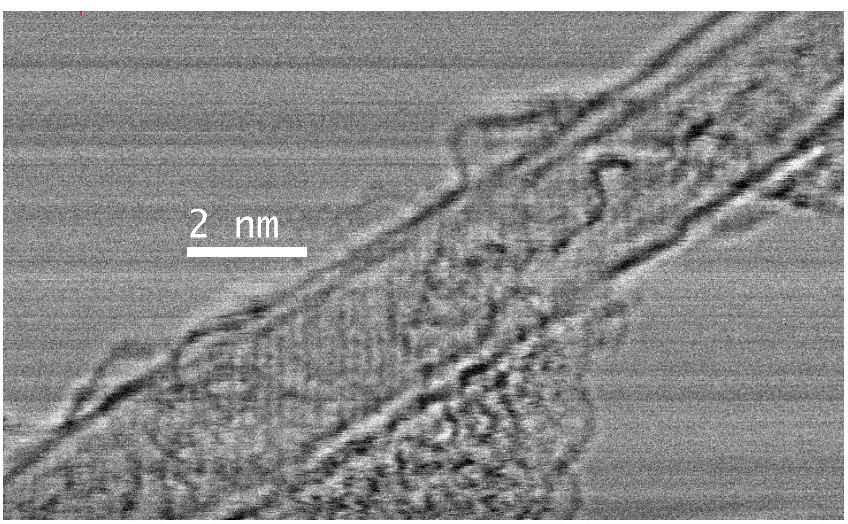


Fig 2. SuperSTEM image showing (100) fringes which reveal the chirality of a double-walled tube.

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