# Engineered Control of the Diameter of Single Walled Carbon Nanotubes

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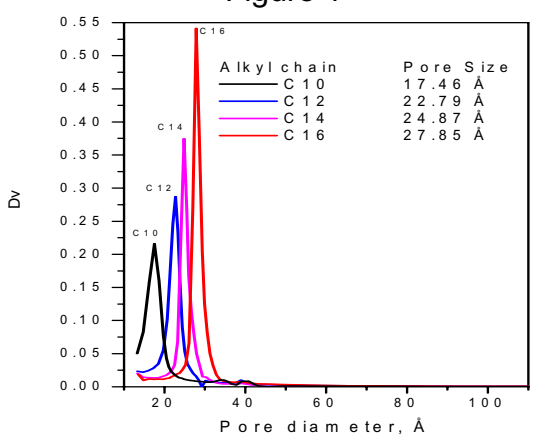
Properties of single walled carbon nanotubes (SWNT) depend on the tube diameter providing an incentive to find a method that selectively produces a preselected size. Metal substituted MCM-41 provides good selectivity and flexibility to vary the SWNT average diameter with a distribution of about ±0.06 nm by catalyst design. We have synthesized SWNT with average diameters in the range of 0.5 – 0.9 nm with this narrow distribution. The average diameter of the SWNT produced linearly correlates with the pore size of the Co-MCM-41 catalyst used and is controlled by the size of the metal cluster formed during synthesis. Metal cluster size is controlled by the pore size (radius of curvature), pretreatment conditions and the loading of the metal incorporated into the wall of the MCM-41 mesoporous molecular sieve. The process is robust and controllable and the catalyst is stable under reaction conditions.

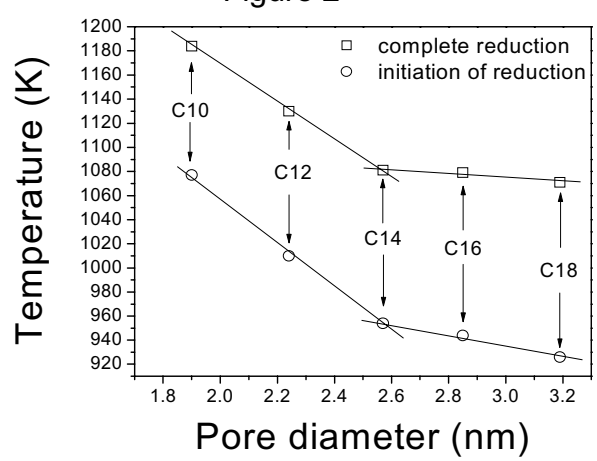
We have shown that well-ordered mesoporous molecular sieves substituted with transition metals can be used as templates for the in-situ catalytic synthesis of SWNT [1]. The pore diameter of the MCM-41 template is highly controllable and uniform (see [2] and figure 1 below) and affects the reducibility of the catalytic component in the framework (figure 2). The data in these figures is for Co-MCM-41 catalysts of different pore sizes with 1% by weight of cobalt substituted into the pore framework.

Figure 1




Pore size distribution of Co-MCM-41 catalysts synthesized with different alkyl chain lengths

Figure 2




Temperature programmed reduction of Co in catalysts with different pore diameters

The catalysts are pretreated in hydrogen at 775K for 30 minutes prior to nanotubes synthesis by CO disproportionation. X-ray absorption measurements show that after the pretreatment the metal is still largely unreduced and dispersed in the MCM-41 framework.

In-situ X-ray absorption measurements taken during pretreatment and reaction with CO show that further reduction of the metal catalyst takes place during exposure to CO. X-ray absorption fine structure (EXAFs) analysis suggest that the mechanism responsible for SWNT diameter control is the effect of the radius of curvature of the MCM-41 pore wall on the size of sub-nm metal clusters formed. From the Co-Co coordination number determined in the EXAFs analysis, the clusters formed during reaction vary from 10 to 30 metal atoms. The size of the clusters is controlled both by the pore diameter and reduction conditions. This effect is controllable and allows a narrow cut of a pre-selected tube size to be produced because the controlled size metal clusters likely serve as SWNT nucleation sites, as depicted in Figures 3 and Figure 4 below. By understanding how the radius of curvature affects the formation and stability of the sub-nanometer metal clusters we can provide a basis for SWNT diameter control. We have produced carbon nanotubes with extremely narrow diameter distribution. A theoretical basis for predicting diameter and its distribution combined with low-level boron doping will likely provide a means to *preselect* electronic properties. It is important to note that this is not a physical templating mechanism but rather depends on controlling the properties of metal clusters formed in the MCM-41 pores. Formation and stabilization of sub-nm metallic clusters has broad reaching applications beyond our work with carbon nanotubes for both catalysis and electronic device design.

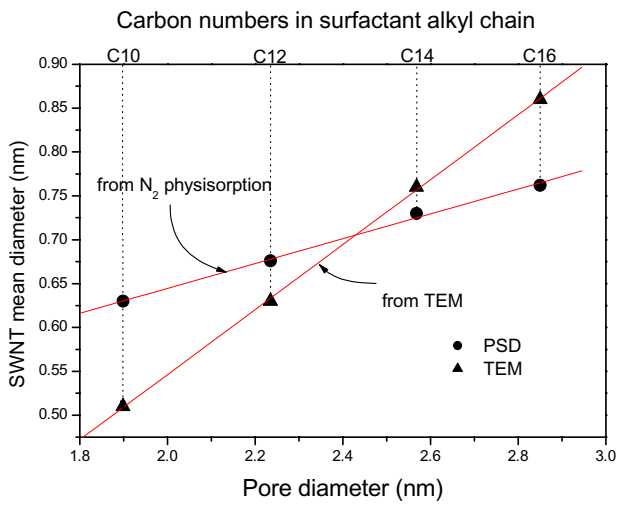



Figure #3. SWNT diameter produced with catalysts having different pore sizes.

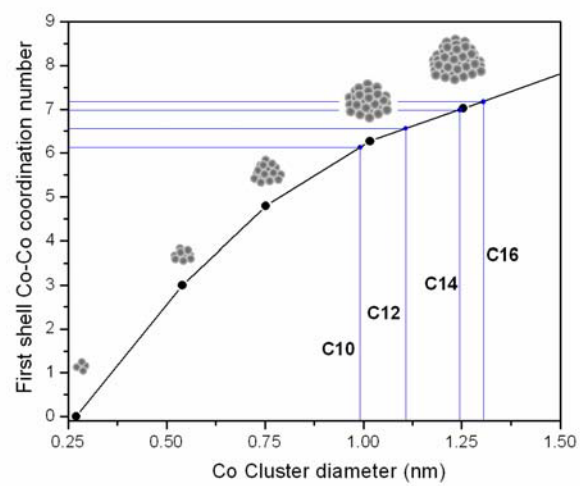



Figure #4 Metal cluster size from EXAFS

Note on Figure# 3 above that one of the tube size measurements was done by physisorption of nitrogen in the tubes showing they are open ended. This is not likely an artifact as the volume of $N_2$ accounted for is near that of the tube volume calculated using the known amount of carbon and the tube diameter from averaging on the order of 60 TEM measurements from different parts of the sample. The carbon nanotube growth

mechanism most quoted in the literature consists of the precipitation of the carbon dissolved in a metallic particle. Growth from metallic clusters consisting of 10 to 30 atoms, as is the case with our single walled nanotubes (SWNT) of carbon grown on Co-MCM-41 catalysts, does not likely follow this mechanism simply because the solubility of carbon in such small metallic clusters is likely very low as observed in earlier work on reforming catalysts. There is a minimum cluster size needed to initiate nanotube growth likely related to the ability of the cluster to dissociate CO.

This talk will compare our synthesis with other methods and present data from in-situ X-ray absorption measurements on the state of the catalyst during pretreatment and reaction with CO to form carbon nanotubes. Mechanism data on how the catalyst is transformed under reaction conditions is key to the ability to preselect and control the SWNT diameter.

Acknowledgements:

DARPA-DSO Grant No. MDA972-02-1-0010

References

[1] D. Ciuparu, Y. Chen, S. Lim, G.L. Haller and L. Pfefferle, "Uniform-Diameter Single-Walled Carbon Nanotubes Catalytically Grown in Cobalt-Incorporated MCM-41", *J Phys Chem B*, **108**(2) (2004) 503.

[2]. S. Lim, D. Ciuparu, C. Pak, F. Dobek, Y. Chen, D. Harding, L. Pfefferle and G. Haller, "Synthesis and characterization of highly ordered Co-MCM-41 for production of aligned single walled carbon nanotubes (SWNT)", *J Phys Chem B*, **107**(40) (2003) 11048.