

Diameter Tuning of Single-walled Carbon Nanotube Using Co-MCM-41

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Introduction

The unique electronic and mechanical properties of SWNT make them attractive for a large number of applications. Electronic properties of SWNT depend on their diameter and chirality.[1] For the typical diameters at which SWNT are grown, there are about 100 different chiralities.[2] Progress on applications has been hindered by quality issues in commercial SWNT and lack of a commercially viable separation process.

Metal incorporated MCM-41 has proven to be a valuable framework for the growth of narrowly distributed single-walled carbon nanotube (SWNT) producing samples with a wide range of different mean diameters. The ability to obtain narrow diameter distributions at different mean diameters is important for applications that require particular (n,m) nanotubes. Separation processes work best when a large fraction of the desired component is present.

In this work we describe the use of C10 Co-MCM-41 under different reaction temperatures to “tune” the mean diameter of the distribution. C10 is different from other templates we use because the pore size is smaller and the silica may be more mobile as evidenced by slightly lower stability.

Materials and Methods

For the results reported here we used a C10 MCM-41 framework substituted with 3 wt% Co having a mean pore diameter of 1.8 nm by the BJH method. The catalysts used in this study were synthesized at a pH of 10.5 by the method described in reference 3. SWNT was produced by catalytic disproportionation of CO flowing over a bed of the Co-MCM-41 catalyst maintained at constant reaction temperature. Before CO disproportionation, pretreatment involving nearly complete reduction was found in earlier studies to be important for both high yield and good selectivity.[3] SWNT in the product was analyzed by a variety of techniques including thermal gravimetric analysis (TGA), Raman spectroscopy, fluorescence spectroscopy (FLS), near-infrared (NIR) spectroscopy, and transmission electron microscopy (TEM). The study of Co particle size was conducted using X-ray absorption spectroscopy (XAS).

Results and Discussion

The diameter of SWNT produced from carbon monoxide disproportionation over C10 Co-MCM-41 can be simply engineered by changing the reaction temperature. The diameter shifts systematically over a broad diameter range (from 0.6-0.8 nm to 1.8-2.0 nm) as the reaction temperature increases from 550 °C to 950 °C verified by TEM (Fig 1 (b)), Raman (Fig 1 (a)), FLS and NIR. The average size of the Co nanoparticles fitted from Extended X-Ray Absorption Fine Structure (EXAFS) results and observed from TEM images agrees with each other, and also the particle size and the corresponding carbon nanotube diameter matches well. Although only Raman at 785 nm is shown here, NIR and FLS agree with these results. The

control of SWNT diameter is achieved via the control of Co particle size in this two stage reaction. After almost complete reduction under hydrogen, the Co particle size is finally determined by the CO reaction stage. Silica is believed to occlude the Co in the pre-reduction step. Carbon monoxide facilitates the migration of small Co clusters and brings them to the surface of MCM-41 pore wall. The competition between the Co migration and carbon deposition determines the size of the Co nanoparticle, thus determines the diameter of SWNT. The lower temperature reaction provides a robust means to obtain very small diameter (0.64 nm and smaller) SWNT which is the strongest 1-D material and exhibit unusual, unpredicted electronic properties.

Significance

SWNT produced by this method has a narrow diameter distribution and is produced at high yield [3]. It also has extremely high surface area [3] and the Co particle and MCM-41 framework can be easily removed, which suggests many promising applications in various fields such as bio-medical engineering, environmental engineering, and new catalytic support.

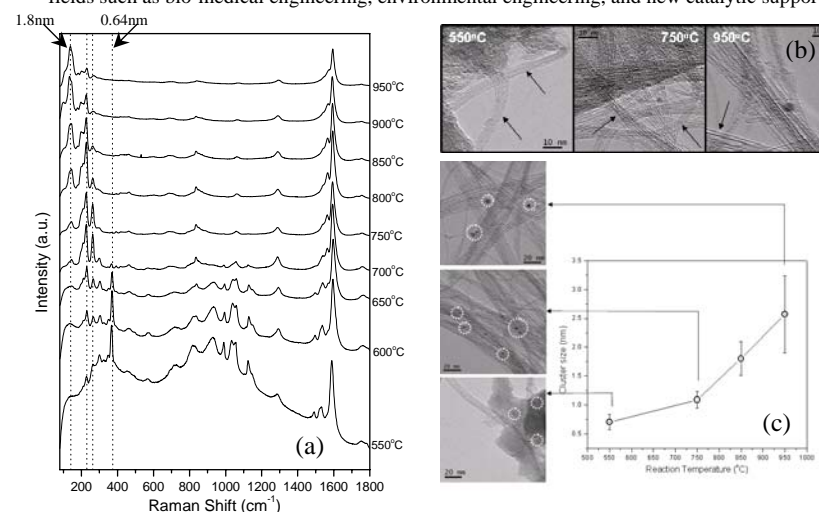


Figure 1. (a) Raman spectra at excitation 785 nm; (b) TEM images; (c) Cobalt cluster size determined by EXAFS fitting and TEM images indicating cluster size, for the as-synthesized SWNT samples pre-reduced at 750 °C and reacted at temperatures from 550 °C to 950 °C.

References

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