

SELECTIVE SYNTHESIS OF SUB-NANOMETER DIAMETER SEMICONDUCTING SWNTS

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Introduction

SWNTs are one-dimensional systems with exceptional chemical and electronic properties, and a vast number of emerging applications [1-3]. To date, much research effort has been dedicated to produce SWNT material with a narrow diameter distribution and specific (n, m) indices. Synthesis of nanotubes with specific (n, m) index is important for the advancement of SWNTs in electronic applications. The general mechanism by which SWNT are produced consists of exposing catalytic transition metal particles (especially Fe, Co and Ni) to a carbon feedstock (CO, ethane, acetylene etc.) at high temperatures (between 500 and 1000 °C) and varying pressures. When the catalyst particles become saturated with carbon, the growth of SWNTs is initiated by the formation of a stable carbon cap at the surface of the particle followed by addition of carbon atoms at the growing end of the cap to form a nanotube. The diameter and symmetry of the carbon cap should closely match that of the metal particle [4,5]. Previously, Ding *et al.* [6] showed that the interaction between the end atoms of a growing SWNT and the catalyst metal atoms has high bond energy, and the enthalpy of SWNT formation is substantially reduced when the number of carbon-metal bonds is maximized. A key factor in diameter selective synthesis of SWNTs is therefore the size of the catalyst particles [5,6]. We have previously shown that diameter selective growth of SWNT can be achieved using MCM-41 mesoporous silica templates isomorphously substituted with Co [7, 8].

Here, we demonstrate an improved synthesis method in which a second transitional metal (Mn) is added to the aforementioned Co-MCM-41 monometallic system. The second metal component does not form metallic particles during synthesis due to its high stability against reduction. Instead Mn ions highly dispersed in the silica substrate; act as anchoring sites for small Co particles preventing them from sintering into large inert particles [9]. Similar results were obtained with a CoCr-MCM-41 bimetallic system [10, 11]. A combined photoluminescence (PL) and Raman study showed

that the CoMn-MCM-41 catalyst with a molar ratio of 1:3 favors the growth of semiconducting, sub-nanometer diameter SWNTs (sub-nm SWNTs). Importantly, with decreasing synthesis temperature, a gradual increase in the proportion of semiconducting sub-nm SWNTs formed is observed. In addition, strong intermediate frequency modes (IFMs) are observed in the Raman spectra excited with $\lambda_{\text{excitation}}$ at 785, 855 and 1064 nm.

Results and Discussion

A CoMn-MCM-41 catalyst with 3% metal loading (Co:Mn in a molar ratio of 1:3) was synthesized by isomorphous substitution of metal in the silica framework. A 16 carbon atom alkyl chain length was used to template the MCM-41 yielding an average pore diameter of about 3 nm as determined by nitrogen physisorption measurements. Briefly, sub-nm SWNTs were prepared using the CoMn-MCM-41 catalyst (~200 mg) from a thermal disproportionation of CO (1000 sccm) at 600, 700 and 800 °C in a quartz tube (dia. ~ 18 mm) reactor. The CoMn-MCM-41 catalyst was reduced (flowing hydrogen at 1000 sccm, 700°C, 1 atm.) prior to CO disproportionation. The products were extensively characterized using transmission electron microscopy (TEM), Extended X-Ray Absorption Fine Structure (EXAFS), Photoluminescence (PL), and Raman spectroscopy.

PL has been used extensively for identifying (n, m) indices of semiconducting SWNTs and their relative abundance. The excitonic contributions to the SWNT electronic properties make precise (n, m) indexing difficult, however estimates are possible. (n, m) indices of the most abundant sub-nm SWNT are identified in the PL spectra, and their relative abundance was determined from direct measurements of the peak intensities (15 % accuracy). Consistent with the Raman analysis discussed below, the dominant semiconducting sub-nm SWNT is the (6,5) with a relative abundance of ~40% in all samples with a maximum of ~45% at 700 °C. It should be mentioned that the smallest sub-SWNT accessible in our PL experiments is the (7,3) with a diameter of 0.706 nm, although SWNTs of smaller diameter were identified in our samples by TEM and Raman spectroscopy as shown next.

Resonant Raman spectra were collected at 7 different laser excitation wavelengths for each sample: 488, 514, 532, 647, 785, 855 and 1064 nm. Apart from the radial breathing modes (RBMs), the disorder band (D-band) and the tangential stretching modes (G-band), a rich set of intermediate frequency modes (IFMs) are observed in the samples reacted at the lower temperature which contain mainly sub-nm semiconducting SWNTs. These strong IFMs were also observed in SWNTs grown on a Co-Cr catalyst at 600 °C [11]

where small diameter semiconducting SWNTs were also observed. Following Kataura *et al.* [12] several authors have approximated the tight binding calculations to obtain a simple relationship between the electronic transition energy (E_{ii}) and d_t . According to the empirical Kataura plot proposed by Weismann *et al.* [13], the set of wavelengths (488-1064 nm) used for characterizing our samples can excite both semiconducting tubes with diameters between 0.5 -1.75 nm and metallic tubes with diameters between 0.6-2 nm. We assigned the (n , m) indices using RBMs observed in the resonance Raman spectra of sub-nm SWNTs. Such indexing is possible in case of sub-nm SWNTs ($\omega_{\text{RBM}} > 240 \text{ cm}^{-1}$) as the number of chiralities that can be resonant in the excitation window of $488 < \lambda_{\text{excitation}} < 1064 \text{ nm}$ is limited [12]. Using Raman and PL spectra in tandem, the (n , m) indices were identified as follows: (i) d_t is estimated from the observed ω_{RBM} using Eqn. 1, and the chiral angles were computed from the E_{ii} values obtained through the best fit equation to the empirical Kataura plot described in Ref. 12. (ii) A chiral vector, obtained from a given d_t and its chiral angle of the previous step, was then used along with PL spectra to uniquely identify the (n , m) index.

$$\omega_{\text{RBM}} = \frac{223.5 \text{ cm}^{-1} \text{ nm}}{d_t} + 12.5 \text{ cm}^{-1} \dots \dots \dots (1)$$

Conclusion

A simple and scalable approach for the direct production of diameter selective semiconducting sub-nm SWNT was demonstrated using a CoMn-MCM-41 bimetallic catalyst. Raman and PL spectra were used in tandem for identifying (n , m) indices of these sub-nm SWNT. In addition the effect of synthesis temperature on diameter and (n , m) index of sub-SWNTs was also explained. New features observed in the Raman spectra of sub-nm SWNT (IFM and S-shaped dispersion of G-band) were presented.

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