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Towards the Growth of Monochiral Single-walled Carbon Nanotubes on MgO supported FeCu Bimetallic Catalysts

Maoshuai He[1], Alexander I. Chernov[2], Elena Obraztsova[2], Hua Jiang[3], Juha Lehtonen[1], Esko I. Kauppinen[3*]

[1]Department of Biotechnology and Chemical Technology, Aalto University School of Chemical Technology,
[2]A.M. Prokhorov General Physics Institute RAS, 38 Vavilov Street, 119991 Moscow, Russia
[3]Department of Applied Physics and Center for New Materials, Aalto University School of Science.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have demonstrated promise of wide applications in catalysis, paper batteries and nanoelectronics because of their unique structures and extraordinary electronic properties. Up to now, their structural diversity is still a major hurdle for achieving optimal performances in many of their potential fields. To realize most potential applications of SWNTs, one prerequisite is the ability to produce a large quantity of SWNTs with only a few chirality indices or preferential semiconducting/metallic species. In addition, gaining insights in the SWNT growth mechanisms is of utmost importance for guiding design of new catalyst systems. A number of monometallic catalyst systems, such as Co-SiO_2 [1], Ni-SiO_2 [2] and calcined stainless steel [3] have been developed in our group for selective growth of SWNTs. However, owing to their elemental compositions related equilibrium morphologies of the nanocrystals [1,2] or the relative high growth temperature [3] required to reduce the catalyst, the produced SWNTs do not show very narrow chirality distributions. In this contribution, we present our recent advances in chirality controlled growth of SWNTs on a FeCu-MgO catalyst and further, to understand the growth mechanism by means of an *in-situ* environmental electron transmission electron microscopy (ETEM).

2. Experimental section

The The FeCu-MgO catalyst was prepared by consecutive deposition of Cu and Fe onto the MgO support. Carbon nanotube growth was carried out in a cold-wall CVD micro-reactor (Linkam CCR1000). The catalyst was put into a resistive heating crucible and heated at a flow rate of 50 standard cubic centimeters per minute (sccm) argon. Once the desired temperature was reached, the argon flow was replaced by 50 sccm CO, and the growth process lasted for 15 min. After the growth process, CO was changed to argon and the system was cooled down under the protection of argon.

The *In situ* ETEM experiments were performed on an aberration corrected FEI Titan 80-300FEG ETEM operated at 300 kV. The FeCu-MgO catalyst powder was dispersed on a bare Au grid, which was then loaded in a specimen holder and later inserted into the TEM chamber for *in situ* experiments. CO at a flow rate of 2 sccm was introduced into the microscope chamber and kept at a pressure of 290 Pa.

3. Results and discussions

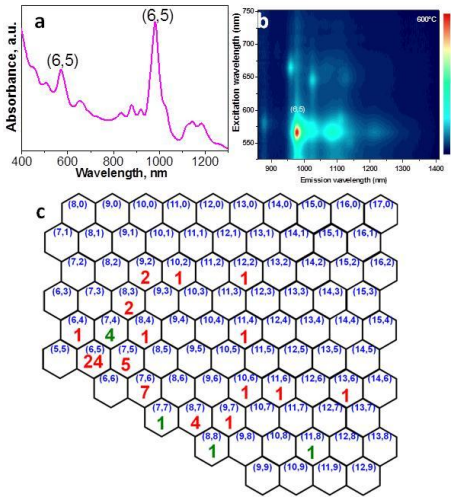

Figure 1. (a) UV-vis-NIR absorption spectrum and (b) Photoluminescence map of SWNTs grown at 600 °C. (c) Chirality map of SWNTs grown on FeCu/MgO catalyst. The (n,m) populations were labeled with numbers in the hexagonal cell. Red numbers and green numbers correspond to semiconducting and metallic SWNTs, respectively.

Figure 1a and 1b show the UV-vis-NIR absorption and photoluminescence (PL) spectroscopy characterization results on the SWNTs grown on the FeCu bimetallic catalyst at 600 °C. Clearly, the SWNTs has a very high chirality selectivity to (6,5) tube [4]. The PL signal ratio of (6,5)/(n,m) has been used to evaluate the relative quantities of (6,5) tubes. The signal intensity ratio of (6,5)/(7,5), (6,5)/(8,4) and (6,5)/(7,6) is 5, 7 and 13, respectively. All the values are higher than that shown in CoMoCAT tube dispersion. In order to evaluate quantitatively the helicity distribution of the SWNTs, we used electron diffraction to characterize the chiralities of well dispersed SWNTs. Figure 1c presents the chirality distributions of the FeCu grown SWNTs. Helicity statistics clearly show that the (6,5) tube is the major species detected in the sample (40%). More important, the ED recording results show a semiconducting content of 88%. Different from other selective semiconducting SWNT growth, such as plasma or ultraviolet CVD, which preferentially destroy metallic SWNTs, this methodology produces SWNTs without degrading their properties.

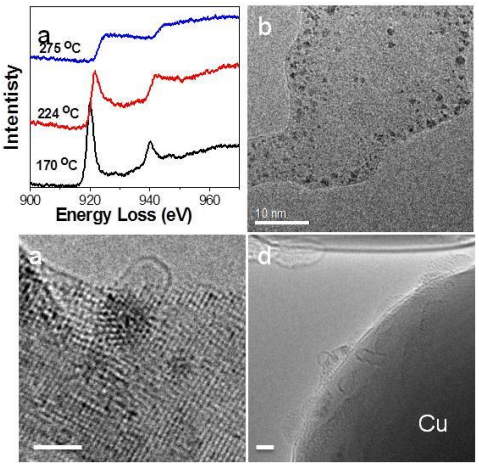

Figure 2. (a) Evolution of the electron energy-loss spectra of Cu phase during reduction in CO atmosphere (290 Pa) at different temperatures. (b) A TEM image showing the formation of small particles on MgO at 600 °C. (c) An *in situ* TEM image showing the formation of a SWNT on an MgO supported Fe particle. (b) An In situ TEM image showing the growth of SWNTs on metallic Cu supported Fe particles.

ETEM and EELS were used to monitor the nucleation of the catalytic Fe particles, the evolution of the CuO phase as well as the growth of SWNTs [5]. The characteristic $L_{2,3}$ edges of CuO (Fig. 2a) in the EEL spectrum shows that no reduction occurred at temperatures below 180 °C, while partial reduction of Cu^{2+} ions to Cu^{+} or Cu^{0} took place in the temperature range from 180 to 275 °C. Finally, complete reduction of CuO to metallic Cu was observed at temperatures above 275 °C. When the temperature exceeded 600 °C, the formation of small particles (< 3 nm) on the support surface were observed (Fig. 2b). EELS characterization revealed that the MgO-supported nanoparticles contain both Fe and Cu. When CO is further introduced, SWNTs start to grow on the Fe nanoparticles located not only on MgO (Fig. 2c), but also on metallic Cu particles (Fig. 2d).

Based on the in situ ETEM studies and other ex situ characterization results, detailed growth mechanisms of SWNTs on FeCu/MgO was proposed [5]. Before introducing CO, Cu is present in the catalyst as CuO particles (> 50 nm) and also as a solid solution with MgO. The CuO phase is reduced to metallic Cu particles in the catalyst after the CO introduction at 600 °C. Small diameter (< 3 nm) metallic Cu particles are extracted from the solid solution and large Cu particles are obtained from reducing CuO particles (> 50 nm) originally located on the MgO surface (Step I in Fig. 3). The formation of the Cu^{0} phase marks the onset of the reduction of the intimate Fe phase to Fe^{0} through the proposed spillover of CO species absorbed on Cu^{0}. As a result, Fe oxide located both in the solid solution and on the large Cu particle surfaces is reduced to metallic Fe nanocrystals stabilized by their supports (Step II in Fig. 3). Consequently, growth of SWNTs on the Fe nanocrystals is achieved by prolonged exposure to CO (Step III in Fig. 3).

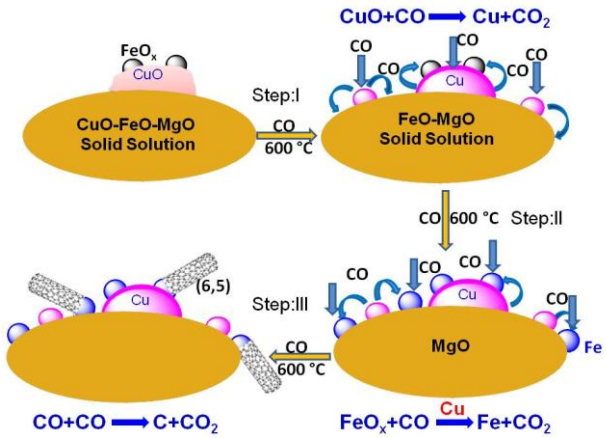

Figure 3. Schematic illustration of SWNT growth on the FeCu-MgO catalyst.

4. Conclusions

SWNTs rich in (6,5) species were successfully grown on MgO supported FeCu catalyst. The high yield of (6,5) tubes was confirmed by the ED characterization. Furthermore, these nanotubes were shown to be predominantly semiconducting (88%). The preferential growth of SWNTs is attributed to the low growth temperature, under which Fe nanoparticles can be reduced with the aid of Cu through a proposed spillover mechanism. Such FeCu catalyst is anticipated to be a suitable system for many applications in other CO association/dissociation related catalytic reactions, like Fisher-Tropsch synthesis.

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