Selective growth of SWNTs on partially reduced monometallic cobalt catalyst

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SiO2 supported cobalt (Co) catalyst could be partially reduced and anchored by unreduced Co ions during a carbon monoxide (CO) chemical vapor deposition (CVD) process. This resulted in the formation of sub-nanometre metallic Co clusters catalyzing the growth of single-walled carbon nanotubes (SWNTs) with a narrow diameter distribution.

SWNTs are very attractive one-dimensional materials with a variety of potential applications, such as electron-field emission, electrochemical probes, membranes for microfluidic devices, and nanoelectronic devices. The performance of SWNT-based materials depends greatly on the diameter and chirality of the nanotube. The ultimate goal in carbon nanotube production is to find a catalytic system that would allow for the growth of SWNTs of a single helicity. Significant work has been conducted to achieve this goal in the area of selective growth, which is aimed at lowering the reaction work. However, the introduction of MoOx/C13 has been conducted to achieve this goal in the area of selective growth.

In this work, we demonstrate the low temperature growth of SWNTs on Co grafted SiO2 (Grace 432 silica, 0.5–1.0 mm particle size, surface area 320 m2 g−1) catalyst deposited by the ALD technique. The precursor used for the deposition was cobalt(III) acetylacetonate (Co(acac)3, Aldrich, 98%). The entire ALD process was carried out at a reduced pressure of 6–10 kPa. Prior to deposition, the silica support was preheated at the ALD reactor at 400 °C for 5 h in a nitrogen atmosphere. The Co(acac)3 precursor was then evaporated at 190 °C and passed through the silica bed. After deposition for 6 h and flushing with nitrogen, the catalyst was annealed at 450 °C with air for 4 h to remove the acac-ligands. The catalyst thus produced was thereafter introduced into a CVD set-up for growing SWNTs. The catalyst was heated to the desired temperature (300 °C to 900 °C) under an argon (Ar) flow (50 cm3 min−1) at atmospheric pressure. After reaching the desired temperature, CO (50 cm3 min−1) replaced Ar and the growth process lasted for 10 min.

The Co concentration on the SiO2 support is 8.0 atomic percent, which was determined by X-ray photoelectron spectroscopy (XPS, ESCA SSX-100). As demonstrated in the previous studies, X-ray diffraction patterns of the catalyst showed very weak reflections which suggests the possible presence of small particles. The extent of reduction is

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scale bars are 500 nm in all images.

It was found that carbon nanotubes can grow on the Co catalyst in a wide temperature window (500 °C–900 °C). Fig. 2 displays scanning electron microscope (SEM, Leo Gemini 982) images of the carbon nanotubes grown at temperatures ranging from 550 °C to 700 °C. Carbon nanotubes, with high density, can be observed on samples grown in this temperature range (Fig. 2). Carbon nanotubes can even grow at 500 °C, but the density is rather low. This observation is in agreement with the Raman spectroscopy (He–Ne laser, 632.8 nm, JY LabRam 300) characterization result (Fig. 3a), which shows a high D mode intensity for carbon nanotubes grown at 500 °C. The intensity ratio of G mode to D mode, which is related to the quality of carbon nanotubes, increases with increasing growth temperature (6, 22 and 23 for carbon nanotubes grown at 500 °C, 550 °C and 700 °C, respectively). Carbon nanotube samples grown at 600 °C were finely ground using an agate mortar and collected on a carbonized copper grid for transmission electron microscope (TEM, Philips CM-200FEG) characterization, besides SWNTs and small diameter catalyst particles, no other form of carbon was observed (Fig. 3b).

The diameter of SWNTs grown at different temperatures was evaluated by the radial breathing mode (RBM) frequencies in the Raman spectra. For SWNTs grown at 700 °C, the relative intensity of the RBM centered at 190 cm⁻¹ (1.26 nm, \(\omega = 223.5/\Delta + 12.5\)) is relatively high. When the reaction temperature is lowered, the intensity of the RBM peak at 190 cm⁻¹ decreases gradually, and the RBM peaks centered at 280 cm⁻¹ ((7,5) tube) and 290 cm⁻¹ ((8,3) tube) become much more dominant. Meanwhile, the intensities of intermediate frequency modes, which correlate with small diameter SWNTs, become significant in the Raman spectra of samples grown at low temperatures.

UV-vis-NIR absorption spectroscopy (Perkin Elmer Lambda 950) was also used to characterize the suspensions of SWNTs grown at different temperatures. To disperse SWNTs, as-synthesized SWNTs were mixed with sodium cholate aqueous solution (2 wt%) and sonicated at 80 W (tip sonicator) for 60 min, the dispersions were centrifuged at 50 000 g for 60 min to remove the SiO₂ support and metallic particles (the centrifugation does not affect the SWNT diameter distribution). Only a few SWNT species, such as (6,4), (6,5), (7,5), (8,3), (8,4) and (7,6) were observed in the suspension of SWNTs grown at 600 °C (Fig. 4a). This is well in agreement with the photoluminescence (PL) excitation spectra.
In summary, we have demonstrated the selective growth of SWNTs on partially reduced monometallic Co catalyst with low temperature CVD. Because of the modest reduction temperature of the catalyst, the catalyst could be partially reduced by CO and anchored on the surface by unrebuilt CO ions without a high temperature H$_2$ pre-reduction process. As-formed sub-nanometre Co clusters can thus catalyze the growth of small diameter SWNTs with a narrow diameter distribution. Although ALD is not an efficient technique for the preparation of catalyst in large quantities, similar catalyst could be prepared using impregnation or co-precipitation techniques by selecting proper precursors and a subsequent calcination process.

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**Notes and references**