High temperature growth of single-walled carbon nanotubes with a narrow chirality distribution by tip-growth mode

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HIGHLIGHTS

- Porous magnesia supported cobalt catalyst affords tip-growth of carbon nanotubes.
- Nanotubes possess narrow chirality distribution with enriched (6, 5) species.
- Lift-off inhibits particle coalescence, favoring small diameter nanotube growth.
- Small-diameter carbon nanotubes form earlier than large-diameter counterparts.

ARTICLE INFO

ABSTRACT

An MgO supported Co catalyst prepared by atomic layer deposition was applied for the growth of single-walled carbon nanotubes (SWNTs). Different from other catalysts, which generally nucleate SWNTs by base-growth mode, the Co-MgO catalyst uniquely generates SWNTs by tip-growth mode, indicating a weak metal-support interaction. During chemical vapor deposition process, the lift-off of Co nanoparticles from support inhibits the aggregation of Co nanoparticles and favors the synthesis of small-diameter SWNTs with a narrow chirality distribution, even at a high reaction temperature. Particularly, product grown at 800 °C maintains a preferential synthesis of small-diameter (6, 5) SWNTs. The enrichment of (6, 5) SWNT arises from the combination of SWNT-catalyst interface thermodynamics with growth kinetic. The growth dynamics of SWNTs was further investigated by *in situ* Raman spectroscopy, which revealed that SWNTs with smaller diameters appeared prior to the growth of large-diameter counterparts.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have brought worldwide attentions because of their fascinating physical and chemical properties [1]. The properties of SWNTs with geometrical structures determined by chiral indices (n, m), could differ from each other even they possess similar diameters. Such a structural diversity greatly hinders their potential applications in nanoelectronics, where SWNTs with uniform properties are demanded [2]. Aiming to separate SWNTs with different chiralities, a number of strategies have been developed to amplify their

structural differences [3,4]. Nevertheless, the separation techniques generally suffer from several drawbacks [5], such as low yield, high cost, deterioration of pristine tube properties, and so on. Consequently, direct synthesis of SWNTs with a high chirality selectivity by the chemical vapor deposition (CVD) technique is considered as the most promising approach [6–14].

There are many parameters involved in the CVD process, including gas feedstock [15], reaction temperature [8,9], reaction pressure [16] and catalyst [12]. All the parameters have been demonstrated to affect kinetics and thermodynamics of SWNT growth. Preliminary

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correlations between SWNT growth and CVD parameters have been proposed theoretically [17–19]. Among all the parameters, catalyst is demonstrated to play vital roles during SWNT growth [12–14,20]. The past twenty years witnessed the development of catalysts for chirality-selective growth of SWNTs [12]. Many supported catalyst systems, including CoMoCAT [6], FeRu/SiO$_2$ [8], FeCu/MgO [9], Co/TUD-1 [7], CoPt/SiO$_2$ [21] and Co$_x$Mg$_{1-x}$O [10,11], have been well developed for the preferential growth of near-armchair SWNTs, like (6, 5) and (9, 8) SWNTs. In these catalysts, transition metal nanoparticles, which are generated upon reduction, catalyze the growth of SWNTs. In order to facilitate the synthesis of SWNTs with a narrow chirality distribution, metallic nanoparticles must be well anchored either on a second metal or on a support to inhibit the aggregation of metal particles, that is, a catalyst nucleates a nanotube by the base-growth mode. This is natural because the small size nanoparticles usually have strong interactions with the support and tend to promote carbon nanotube growth by the base-growth mode [22]. At high reaction temperatures, although the growth mode does not change, such anchoring effects could be lost, causing the coalescence of reduced metallic particles and the subsequent formation of large-diameter SWNTs [8,9]. Therefore, chirality-selective synthesis of SWNTs was mainly achieved at low reaction temperatures by a base-growth mode [6–9,12]. Growth of SWNTs with a narrow chirality distribution on small-diameter metallic particles with a weak metal-support interaction, i.e. a tip-growth mode, has been scarce [11]. In addition, high temperature synthesis of SWNTs is favored as the quality of obtained SWNTs can be high. Recent advances on chirality-specific growth of SWNTs on solid catalysts [13,14] move a huge step forward in the high temperature synthesis. However, such kinds of SWNT growth are limited on flat surfaces, and bulk growth of SWNTs with a narrow chirality distribution at relatively high temperatures has been challenging [21].

To fill this gap, we herein systematically investigate the growth of SWNTs on a Co-MgO catalyst by a tip-growth mode. The correlation between the onset temperature for catalyst reduction and the threshold temperature for SWNT growth will be revealed. SWNTs grown in the temperature range of 550–800 °C are thoroughly characterized by optical techniques, which show that although a gradual diameter increase is observed with the increasing reaction temperature, the product grown at 800 °C maintains the enrichment of (6, 5) SWNTs. In comparison with the chirality distribution of SWNTs synthesized on Co-SiO$_2$ catalyst by a base growth mode at high temperatures, the mystery behinds the unique SWNT chirality distribution achieved on the Co-MgO catalyst will be disclosed. Particularly, the enrichment of (6, 5) SWNT in the product will be explained in the frame of SWNT growth thermodynamics and kinetics. Furthermore, *in situ* Raman spectroscopy will be applied to clarify the growth dynamics of SWNTs at a high reaction temperature.

2. Experimental

2.1. Preparation of Co-MgO catalyst and Co-SiO$_2$ catalyst by atomic layer deposition (ALD)

ALD deposition of Co onto a porous MgO support was performed on a F120 reactor. The adopted Co precursor is cobalt (III) acetylacetonate (Co(acac)$_3$, 98%, Aldrich). Prior to reaction, the MgO support was heated in the reactor at 400 °C for 5 h in N$_2$ to remove possible absorbed H$_2$O molecules [9]. The Co(acac)$_3$ precursor was then evaporated at 190 °C and passed through the MgO bed. Such a deposition step lasted 6 h. Finally, the ALD system was purged with N$_2$ to flush away the unreacted precursor and the catalyst was annealed in air flow to remove the residual organic ligands [11,23].

Co-SiO$_2$ catalyst was prepared by the same procedure except that the support was replaced by SiO$_2$ (Grace 432 silica with a surface area of 320 m^2/g) [23].

2.2. Characterizations of Co-MgO catalyst

X-ray Diffraction (XRD) characterization of the catalyst was carried out with a Panalytical diffractometer using a Cu Kα radiation (λ = 0.1542 nm). The 2θ scan ranges from 10° to 90°. X-ray photoelectron spectroscopy (XPS) was performed with a Surface Science Instruments SSX-100 ESCA spectrometer using monochromatic Al Kα X-rays (1486.6 eV) and an electrostatic hemispherical analyzer. To study the reducibility of the catalyst, the catalyst had been reduced in flowing H$_2$ at 500 °C for 1 h before being transferred into the measurement chamber in an inert atmosphere.

H$_2$ temperature-programmed reduction (TPR) measurement was done with an Altamira Instruments AMI-200R catalyst characterization system. Approximately 100 mg catalyst was loaded into a "U" shape quartz cell. A mixture of H$_2$ and Ar was introduced into the quartz cell, which was heated to over 800 °C with a rate of 10 °C/min. H$_2$ consumption was monitored by the formation of H$_2$O using a Hiden mass spectrometer [23].

2.3. CVD synthesis of SWNTs

Carbon nanotube synthesis on Co-MgO catalyst was carried out in a cold wall CCR-1000 micro-reactor [9,10,23]. A resistive heating crucible was applied to load catalyst, which was subsequently heated to desired temperature (550–800 °C) in a flow of Ar. After stabilization, CO was introduced into the reactor and the growth lasted 15 min. The system was finally cooled down in Ar.

For comparison, CVD growth was also performed on Co-SiO$_2$ catalyst using exactly the same procedure.

2.4. Characterizations of SWNTs by optical techniques

As prepared carbon nanotubes were subjected to Raman spectroscopy (Horiba Jobin Yvon LabRam 300) characterizations. Two excitation laser wavelengths, 632.8 nm and 514 nm, were adopted to detect the products. The produced carbon nanotubes were purified by a hydrochloride acid followed by rinsing with capacious H$_2$O. The purified samples were subsequently dispersed in a sodium cholate hydrate (NaC) aqueous solution by a probe-type sonicator. After centrifugation, the SWNT dispersion was subjected to UV–vis–NIR absorption (PerkinElmer Lambda-950 spectrometer) and photoluminescence (Horiba Jobin-Yvon NanoLog-4) investigations. It is noted that for Co-SiO$_2$ grown SWNTs, the as-produced nanotubes were directly dispersed in NaC aqueous solution without any purification process.

2.5. In situ Raman investigations on SWNT growth at 800 °C

In situ monitoring of SWNT growth was also performed on both Co-MgO and Fe-MgO [24] with the CCR1000 reactor. The excitation laser wavelength of 514 nm was chosen and the laser power was adjusted to ~1.0 mW to minimize the heating effect of the laser. Both excitation and collection occur through a 50× microscope objective with a long working distance. After catalyst loading and reaching the desired temperature in Ar, CO was switched on and the SWNT growth process was monitored by Raman spectroscopy.

3. Results and discussion

Impregnation is a widely used technique for preparing catalysts of synthesizing SWNTs [6,8,10,11]. In our previous work [10,11], we have systematically investigated an impregnation-prepared Co$_x$Mg$_{1-x}$O catalyst for highly selective growth of (6, 5) SWNTs at low reaction temperatures (500–600 °C). It is revealed that the epitaxial relationship between the MgO support and the reduced Co nanoparticles play an important role in biasing (6, 5) species. Compared to the impregnation technique, ALD usually affords catalysts with high metal dispersions