Selective growth of SWNTs on partially reduced monometallic cobalt catalyst

Maoshuai He,*^{*a*} Alexander I. Chernov,^{*b*} Pavel V. Fedotov,^{*b*} Elena D. Obraztsova,^{*b*} Emma Rikkinen,^{*a*} Zhen Zhu,^{*c*} Jani Sainio,^{*d*} Hua Jiang,^{*c*} Albert G. Nasibulin,^{*c*} Esko I. Kauppinen,*^{*ce*} Marita Niemelä^{*a*} and A. Outi I. Krause^{*a*}

Received 23rd July 2010, Accepted 4th November 2010 DOI: 10.1039/c0cc02751k

 SiO_2 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.1 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.² Significant work has been conducted to achieve this goal in the area of selective growth,³⁻⁶ which is aimed at lowering the reaction temperature of a specific catalyst to obtain a narrow chirality distribution of SWNTs. Co-based catalysts were usually selected due to the possibility of forming cobalt carbonyl-like species which act as precursors for growing SWNTs³⁻⁵ in a CO CVD process. To grow SWNTs, it is first necessary to fully reduce the catalyst in a hydrogen (H₂) atmosphere. However, during the reduction, the Co species are highly mobile and tend to form large particles which result in the growth of multiwalled carbon nanotubes (MWNTs). To constrain the mobility of the Co species on the support, either a MoO_x (CoMoCAT process) or a MCM-41 mesoporous support has to be introduced.3-5

However, the introduced MoO_x will finally result in the formation of an Mo_2C impurity which is difficult to remove from the SWNTs produced.⁴ Instead, Co incorporated in MCM-41 has recently proven to be a good template for the growth of SWNTs with a narrow diameter distribution: the

size of the Co nanoparticles was well controlled by the occlusion of the MCM-41 framework.^{3,5} Nevertheless, the use of an expensive MCM-41 mesoporous material as a template limits the scale-up potential of SWNT production. To develop an economically viable method, it is desirable to develop a monometallic catalyst on an ordinary support for synthesizing high quality SWNTs with only a few species.

Atomic layer deposition (ALD) allows the production of a catalyst on a support with better dispersion^{7,8} than impregnation⁹ or co-precipitation techniques. The reason for the high dispersion is that the catalyst precursor is attached to the support via a chemical reaction with the surface functional groups. For example, Haller et al. have synthesized Co grafted SBA-15 through the ALD technique for growing high quality SWNTs at high temperatures.⁷ It was also discovered that the Co ions were substituted for silicon and formed a tetrahedral structure,⁷ which could be the surface cobalt silicate (Co_2SiO_4) .⁹ This enhanced the metal-support interaction and provided a good yield in the SWNT synthesis even on a catalyst prepared by the impregnation technique.⁹ Nevertheless, due to the necessarily high catalyst pre-reduction and lack of anchor site, the use of these catalysts did not lead to the selective growth of SWNTs.7,9

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 $320 \text{ m}^2 \text{ g}^{-1}$) catalyst deposited by the ALD technique.⁸ 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 (6-10 kPa). Prior to deposition, the silica support was preheated in 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-up⁶ for growing SWNTs. The catalyst was heated to the desired temperature (500 °C to 900 °C) under an argon (Ar) flow $(50 \text{ cm}^3 \text{ min}^{-1})$ 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,¹⁰ X-ray diffraction patterns of the catalyst showed very weak reflections which suggests the possible presence of small particles. The extent of reduction is

^a Department of Biotechnology and Chemical Technology, School of Science and Technology, Aalto University, PO Box 16100, FI-00076 Aalto, Finland. E-mail: maoshuai.he@hut.fi; Fax: +358 947022622; Tel: +358 947022874

^b A.M. Prokhorov General Physics Institute RAS, 38 Vavilov Street, 119991 Moscow, Russia

^c NanoMaterials Group, Department of Applied Physics and Center for New Materials, School of Science and Technology, Aalto University, PO Box 15100, FI-00076 Aalto, Finland. E-mail: esko.kauppinen@hut.fi; Fax: +358 947023517; Tel: +358 405098064

^d Department of Applied Physics, School of Science and Technology,

Aalto University, PO Box 11100, FI-00076 Aalto, Finland ^e VTT Biotechnology, PO Box 1000, FI-02044, Espoo, Finland



Fig. 1 H_2 -TPR pattern of Co–SiO₂ synthesized by ALD from Co(acac)₃ as a precursor.

relatively low at a temperature below 700 °C, as estimated by a temperature programmed reduction (TPR) profile (Fig. 1) which was obtained from monitored H₂ consumption by a Hiden mass spectrometer (AMI-200R catalyst characterization system). The low extent of reduction obtained is in agreement with our previous studies,⁸ wherein the degree of reduction of Co/SiO₂ catalyst reduced at 550 °C in H₂ was ranging from 4% to 28% depending on the content of Co. Meanwhile, the TPR pattern shows that the reduction started at around 500 °C and continued to well above 800 °C implying a possible formation of Co₂SiO₄ during the catalyst preparation process.^{9,10} Based on the binary CoO and SiO₂ phase diagram,^{11a} the formation of Co₂SiO₄ can only start to occur at around 900 °C. However, considering the small size of Co and the presence of H2O^{11b} which results from the decomposition of the $Co(acac)_3$, the formation of surface Co_2SiO_4 is highly plausible during the catalyst preparation process.

It was found that carbon nanotubes can grow on the Co catalyst in a wide temperature window ($500 \,^{\circ}C-900 \,^{\circ}C$). Fig. 2 displays scanning electron microscope (SEM, Leo Gemini 982) images of the carbon nanotubes grown at temperatures ranging from 550 $^{\circ}C$ to 700 $^{\circ}C$. Carbon nanotubes, with high density, can be observed on samples grown in this temperature range (Fig. 2). Carbon nanotubes can even grow at 500 $^{\circ}C$, 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 $^{\circ}C$. The intensity ratio of G mode to D mode, which is related to the quality of carbon nanotubes, increases with increasing growth



Fig. 2 SEM images of SWNTs grown on Co–SiO₂ catalyst at different temperatures: (a) 550 °C, (b) 600 °C, (c) 650 °C and (d) 700 °C. The scale bars are 500 nm in all images.



Fig. 3 (a) Raman spectra (632.8 nm) of the as-synthesized SWNTs grown at a temperature of 500 °C, 550 °C, 600 °C, 650 °C and 700 °C. All the spectra were normalized with G intensity. (b) TEM image of SWNTs grown at 600 °C.

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, $\omega = 223.5/d + 12.5$)¹² is relatively high. When the reaction temperature is lowered, the intensity of the RBM peaks 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,³ 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 000g 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



Fig. 4 (a) UV-vis-NIR absorption spectra of sodium cholate dispersed SWNTs grown at a temperature of 600 °C and 700 °C. M_{11} , S_{22} and S_{11} represent the lowest metallic, second lowest semiconducting and lowest semiconducting absorption, respectively. (b) The contour plot of normalized photoluminescence emission intensities under the various excitation energies for SWNTs grown at 600 °C.



Fig. 5 Schematic illustration of SWNT growth on a partially reduced Co–SiO₂ catalyst.

mapping (Horiba Jobin-Yvon NanoLog system with InGaAs CCD detection) result (Fig. 4b). The most bright PL peak corresponds to the (6,5) nanotubes, and its intensity is two times higher than that of the second brightest peak corresponding to (7,5) tubes. Compared to the SWNTs grown on CoMoCAT at ambient pressure,¹³ the monometallic Co catalyzed SWNTs consist of much smaller diameter species. It is noteworthy that although predominant small diameter (6,5) tubes were produced in the Co–MCM-41 SWNTs³ and commercial grade CoMoCAT SWNTs, it was indeed the applied high pressure¹⁴ during the growth processes that induced the growth of small diameter SWNTs.

As reported in the previous work,^{3,5,6} the SWNT diameter shifts towards a large value and the diameter distribution gets broad with increasing growth temperature. From the comparison of absorption spectra between SWNTs grown at 600 °C and those grown at 700 °C (Fig. 4a), it can be clearly seen that the absorption peaks of large diameter SWNTs, such as (7,6), (8,4) and (8,7) tubes, become significant in the absorption spectra of SWNTs grown at 700 °C.

It is necessary to elucidate the mechanism for the successful growth of SWNTs at low temperature from the Co-SiO₂ catalyst. The reducibility of Co can be strongly influenced by the catalyst preparation method and the calcination treatment.^{8,9} It has been reported that SWNTs could hardly be grown at low temperatures (<700 °C) on monometallic Co deposited onto SiO₂ support by impregnation.^{13,15} The previous failed attempts to grow SWNTs are most likely related to the high reducibility of the impregnated Co-SiO₂ catalyst, since the H2-TPR spectrum of the impregnated catalyst mainly showed low reduction peaks between 200 °C to 600 °C.¹³ After reduction at 700 °C in H₂, due to the lack of anchoring sites on the support,^{13,15} all of the Co was reduced and tended to form large particles having a direct implication on the nucleation of MWNTs.¹⁵ While in the case of the catalyst used in this study, based on its H₂-TPR pattern (Fig. 1), the reduction takes place in the temperature range of 500 °C-850 °C. Thus, in the carbon nanotube growth process with a growth temperature investigated here (500 °C-700 °C), only part of the Co²⁺ is reduced and the residual Co²⁺ and Co⁺ act as anchoring sites, which constrain the mobility of the reduced cobalt species thus facilitating the formation of sub-nanometre Co clusters.¹⁶ Once CO is dissociated and the Co clusters are saturated with carbon, small diameter SWNTs will nucleate and protrude out, as shown in the schematic illustration of Fig. 5.

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 unreduced 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.

This work was supported by TEKES, Academy of Finland (Project Nos 128445 and 128495), CNB-E project in Aalto University through the Multidisciplinary Institute of Digitalization and Energy (MIDE) program, European FP6 Project 033350, Project RFBR-09-02-91076 and Project ROSNAUKA 02.523.12.3020. We thank Dr Sanna Airasinen, MSc Kati Vilonen and MSc Sonja Kouva for their help in preparing this manuscript and experimental support.

Notes and references

- M. S. Dresselhaus, G. Dresselhaus and P. Avouris, "Carbon Nanotubes: Synthesis, Structure, Properties, and Applications", Springer-Verlag, 2000.
- 2 A. Hirsch, Angew. Chem., Int. Ed., 2009, 48, 5403-5404.
- 3 N. Li, X. M. Wang, F. Ren, G. L. Haller and L. D. Pfefferle, J. Phys. Chem. C, 2009, 113, 10070–10078.
- 4 S. M. Bachilo, L. Balzano, J. E. Herrera, F. Pompeo, D. E. Resasco and R. B. Weisman, J. Am. Chem. Soc., 2003, 125, 11186–11187.
- 5 Y. Chen, L. Wei, B. Wang, S. Y. Lim, D. Ciuparo, M. Zheng, J. Chen, C. Zoican, Y. H. Yang, G. L. Haller and L. D. Pfefferle, *ACS Nano*, 2007, 1, 327–336.
- 6 M. S. He, A. I. Chernov, P. V. Fedotov, E. D. Obraztsova, J. Sainio, E. Rikkinen, H. Jiang, Z. Zhu, Y. Tian, E. I. Kauppinen, M. Niemelä and A. O. I. Krause, *J. Am. Chem. Soc.*, 2010, **132**, 13994–13996.
- 7 C. Wang, S. Lim, G. Du, C. Zoican Loebick, N. Li, S. Derrouiche and G. Haller, J. Phys. Chem. C, 2009, 113, 14863–14871.
- 8 L. B. Backman, A. Rautiainen, A. O. I. Krause and M. Lindblad, *Catal. Today*, 1998, 43, 11–19.
- 9 N. Li, X. M. Wang, S. Derrouiche, G. L. Haller and L. D. Pfefferle, ACS Nano, 2010, 4, 1759–1767.
- 10 L. B. Backman, A. Rautiainen, M. Lindblad, O. Jylhä and A. O. I. Krause, *Appl. Catal.*, *A*, 2001, **208**, 223–234.
- (a) D. P. Mosse and A. Muan, *Trans. AIME*, 1965, 233, 1448–1450;
 (b) E. Kondoh, R. A. Donaton, S. Jin, H. Bender, W. Vandervorst and K. Maex, *Appl. Surf. Sci.*, 1998, 136, 87–94.
- 12 S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley and R. B. Weisman, *Science*, 2002, 298, 2361–2365.
- 13 B. Wang, Y. H. Yang, L. J. Li and Y. Chen, J. Mater. Sci., 2009, 44, 3285–3295.
- 14 B. Wang, L. Wei, L. Yao, L. J. Li, Y. H. Yang and Y. Chen, J. Phys. Chem. C, 2007, 111, 14612–14616.
- 15 W. E. Alvarez, B. Kitiyanan, A. Borgna and D. E. Resasco, *Carbon*, 2001, **39**, 547–558.
- 16 S. Y. Lim, C. Wang, Y. H. Yang, D. Ciuparu, L. Pfefferle and G. L. Haller, *Catal. Today*, 2007, **123**, 122–132.