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Sulfur doped Co/SiO\textsubscript{2} catalysts for chirally selective synthesis of single walled carbon nanotubes†

Hong Wang, Kunli Goh, Rui Xue, Dingshan Yu, Wenchao Jiang, Raymond Lau and Yuan Chen*

Monochiral single-walled carbon nanotubes have many potential uses, especially in the field of electronics and medical applications. Here we demonstrate a method to activate three types of Co/SiO\textsubscript{2} catalysts via sulfur-doping for the synthesis of tubes with a narrow chiral distribution around (9,8) chirality.

Electronic and optical properties of single-walled carbon nanotubes (SWCNTs) are correlated with their geometric structures, i.e. chirality index \((n,m)\). Thus, many potential applications require the use of monochiral SWCNTs. Chirally selective synthesis of nanotubes is the ultimate goal in SWCNT production, which remains a great challenge. In common growth methods, i.e. chemical vapor deposition (CVD), carbon precursors decompose at high temperature to form atomic carbon species, which then nucleate into one-dimensional tubes on catalytic particles. Theoretical studies suggest that catalysts play a critical role in the \((n,m)\) selectivity. To control SWCNT \((n,m)\) structures, the size of catalytic particles need to be first confined in a suitable range. However, metal species are mobile and form particles of various sizes at high growth temperatures, which eventually results in the growth of multiwalled carbon nanotubes (MWCNTs), graphite and amorphous carbon.

Co catalysts supported on silica substrates (Co/SiO\textsubscript{2}) are the most often used catalysts for \((n,m)\) selective growth of SWCNTs. Several approaches have been used to control the nucleation of Co, e.g. stabilizing Co clusters in bimetallic alloys, incorporating Co ions into mesoporous substrates, forming dispersed surface Co silicates, anchoring reduced Co atoms by unreduced Co ions, and creating strong interfacial Co-Si interactions. Most of these approaches only result in the selective growth of small-diameter (6,5) tubes. Some previous studies had shown that when sulfur (S) species are added to carbon precursors, it can promote the growth rate and yield of the nanotubes, and change MWCNT diameters. However, to the best of our knowledge, no work has been reported on the direct doping of S in solid catalysts to control metal particles for SWCNT growth.

In this work, we have demonstrated that non-selective Co/SiO\textsubscript{2} catalysts can be converted into efficient chiral selective catalysts by S doping. SWCNTs were characterized by photoluminescence (PL), UV-vis-near-infrared (UV-vis-NIR) absorption and Raman spectroscopies. Catalysts were characterized by elemental analysis, temperature programmed reduction (H\textsubscript{2}-TPR), and UV-vis diffuse reflectance spectroscopy. The molecular structural changes of Co species on SiO\textsubscript{2} caused by S doping are believed to be responsible for the chiral selectivity.

Three Co/SiO\textsubscript{2} catalysts with 1 wt% Co were prepared by the impregnation method using Co precursors, including Co(acac)\textsubscript{2}, CoCl\textsubscript{2}, and Co(NO\textsubscript{3})\textsubscript{2}, respectively (see ESI† for details). Catalysts were introduced into a CVD reactor, and first reduced under pure H\textsubscript{2} (1 bar, 50 sccm) from room temperature to 540 °C at 20 °C min\textsuperscript{-1}, then further heated to 780 °C under an Ar flow (1 bar, 50 sccm). At 780 °C, pressured CO (6 bar, 200 sccm) replaced Ar, and the SWCNT growth lasted for 1 h. As-synthesized SWCNTs were characterized by Raman spectroscopy, UV-vis-NIR absorption spectroscopy, PL, temperature programmed reduction (H\textsubscript{2}-TPR), and PL and UV-vis-NIR absorption spectroscopies for the chiral selectivity.

PL maps in Fig. 1a–f show that two undoped Co/SiO\textsubscript{2} catalysts (Co(acac)/SiO\textsubscript{2} and CoCl/SiO\textsubscript{2}) resulted in small-diameter tubes (<0.9 nm), such as (6,5), (7,5), (7,6) and (8,4). Co(N)/SiO\textsubscript{2} is not active for SWCNT growth. This is in agreement with previous studies using various SiO\textsubscript{2} supported Co catalysts. In contrast, after doping with S, the major \((n,m)\) products are large-diameter tubes (>1.1 nm), such as (9,8), (9,7), (10,6), and (10,9). The abundance of these
Doping sulfate ions into metal oxides has created various solid acid catalysts, such as SO\(_4^{2−}/\)ZrO\(_2\), SO\(_4^{2−}/\)TiO\(_2\), and SO\(_4^{2−}/\)Fe\(_2\)O\(_3\). Based on our characterization of the Co/SiO\(_2\) catalysts, we propose the following mechanism to explain their (n,m) selectivity in SWCNT growth. As shown in Fig. 3, undoped Co/SiO\(_2\) catalysts contain CoO\(_x\) Co hydrosilicate, and surface Co silicates, which are evident from their H\(_2\)-TPR profiles and UV-vis spectra. Surface Co silicates on CoACAC/SiO\(_2\) and CoCl/SiO\(_2\) would be reduced and nucleated into small Co nanoparticles,
which are selective toward small-diameter SWCNTs,17 as shown in Fig. 1. CoO on CoN/SiO2 is reduced to form large Co particles, which are not selective to SWCNTs. Doping S through H2SO4 leads to the formation of chelating bidentate SO42−, where one S atom is linked to one Co atom through two O atoms, a common structure found in sulfate promoted metal oxide catalysts.30 This is supported by the sharp peaks at 493–506 nm in the UV-vis spectra. Windle et al. showed that adding triphosphate or carbon disulfide in gas phase would restrict the growth of Fe particles for selective growth of (9,9).12 Similarly, we propose that the co-existence of S atoms near Co atoms may limit the nucleation of Co and/or form Co–S compounds, which changes the selectivity of the catalysts to favor the formation of (9,8). As discussed in our previous study,26 the selectivity toward (9,8) may be attributed to the close match between carbon caps and the most stable Co particles in their size range, as well as the higher growth rate of high chiral angle tubes.33 As active Co nanoparticles are embedded under or near SiO2 surface, we are still unable to quantify their size and composition in transmission electron microscopy analysis (see Fig. S3 in the ESI†). Furthermore, we propose a reaction between H+ ions and CoOx releasing Co ions to form well dispersed Co hydrosilicate and surface Co silicate on SiO2, which would increase the selectivity toward SWCNTs. This is suggested by the increased SWCNT selectivity of CoN/SiO2/S. To further verify the proposed mechanism, we doped CoN/SiO2 using (NH4)2SO4. We expected the same effect from SO42−, but selectivity toward SWCNTs may be compromised since NH4+ is less reactive than H+. As shown in Fig. S4–S7 in the ESI†, [NH4]2SO4 doped CoN/SiO2 can result in the growth of (9,8) nanotubes because of S doping. However, it is less selective to SWCNTs as compared to CoN/SiO2/S. This provides strong credibility to our proposed mechanism.

In conclusion, we have demonstrated a method to convert three types of Co/SiO2 catalysts, which are either inactive for the SWCNT growth or only selective to small-diameter nanotubes, into chirally selective catalysts to grow SWCNTs enriched with large-diameter (9,8) tubes (up to 40.5%) by doping catalysts with S. We also proposed in the mechanism that S atoms near Co atoms assist the formation of Co nanoparticles which are selective to (9,8) tubes. Moreover, H+ ions may react with CoOx to form well dispersed Co hydrosilicate and surface Co silicate on SiO2, which increases the selectivity to SWCNTs.

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Notes and references