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<th>Sulfur doped Co/SiO₂ catalysts for chirally selective synthesis of single walled carbon nanotubes</th>
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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/SiO2 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/SiO2) 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/SiO2 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, H2 temperature programmed reduction (H2-TPR), and UV-vis diffuse reflectance spectroscopy. The molecular structural changes of Co species on SiO2 caused by S doping are believed to be responsible for the chiral selectivity.

Three Co/SiO2 catalysts with 1 wt% Co were prepared by the impregnation method using Co precursors, including Co(n) acetylacetone (Co(acac)x, Sigma-Aldrich, 97%), Co(n) chloride (CoCl2, Alfa Aesar, 97%), and Co(n) nitrate hexahydrate (Co(NO3)2.6H2O, Sigma-Aldrich, 99.999%). They are denoted as CoACAC/SiO2, CoCl2/SiO2, and CoN/SiO2, respectively. To add S, the calcined Co/SiO2 catalysts were impregnated by dilute sulfuric acid (H2SO4, 0.04 mol L−1) at 8 mL solution per g catalyst ratio for 1 h. The resulting S doped catalysts were marked as CoACAC/SiO2/S, CoCl2/SiO2/S, and CoN/SiO2/S, respectively (see ESI† for details). Catalysts were introduced into a CVD reactor, and first reduced under pure H2 (1 bar, 50 sccm) from room temperature to 540 °C at 20 °C min−1, and then further heated to 780 °C under an Ar flow (1 bar, 50 sccm). At 780 °C, pressurized CO (6 bar, 200 sccm) replaced Ar, and the SWCNT growth lasted for 1 h. As-synthesized SWCNTs with catalysts were first characterized by Raman spectroscopy, and then dissolved in NaOH aqueous solution (1.5 mol L−1) to remove SiO2. The carbon deposits were then dispersed in 2 wt% sodium dodecyl benzene sulfate (SDBS, Aldrich) D2O solution. The SWCNT suspension obtained after centrifugation at 50 000 g was characterized by PL and UV-vis-NIR absorption spectroscopies (see ESI† for details).

PL maps in Fig. 1a–f show that two undoped Co/SiO2 catalysts (CoACAC/SiO2 and CoCl2/SiO2) resulted in small-diameter tubes (<0.9 nm), such as (6,5), (7,5), (7,6), and (8,4). CoN/SiO2 is not active for SWCNT growth. This is in agreement with previous studies using various SiO2 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
four species calculated using their PL intensity is 52.4–69.1% of all semiconducting species identified, out of which, 32.7–40.5% is (9,8) [see Tables S1–S3 in the ESI†]. PL results were corroborated by UV-vis-NIR absorption spectra. Fig. 1g shows that SWCNTs from CoACAC/SiO2 and CoCl/SiO2 have intense absorption peaks at 992, 1025 and 1137 nm from (6,5), (7,5), (7,6), and (8,4). SWCNTs grown on Co/N/SiO2 have weak absorption peaks. In contrast, Fig. 1h shows that SWCNTs grown on S doped catalysts all have strong absorption peaks at 1420 and 818 nm, corresponding to the $E_{22}$ and $E_{11}$ transitions of metallic (9,6) and (10,10) (1.36 nm) or the $E_{22}$ transition of semiconducting (6,5). A few other absorption peaks below 700 nm can be assigned to either the $E_{11}$ transition of metallic (9,6) (1.02 nm) and (10,10) (1.36 nm) or the $E_{22}$ transition of semiconducting (6,5). Since the intensity of (6,5) PL peaks in Fig. 1d–f is low, the absorption peaks below 700 nm in Fig. 1h are likely to be from those metallic tubes. SWCNTs were further characterized by Raman spectroscopy under two excitation lasers (785 and 514 nm). Raman results (see Fig. S1 in the ESI†) agree with the findings from PL and UV-vis-NIR. Overall, the three spectroscopic techniques have demonstrated that S doping can shift the ($n,m$) selectivity of Co/SiO2 catalysts from small-diameter tubes near (6,5) to large-diameter tubes with a narrow distribution around (9,8).

Co species deposited on SiO2 would first be partially reduced in H2, and then nucleated into Co nanoparticles to initiate SWCNT growth. The change in ($n,m$) selectivity shown in Fig. 1 may be attributed to the changes in Co species caused by S doping. Firstly, we conducted an elemental analysis of S doped catalysts.

Firstly, we conducted an elemental analysis of S doped catalysts. PL maps and UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown on undoped and S doped Co/SiO2 catalysts. PL maps: (a) CoACAC/SiO2, (b) CoCl/SiO2, (c) CoN/SiO2, (d) CoACAC/SiO2/S, (e) CoCl/SiO2/S, and (f) Co/N/SiO2/S. Some major ($n,m$) species identified on PL maps are marked. Absorption spectra: undoped (g) and S doped (h). The shaded pink indicates the $E_{11}$ absorption band and the shaded blue shows the overlapping $E_{22}$ and $E_{11}$ bands.
which are selective toward small-diameter SWCNTs, 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. This is supported by the sharp peaks at 493–506 °C in the TPR profiles and the broad peak around 535 nm in the UV-vis spectra. Windle et al. showed that adding thiophene or carbon disulfide in gas phase would restrict the growth of Fe particles for selective growth of (9,9). 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, 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. 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 hydroxosilicate 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 Co3+ to form well dispersed Co hydroxosilicate and surface Co silicate on SiO2, which increases the selectivity to SWCNTs.

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Notes and references