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# Sulfur doped Co/SiO$_2$ catalysts for chirally selective synthesis of single walled carbon nanotubes†

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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/SiO$_2$ 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*).[1] 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.[2–7] To control SWCNT (*n*,*m*) structures, the size of catalytic particles need to be first confined in a suitable range.[7–9] 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$_2$) are the most often used catalysts for (*n*,*m*) selective growth of SWCNTs.[10–20] Several approaches have been used to control the nucleation of Co, *e.g.* stabilizing Co clusters in bimetallic alloys,[10,12,20] incorporating Co ions into mesoporous substrates,[11,14,16] forming dispersed surface Co silicates,[17] anchoring reduced Co atoms by unreduced Co ions,[18] and creating strong interfacial Co–Si interactions.[19] 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.[21–24] 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$_2$ 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, H$_2$ temperature programmed reduction (H$_2$-TPR), and UV-vis diffuse reflectance spectroscopy. The molecular structural changes of Co species on SiO$_2$ caused by S doping are believed to be responsible for the chiral selectivity.

Three Co/SiO$_2$ catalysts with 1 wt% Co were prepared by the impregnation method using Co precursors, including Co(II) acetylacetonate (Co(acac)$_2$, Sigma-Aldrich, 97%), Co(II) chloride (CoCl$_2$, Alfa Aesar, 97%), and Co(II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich, 99.999%). They are denoted as CoACAC/SiO$_2$, CoCl/SiO$_2$, and CoN/SiO$_2$, respectively. To add S, the calcined Co/SiO$_2$ catalysts were impregnated by dilute sulfuric acid (H$_2$SO$_4$, 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/SiO$_2$/S, CoCl/SiO$_2$/S, and CoN/SiO$_2$/S, respectively (see ESI† for details). Catalysts were introduced into a CVD reactor, and first reduced under pure H$_2$ (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, pressured 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 SiO$_2$. The carbon deposits were then dispersed in 2 wt% sodium dodecyl benzene sulfate (SDBS, Aldrich) D$_2$O 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/SiO$_2$ catalysts (CoACAC/SiO$_2$ and CoCl/SiO$_2$) resulted in small-diameter tubes (<0.9 nm), such as (6,5), (7,5), (7,6) and (8,4). CoN/SiO$_2$ is not active for SWCNT growth. This is in agreement with previous studies using various SiO$_2$ supported Co catalysts.[15,17,25] 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

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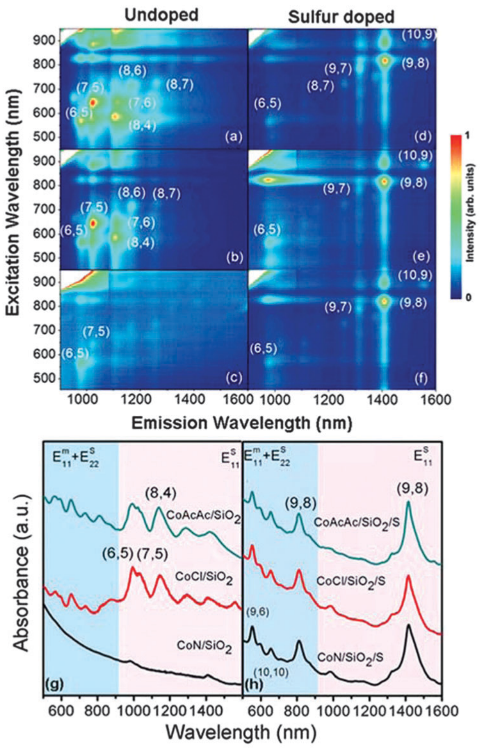

**Fig. 1** PL maps and UV-vis-NIR absorption spectra of SDBS-dispersed SWCNTs grown on undoped and S doped Co/$SiO_2$ catalysts. PL maps: (a) CoACAC/$SiO_2$, (b) CoCl/$SiO_2$, (c) CoN/$SiO_2$, (d) CoACAC/$SiO_2$/S, (e) CoCl/$SiO_2$/S, and (f) CoN/$SiO_2$/S. Some major (*n*,*m*) species identified on PL maps are marked. Absorption spectra: undoped (g) and S doped (h). The shaded pink indicates the $E_{11}^{S}$ absorption band and the shaded blue shows the overlapping $E_{22}^{S}$ and $E_{11}^{M}$ bands.

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/$SiO_2$ and CoCl/$SiO_2$ have intense absorption peaks at 992, 1025 and 1137 nm from (6,5), (7,5), (7,6), and (8,4). SWCNTs grown on CoN/$SiO_2$ 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 $E_{11}^{S}$ and $E_{22}^{S}$ transitions of (9,8). A few other absorption peaks below 700 nm can be assigned to either the $E_{11}^{M}$ transition of metallic (9,6) (1.02 nm) and (10,10) (1.36 nm) or the $E_{22}^{S}$ 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/$SiO_2$ catalysts from small-diameter tubes near (6,5) to large-diameter tubes with a narrow distribution around (9,8).

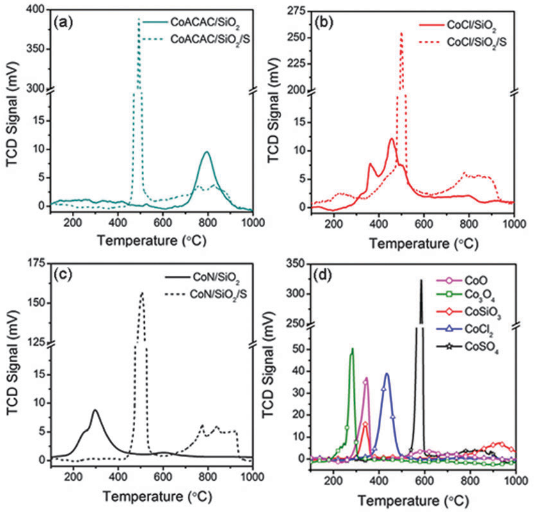

**Fig. 2** $H_2$-TPR profiles of undoped and S doped Co/$SiO_2$ catalysts and several Co references (CoO, $Co_3O_4$, $CoSiO_3$, $CoCl_2$ and $CoSO_4 \cdot 7H_2O$).

Co species deposited on $SiO_2$ would first be partially reduced in $H_2$, 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. The S content in CoACAC/$SiO_2$/S, CoCl/$SiO_2$/S, and CoN/$SiO_2$/S was found to be 0.91, 1.17 and 0.83 wt%, respectively. This confirms the existence of S. Next, $H_2$-TPR was employed to study the reducibility of Co species. Fig. 2 shows that CoACAC/$SiO_2$ displays a peak around 797 °C, which is due to the surface Co silicate.[17] CoCl/$SiO_2$ has multiple peaks at 360–800 °C, which may come from the reduction of CoO, $CoCl_2$, and surface Co silicate. CoN/$SiO_2$ possesses a broad peak around 290 °C which can be attributed to $Co_3O_4$ and CoO. In contrast, all the TPR profiles of the three S doped Co/$SiO_2$ catalysts have a sharp peak at 493–506 °C, similar to our recently reported chiral selective $CoSO_4$/$SiO_2$ catalyst.[26] In addition, it is observed that the $CoO_x$ peaks of undoped catalysts become significantly smaller after S doping, and new peaks around 800 °C appear on CoCl/$SiO_2$/S and CoN/$SiO_2$/S. This observation suggests the formation Co hydrosilicate or surface Co silicate,[27] while the 797 °C peak of CoACAC/$SiO_2$ becomes smaller. Lastly, UV-vis diffuse reflectance spectroscopy was used to probe the surface chemistry of the catalysts. As shown in Fig. S2 in the ESI,† CoACAC/$SiO_2$ has two peaks around 570 and 650 nm, suggesting the formation of surface Co silicates.[28] The spectrum of CoCl/$SiO_2$ shows two broad peaks at 550 and 720 nm, indicating the presence of $CoO_x$ and $CoCl_2$. The spectrum of CoN/$SiO_2$ is similar to that of $Co_3O_4$, having two broad peaks at ~400 and 720 nm, which can be assigned to the transitions of octahedral configured $Co^{3+}$ ions.[29] In contrast, all the three S doped Co/$SiO_2$ catalysts have a broad peak around 535 nm, similar to that of $CoSO_4$, and this suggests the existence of Co species bonded to $SO_4^{2-}$.

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 $SO_4^{2-}/Fe_2O_3$.[30,31] 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,

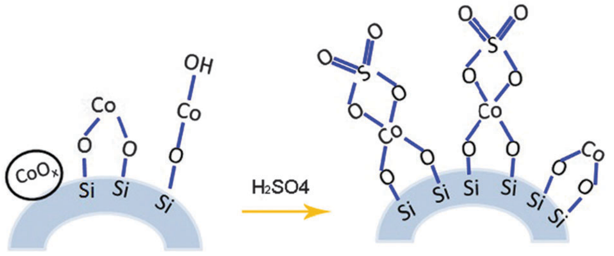

**Fig. 3** Schematic illustration of changes in Co species on Co/SiO$_2$ catalysts caused by S doping.

which are selective toward small-diameter SWCNTs,[17] as shown in Fig. 1. CoO$_x$ on CoN/SiO$_2$ is reduced to form large Co particles, which are not selective to SWCNTs. Doping S through $H_2SO_4$ leads to the formation of chelating bidentate $SO_4^{2-}$, 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 °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).[32] 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 SiO$_2$ 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 CoO$_x$, releasing Co ions to form well dispersed Co hydrosilicate and surface Co silicate on SiO$_2$, which would increase the selectivity toward SWCNTs. This is suggested by the increased SWCNT selectivity of CoN/SiO$_2$/S. To further verify the proposed mechanism, we doped CoN/SiO$_2$ using $(NH_4)_2SO_4$. We expected the same effect from $SO_4^{2-}$, but selectivity toward SWCNTs may be compromised since $NH_4^+$ is less reactive than H$^+$. As shown in Fig. S4–S7 in the ESI,† $(NH_4)_2SO_4$ doped CoN/SiO$_2$ can result in the growth of (9,8) nanotubes because of S doping. However, it is less selective to SWCNTs as compared to CoN/SiO$_2$/S. This provides strong credibility to our proposed mechanism.

In conclusion, we have demonstrated a method to convert three types of Co/SiO$_2$ 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 CoO$_x$ to form well dispersed Co hydrosilicate and surface Co silicate on SiO$_2$, which increases the selectivity to SWCNTs.

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