Chiral-Selective Growth of (9,8) Single Walled Carbon Nanotube Using Sulfate-Promoted Cobalt Catalysts

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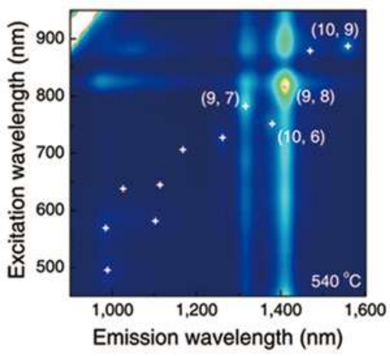

Electronic and optical properties of single-walled carbon nanotubes (SWCNTs) correlate with their chiral structures. Many applications need chirally pure SWCNTs while current synthesis methods cannot produce. We demonstrated that a sulfate-promoted $CoSO_4/SiO_2$ catalyst, which selectively grows large diameter (9,8) nanotubes at 1.17 nm with 51.7 % abundance among semiconducting tubes, and 33.5% over all tube species. After reduction in H_2 at 540 ^{o}C, the catalyst containing 1 wt% Co has a carbon yield of 3.8 wt%, in which more than 90% is SWCNT. The catalyst is also simple to synthesize for scalable production of SWCNTs. As compared to other Co catalysts used for SWCNT growth, the $CoSO_4/SiO_2$ catalyst is unique with a narrow Co reduction window under H_2 centered at 470 °C, which can be attributed to the reduction of highly dispersed $CoSO_4$. X-ray absorption spectroscopy results show that the sulfur content in the catalyst changes after catalyst reduction at different conditions. The sulfur content correlates with the change in SWCNT (n,m) selectivity observed. We can further change the chiral selectivity of the catalyst by changing catalyst calcination temperature. After calcination in air at 400 °C, it has excellent single chiral selectivity towards large diameter (9,8) nanotubes. The selectivity shifts to small diameter nanotubes, when it is calcined at 800 °C. Catalyst characterizations by hydrogen temperature programed reduction, X-ray absorption spectroscopy at the cobalt K-edge and sulfur K-edge suggest that the presence of chelating bidentate SO_4^{2-} bonded with cobalt on the silica surface may limit the aggregation of cobalt and/or form cobalt–sulfur compounds during nanotube growth, leading to the selectivity towards the (9,8) nanotubes. The removal of sulfur at higher calcination temperatures results in the formation of surface cobalt oxides and silicates which shifts the chiral selectivity towards small diameter nanotubes. Our work shows that catalysts incorporated with sulfur compounds have potentials to be further developed for chiral selective growth of SWCNTs.