Chirality selective growth of single-walled carbon nanotubes using W-Co alloy catalyst

論 文 の 内 容 の 要 旨

論文題目　Chirality selective growth of single-walled carbon nanotubes using W-Co alloy catalyst
（W-Co合金触媒を用いたカイラリティ制御単層カーボンナノチューブ合成）

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Ever since their discovery, single walled carbon nanotubes (SWNTs) have attracted intensive attention because of their special electronic properties and potential applications. The diversity of SWNT atomic structures provides a broad window for their applications in nanodevices. However, the candidates for individual devices require SWNT assemblies with homogeneous structure and properties. Unfortunately, the as-grown SWNTs are always a mixture of various chiralities, which hinders their application in nanoelectronics. Since the chirality determines the structure of SWNTs, diameter control and chirality control are the prerequisite to obtain SWNTs with homogeneous properties. Extensive researches have focused on the diameter-control and chirality-control growth of SWNTs. However, it is a critical challenge to grow single-chirality SWNTs. Catalyst plays an important role in the chirality controlled synthesis of SWNTs. Bimetallic catalysts usually possess different catalytic properties than either of their parent metals and thus they have been widely explored in catalytic reactions for SWNTs growth. In this dissertation, the bimetallic will be the focus to selectively control the diameter and chirality of SWNTs.

In order to investigate the mechanism of growth of SWNTs with transmission electron microscopy

(TEM), we develop an in-plane TEM where an etched amorphous SiO_2 window can work as the substrate to directly grow SWNTs with deposited catalyst particles. By using this in-plane TEM method, we successfully study the CuCo bimetallic catalyst which can grow small-diameter of SWNTs at relatively low temperature. An anchoring effect of Cu has been proposed to prevent the active Co catalyst particles from aggregating to large ones, resulting in the production of small-diameter of SWNTs.

Recently, Co_7W_6 clusters were reported to successfully grow a metallic chirality SWNT (12, 6), with over 90% abundance, a zigzag SWNT (16, 0) with near 80% and a semiconducting SWNT (14, 4) with over 97%, by controlling the catalyst structure and growth conditions with a high-temperature reduction and growth [*Nature*, 2014, **510**, 522; *J. Am. Chem. Soc.*, 2015, **137**, 8688]. However, the low yield and short SWNTs inhibits the large-scale applications of the near single-chirality SWNTs. A more simple sputtered W-Co catalyst can selectively grow high-quality (12, 6) SWNTs with better uniformity by low pressure chemical vapor deposition at lower temperature. The abundance of (12, 6) is 50%-70% according to the statistical Raman mapping analysis and optical absorption spectrum of the as-grown SWNTs. Parametric study of the W-Co catalyst system demonstrates that the reduction temperature before growth is critical for the selectivity and the intermediate structure, Co_6W_6C, is identified by the electron diffraction. Moreover, after 5 min-growth the catalyst particles are transformed to Co. The investigation of catalysts discloses the complicated structure changes before and after growth.

The as-reduced catalyst particles are characterized by EDS mapping to further understand the elemental distribution of nanosized particles and an acid treatment experiment is designed to verify the nonexistence of the trifle amount of pure Co phase. The time dependence study confirms that the dynamic evolution of catalyst structure is associated with the selectivity towards (12, 6). The Co_6W_6C is more likely to correlate with the nucleation of (12, 6) cap to achieve a selective growth. A proposed mechanism reveals the elongated nucleation and growth stage which is strongly dependent on the catalyst structure. The evolution of carbon content indicates a possible clue for the understanding of selective growth with Co_6W_6C. The in-plane TEM study with W-Co bimetallic catalyst paves an important way to the final goal of single-chirality synthesis of SWNTs.