Growth modes of single-walled carbon nanotubes on catalysts

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Understanding the growth mechanism of single-walled carbon nanotubes (SWCNTs) and achieving selective growth requires insights into the catalyst structure-function relationship. Using an in situ aberration-corrected environmental transmission electron microscope, we reveal the effects of the state and structure of catalysts on the growth modes of SWCNTs. SWCNTs grown from molten catalysts via a vapor-liquid-solid process generally present similar diameters to those of the catalysts, indicating a size correlation between nanotubes and catalysts. However, SWCNTs grown from solid catalysts via a vapor-solid-solid process always have smaller diameters than the catalysts, namely, an independent relationship between their sizes. The diameter distribution of SWCNTs grown from crystalline Co7W6, which has a unique atomic arrangement, is discrete. In contrast, nanotubes obtained from crystalline Co are randomly dispersed. The different growth modes are linked to the distinct chiral selectivity of SWCNTs grown on intermetallic and monometallic catalysts. These findings will enable rational design of catalysts for chirality-controlled SWCNTs growth.

INTRODUCTION

The relation between catalyst structure and performance plays a critical role in heterogeneous catalysis. The active sites of nanocatalysts have been extensively suggested to be the origin of high selectivity of small molecules (1–5). The chiral structures of the much larger single-walled carbon nanotube (SWCNT) molecules are more complicated, and two chiral indices (n,m) are required to identify them (6). Chirality-pure SWCNTs with the unique properties have shown tremendous application potential in next-generation electronics (7, 8), optoelectronics (9), and biosensing (10). For the rational design of synthetic processes of the chirality-specified SWCNTs, it is of vital importance to attain a deep understanding on how such a helical nanotube grows from a catalyst nanoparticle (11).

The chemical vapor deposition (CVD) of SWCNTs undergoes either a vapor-liquid-solid (VLS) or a vapor-solid-solid (VSS) process depending on the properties of the metal catalysts and CVD conditions (12–14). In a VLS process, the following procedures happened successively: catalyzed decomposition of carbon precursors, dissolution of the resultant carbon species in the molten catalyst, nucleation of tube caps on the catalysts, and further growth of the SWCNTs (15–17). A VSS process undergoes similar procedures, except that the catalysts remain to be solid, and the carbon diffusion is likely to be different. It is generally considered that catalysts play a key role in determining the structure of SWCNTs (11, 16, 18–24). Diameter correlation is the primitive part in the studies of how catalysts affect the structure of the resultant SWCNTs (25). A number of reports addressed the relation of the diameters of nanotubes (dt) and catalyst particles (dNP), presenting a variable d/dNP ratio of ~1 (26, 27) or smaller (28–32). It was proposed that nanotubes grow from the catalyst nanoparticles via two different modes: The tangential mode yields SWCNT with a similar diameter to nanoparticles (d/dNP ≈ 1), whereas the perpendicular mode produces SWCNTs with a diameter smaller than catalyst nanoparticles (d/dNP < 1) (33, 34).

The role of catalysts in determining the structure of the SWCNTs is an important research topic. It has been found that the size and composition of the catalysts remarkably influence the chiral angle distribution (35–37) and the chirality of SWCNTs (38–40). However, the actual mechanism remains fuzzy. More recently, we proposed that the solid-state catalysts with unique crystal structures, such as intermetallic Co7W6, can catalyze the growth of SWCNTs with specified chiralities via VSS processes (41). This strategy has been practiced in a series of examples (42–50). Because the CVD processes usually happen at a high temperature of ~800°C to 1100°C, phase change and the structural and compositional evolution of the catalysts may happen under carbon feeding. Therefore, in situ evidence is essential to establish an unambiguous relation between the catalysts and the structure of SWCNTs grown.

The environmental transmission electron microscope (ETEM) has shown to be an effective tool for directly imaging catalyst and nanotube growth in real time. In earlier dates, the in situ studies using ETEM were often carried out at moderate temperatures of 400°C to 650°C, which are generally lower than the normal CVD process for SWCNTs (42, 51–53). In recent years, ETEM research at much higher temperatures up to 1100°C brought us atomic evidence on the structural stability of intermetallic catalysts under a reactive environment (54) and the subsurface diffusion of carbon species in cobalt nanoparticles associated to the nucleation and growth of SWCNTs (17, 53). These attempts pave the way for the direct observation at the atomic scale of the formation of SWCNTs on catalyst nanoparticles and linking the nanoscaled growth mechanism to the statistics of structure distribution of SWCNTs.

In this work, we present a comprehensive study on the growth modes of SWCNTs on intermetallic Co7W6 and monometallic (Co, Cu, Fe, and Ni) catalysts by investigating the tube-catalyst size correlation.
(fig. S1). Using a state-of-the-art in situ aberration-corrected ETEM to track the nucleation and growth of nanotubes on catalyst nanoparticles, the relation between the state and structure of catalysts and the growth modes of SWCNTs was directly elucidated. The mechanism of the structure-controlled growth of SWCNTs on intermetallic Co₇W₆ was also revealed.

**RESULTS**

**In situ ETEM investigation of SWCNTs grown from intermetallic Co₇W₆ catalysts**

The intermetallic Co₇W₆ catalyst was prepared by using W-Co polyacid clusters as precursors, similar to our previous study (43). We performed the in situ aberration-corrected ETEM to study the growth of SWCNTs on intermetallic Co₇W₆ catalysts at 1000°C with an image resolution of 1.0 Å (see Materials and Methods). To minimize the electron beam damage effect, we also performed the nanotube growth with the electron beam off and then captured the ETEM images with the electron beam on at an acceleration voltage of 80 kV. With the aberration corrector implanted, the states (solid or molten) of nanoparticles can be easily distinguished.

Figure 1 (A and B) depicts the time sequenced ETEM images of a ~1.2-nm SWCNT cap nucleating on a Co₇W₆ nanocrystal at 1000°C in CH₄ (50 Pa). The fast Fourier transform (FFT) derived from the high-resolution ETEM image of this seeded nanocrystal shows characteristic diffractions of Co₇W₆ along the [1₁₀] direction (Fig. 1B, inset). The Co₇W₆ nanocrystals maintained a stable structure during the nucleation of the SWCNT cap. This observation indicates that in the VSS process, carbon atoms migrate on the surface of the solid catalyst nanocrystal to nucleate and grow a nanotube, which is different from the VLS process that endures carbon dissolution into the catalyst. The SWCNT nucleated along the c-axis direction of the Co₇W₆ catalyst, which is consistent with our previous ex situ experimental and theoretical simulation results of (12,6) tubes grown on Co₇W₆ catalysts (43).

Figure 1 (D and E) shows other in situ ETEM images and FFT of cap and SWCNT nucleation on Co₇W₆ nanocrystals. A 1.25-nm SWCNT with a chiral angle (θ) of 0° assigned to (16,0) was observed to grow perpendicular to the (116) plane of the Co₇W₆ catalyst (Fig. 1E), which was consistent with previous theoretical calculations where the (16,0) tube–(116) Co₇W₆ interface presented thermodynamic ascendancy (44). It was found that the nanoparticles in Fig. 1 (A and B) exhibit a hexagonal shape in the projection view, while nanoparticles in Fig. 1 (D and E) are more circular. There are two possible reasons leading to the difference in catalyst morphology. First, the different morphology may be attributed to the different orientation/projection of the nanocrystals. Second, the unclear contour of Co₇W₆ nanocrystals in Fig. 1 (D and E) may be due to the drift/obstacle of silica support, underfocus TEM conditions, and the direction of nanocrystals deviated from zone axis.

We observed that the end of the tubes/caps always attached partially to the edges and partially on the facets of the catalyst nanocrystals as schematically illustrated in Fig. 1C. This indicates that
the atomic edge of a Co$_7$W$_6$ nanocrystal is the active site to initiate the nucleation of a nanotube and the kinetic condition guides the diameter of the tube cap. This perpendicular growth mode resulted in SWCNTs with smaller diameters than the catalyst nanoparticles. It has been demonstrated in our previous study that carbon atoms did not dissolve into Co$_7$W$_6$ nanocrystals (54). Hence, the carbon species should migrate on the surface of the Co$_7$W$_6$ nanocrystal to feed the nucleation and growth of SWCNTs. The less efficient carbon feeding via the VSS process than via the VLS process might be the reason why larger catalyst particles facilitated the growth of SWCNTs.

**Diameter correlation between SWCNTs and catalyst nanoparticles through ex situ TEM**

We performed the CVD growth of SWCNTs on the TEM grids of Si$_x$N$_y$ thin films to perform ex situ TEM investigation. The diameter of the SWCNTs and the size of the catalyst nanoparticles attached on the tubes were measured from the high-resolution TEM (HRTEM) images (fig. S1). The detailed growth condition is shown in table S1. A flux of Ar (200 cm$^3$ min$^{-1}$) through the ethanol bubbler (ice-water bath) (denoted as Ar-ethanol) mixed with H$_2$ (50 cm$^3$ min$^{-1}$) was introduced to grow SWCNTs with a dominant chirality of (12,6) on the Co$_7$W$_6$ catalyst at 1030°C (43). Figure 2A shows a typical TEM image of an SWCNT with a diameter of ~1.3 nm grown from a ~4-nm Co$_7$W$_6$ catalyst. Other HRTEM images presenting the (12,6) SWCNTs grown on Co$_7$W$_6$ nanocrystals with different sizes are shown in fig. S2. When using Ar-ethanol/hydrogen of other flow rates (50:30 and 200:150 cm$^3$ min$^{-1}$) or methanol/hydrogen (200:20 cm$^3$ min$^{-1}$) to grow SWCNTs at 1050°C, we observed ~1.3- and ~1.8-nm SWCNTs growing from larger Co$_7$W$_6$ nanoparticles, respectively (fig. S3). The diameter enrichment here should be the result of the chirality selective growth of SWCNTs on different crystal planes of Co$_7$W$_6$ nanocrystals at corresponding optimum carbon feeding conditions (41). The growth mechanism of tubes on solid Co$_7$W$_6$ catalysts is very different from that on monometallic catalysts. Co$_7$W$_6$ catalysts exhibit a stable surface structure and grow SWCNTs via the surface diffusion of carbon rather than dissolving-precipitation (54).

For comparison, monometallic Cu and Co were used as catalysts to grow SWCNTs at the same condition for Co$_7$W$_6$ (1050°C, Ar-ethanol/hydrogen 200:50 cm$^3$ min$^{-1}$). We observed that the SWCNTs and caps grew in a tangential mode (Fig. 2, B and C, and fig. S4) and the tube/cap diameters were highly dependent on the size of the seeding Co and Cu nanoparticles in a broad range of 2 to 4 nm with $d_t/d_{NP} \approx 1$ (Fig. 2D, open circles and squares). The melting points of bulk Cu and Co are 1083° and 1495°C, respectively, and the melting point of metal nanoparticles often decreases with decreasing particle size (35). Therefore, Cu and Co nanoparticles should be molten at the temperature of 1050°C. We found from ETEM at 1050°C that Cu and Co nanoparticles are in liquid state (fig. S5). Therefore, the SWCNTs should grow from molten Cu and Co catalysts via a VLS process, encountering dissolution of carbon species in precipitation of carbon from, and nucleation of a tube cap on the molten catalyst (11).

**In situ ETEM characterization of SWCNTs grown from solid and molten Co catalysts**

As discussed above, the ex situ statistic measurements on the diameter of catalyst nanoparticles and SWCNTs grown at 1050°C showed that tubes present smaller diameters than Co$_7$W$_6$ nanoparticles and similar diameters to Co and Cu nanoparticles. Is this an intrinsic difference between the VSS and VLS process? We further investigated the nucleation of SWCNTs from Co catalysts in ETEM at 600°C. We found that most of the Co nanoparticles maintained the crystallized/solid state. Both the caps and the tubes exhibited a smaller size than the corresponding Co nanocatalysts (i.e., $d_t/d_{NP} < 1$) (Fig. 3). We also found that a few Co nanoparticles did not exhibit lattice fringes even by tuning the depth of e-beam continuously (Fig. 3D, fig. S7, and movie S2). These Co nanoparticles exhibit the amorphous structure, indicating the molten state. The tubes grown from the molten catalysts possess a similar diameter to the catalyst nanoparticles with $d_t/d_{NP} \approx 1$ (Fig. 3, D and E, open circles). In addition, we noted a notable change in diameter (consequently defects introduced) of SWCNTs grown from the molten catalyst (Fig. 3D and fig. S4). This may be caused by the size change of molten nanoparticles at the very high temperature. These in situ observations of Co catalysts are consistent with the ex situ TEM results. Both the in situ and ex situ results demonstrate the different growth modes of VLS and VSS mechanisms as shown in Fig. 3F.

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However, we must point out that the distribution of the diameters of SWCNTs grown on solid-state Co catalysts was fully random, unlike that of tubes grown from Co-W catalysts that concentrated on a few sizes. This is a crucial difference of the two kinds of catalysts.

We made a statistical analysis of the liftoff plane of solid cobalt catalyst for growing SWCNTs. The catalyst structure was analyzed using Miller indices by FFT to determine the faceted planes that favor the liftoff of nanotubes. It was observed that most of the solid Co catalyst nanoparticles orientated along the low-index zone axes of face-centered cubic (fcc) Co [110] and hexagonal close-packing (hcp) Co [0001] directions. As a result, the SWCNTs/caps were observed to nucleate on low-index fcc Co (111), (002), and hcp Co (1010), (2110) facets (Fig. 4A). When linking the nanotube/cap diameter to the Co crystal planes, we found that the same crystal plane of Co catalysts produced SWCNTs/caps with different diameters (Fig. 4B). This indicates that there is no specific structural correlation between the monometallic Co catalysts and SWCNTs. It was reported that the Co/MgO catalyst showed a selective growth toward (6,5) SWCNTs (42). The reason is that the Co nanoparticles that were stabilized by MgO through lattice mismatch presented a uniform small size and remained in solid state at a temperature of 600°C. Here, the Co catalysts were prepared on Si/SiO₂ wafers or Si₃N₄-TEM grids. The metal-support interaction is much weaker, and no lattice match exists; thus, the Co nanoparticles may melt and aggregate, leading to a nonselective growth.

The tubes grown at 1030°C from Co-W catalysts showed a dominant chirality of (12,6) and hence a focused diameter of 1.24 nm (Fig. 4). Those (12,6) tubes all grow from (0 0 12) planes of Co-W catalysts (fig. S2). Figure 4 again clearly demonstrates the distinct difference between Co and intermetallic Co-W catalysts.

**Comparison of chiral angle distributions of SWCNTs grown on different catalysts**

On the basis of the above in situ and ex situ TEM observations of SWCNTs grown from intermetallic and monometallic catalysts, we further investigated the chiral selectivity of SWCNTs and the effect of carbon feeding conditions on chiral selectivity under the two growth modes. We compared the chiral angle distributions of SWCNTs grown on solid intermetallic Co-W and molten monometallic (Fe, Ni, Co, and Cu) catalysts under a series of carbon feeding conditions at 1050°C. The detailed growth conditions of SWCNTs are shown in table S1.

We chose the selective growth of (14,4) SWCNTs on (1 0 10) planes of intermetallic Co-W catalysts at 1050°C (45) as an example to investigate the effect of carbon feeding conditions on chiral selectivity. The Co-W catalyst was prepared by using H₂ and H₂O vapor at 1050°C (table S1, entry 8), which is different from that prepared under H₂ for growing (12,6) SWCNTs (table S1, entry 2). The chirality of the tubes was characterized by Raman spectroscopy (excitation wavelength: 532, 633, and 785 nm) and electron diffraction. When the flow rates of ethanol carried by Ar and H₂ were 200:40 cm³ min⁻¹,
under a super-rich carbon feeding condition and thus changes the growth kinetics of nanotubes with different chiralities. These correspondences were verified with the intermetallic Co$_7$W$_6$ catalyst. The chiral angle distributions were notably changed when changing the carbon feeding because of the formation and evolution of carbides. However, the diameter of the resultant nanotubes was highly dependent on the sizes of the corresponding catalyst nanoparticles. Yet, there was no atomic-scaled structure correlation between them. When SWCNTs grew from solid Co catalysts, there is no correlation between tubes and catalyst nanoparticles in both diameter and structure. However, when SWCNTs grew from the intermetallic Co$_7$W$_6$ nanocrystals, their chiralities were determined by the structure of the catalyst facets where they nucleated. The catalyst facets exhibit different activities when exposed under various carbon/hydrogen conditions. Under certain carbon feeding conditions, the Co$_7$W$_6$ catalyst facets with suitable activities can nucleate SWCNTs efficiently, resulting in chirality selectivity.

**Discussion**

From all the above, when SWCNTs grew from the molten catalysts, the diameters of the resultant nanotubes were highly dependent on the sizes of the corresponding catalyst nanoparticles. However, kinetics could be a general mechanism of the selective growth of SWCNTs. However, kinetics can play a dominant role, which is often observed when monometal or common alloy catalysts are used. The growth of near (2m,m) SWCNTs with chiral angle enriched at ~19° was reported recently using W, Mo, or Re catalysts, demonstrating a kinetic factor dominant selectivity toward (2m,m) tubes. During the CVD process, W and Mo encountered complicated composition and structure changes with carbon feeding because of the formation and evolution of carbides and Re has a compacted highly symmetric hexagonal crystal structure, weakening the structural effect of the catalysts. Nevertheless, kinetics-controlled enrichment of near (2m,m) SWCNTs can be a strategy to realize the selective growth of certain (2m,m) chiralities. However, with the addition of the structural effect of the catalysts, the selective growth of a wider variety of (n,m) species can be realized, exhibiting the power of the dual control of thermodynamics and kinetics.

In summary, we elucidated the difference in growth modes of SWCNTs on solid-state intermetallic Co$_7$W$_6$ and Co catalysts, as well as various monometallic catalysts by in situ and ex situ studies. The SWCNTs grown on solid-state catalysts via the VSS mechanism presented smaller diameters than those of the catalyst nanoparticles. This might be caused by the inefficient carbon transport and supply on solid catalysts. On a Co$_7$W$_6$ nanocrystal, the tube nucleated from a facet with part of the circumference attached to the margin and the other part attached onto the facet. The chirality
of the tube was determined by the atomic arrangement of the facet. By optimizing the carbon feeding condition, the chirality selectivity can be achieved. However, the solid Co catalyst did not show any chirality selectivity. The SWCNTs grew on molten catalysts via the VLS mechanism, which always exhibited similar diameters to their seeding catalysts ($d_t/d_{NP} \approx 1$). The carbon feeding condition showed no controllable regulation to the chirality of the resultant tubes from VLS processes. These findings depicted the growth mechanism of SWCNTs on different catalysts, clarifying the difference between the VLS and VSS growth process and, more importantly, demonstrating the uniqueness and crucial role of intermetallic Co$_7$W$_6$ catalysts in the chirality-specific synthesis of SWCNTs. Taking into account the previous reports on kinetic control of SWCNTs, we can further conclude that the goal of structure-controlled growth of SWCNTs can

**Fig. 5. Chiral angle distribution of SWCNTs grown on different catalysts.** (A to C) Raman spectra of SWCNTs grown from Co$_7$W$_6$ catalysts at 1050°C. Excitation wavelength: 532 nm. (D to L) Chiral angle distributions of SWCNTs grown from Co$_7$W$_6$ (D to F), Co (G to I), Fe (J), Ni (K), and Cu (L) catalysts at 1050°C. The carbon feeding conditions are indicated in each panel: Ar through the ethanol bubbler is 200, 100, and 50 cm$^3$ min$^{-1}$; the H$_2$ feeding rate is fixed at 40 cm$^3$ min$^{-1}$. 

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be achieved by the careful manipulation on the interfacial structure between the catalyst nanocrystal and the nanotube nucleated together with the optimization of kinetic growth condition.

**MATERIALS AND METHODS**

**Growth of SWCNTs by CVD**

The heteropolyacid cluster \( \text{Na}_{15} \text{[Co(H}_2\text{O})_6]\text{[WO}_3\text{H}_2\text{O}]_3 \text{(P}_2\text{W}_{12}\text{O}_{40})_3] \text{·H}_2\text{O} \) was used as the catalyst precursor. We used three different procedures described in our previous works (43–45) to prepare Co\(_7\)W\(_6\) catalysts and perform CVD growth of SWCNTs on Si/SiO\(_2\) wafers, respectively. The SiN\(_2\) film (thickness: 5 and 10 nm) with defect holes was used as the support instead of the Si/SiO\(_2\) wafer to prepare Co\(_7\)W\(_6\) catalysts and perform CVD growth under the same conditions, which was directly used for ex situ TEM characterization.

The metal salts of Co(OAC)\(_2\), Cu(OAC)\(_2\), FeCl\(_3\), and NiCl\(_2\) were used as catalyst precursors to prepare monometallic nanoparticles, respectively. Then, we performed the growth of SWCNT at 1050°C on SiN\(_2\) grid for ex situ TEM study. The carbon feeding conditions were the same as used in Co\(_7\)W\(_6\) catalysts. The detailed conditions of catalyst preparation and CVD growth are summarized in table S1.

**Ex situ TEM characterization of catalysts**

Ex situ TEM was carried out on four systems: FEI Tecnai F20 (200 kV), FEI Tecnai F30 (300 kV), JEOL 2010F (200 kV), and JEOL 2100F (200 kV). The catalysts were prepared on SiN\(_2\) TEM grids in a tube furnace and then directly used to perform TEM.

**In situ ETEM experiment**

ETEM was carried out on an image aberration-corrected FEI Titan G2 80–300 ETEM microscope (80 kV) with an image resolution of 1.0 Å. For the Co\(_7\)W\(_6\) catalyst, the as-prepared SiO\(_2\) sphere–supported Co\(_7\)W\(_6\) nanoparticles were first ultrasonically dispersed in ethanol and then dropped onto the SiN\(_2\) membrane with microholes and dried in air, which was mounted onto a micro-electron mechanical system (NanoEx-i/v)–based microheater from Thermo Fisher Scientific. The as-prepared specimen was first heated to 700°C in H\(_2\) (100 Pa) for about 30 min to remove organic impurities and then cooled to room temperature. Then, CH\(_4\) (99.9%) was introduced into the TEM chamber. Once the target pressure was reached and stabilized, the specimen was heated again to the target temperature of 1000°C.

For the Co catalyst, the cobalt acetate \([\text{Co(OAC)}_2]/\text{ethanol solution (0.1 mmol liter}^{-1})\] was used. The as-prepared specimen was first heated to 600°C in 30 s and stabilized at 600°C under high vacuum (\(10^{-5}\) Pa) for 10 min with e-beam shut down. During annealing at 600°C, the acetate groups decomposed to carbon and other species (CO, C\(_2\)H\(_4\), and H\(_2\)), acting as reductants to reduce cobalt (II) to metallic Co nanoparticles and also as a solid carbon source to feed the growth of SWCNTs (17).

**Characterization of SWCNTs**

We collected the Raman and ED data based on counting the number of individual SWCNTs independent of tube length. The Raman spectra of SWCNTs were collected with an ARAMIS Jovin Yvon-Horiba LabRam system equipped with 532-, 633-, and 785-nm laser excitations. We chose the laser beam spot of 1 μm in diameter to collect the Raman RBM signal of the SWCNTs. The region with a low density of SWCNTs was selected for Raman measurements to avoid multilayers under a 1-μm laser beam spot. To avoid the repeated collection of Raman data of long SWCNTs, every measurement was performed by moving the laser spot at a step of 5 μm. The assignment of \((n,m)\) chiral angle of SWCNTs was based on the Kataura plot (11).

A JEOL 2010F microscope operated at 200 kV was used and the electron diffraction patterns were recorded with a high-resolution two-dimensional charge-coupled device array. A FEI Tecnai T20 microscope operated at 80 kV was also used to acquire the electron diffraction patterns. The chiral angle of an individually suspended SWCNT was determined from an electron diffraction pattern with a calibration-free intrinsic layer line-spacing method (60).

**SUPPLEMENTARY MATERIALS**

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