

Growth of Single-Walled Carbon Nanotubes with Different Chirality on Same Solid Cobalt Catalysts at Low Temperature

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Currently, designing solid catalysts at high temperature is the main strategy to realize single-walled carbon nanotubes (SWNTs) with specific chirality, meaning it is very hard and challenging to create new catalysts or faces to fit new chirality. However, low temperatures make most catalysts solid, and developing solid catalysts at low temperature is desired to realize chirality control of SWNTs. A rational approach to grow SWNTs array with different chiralities on same solid Co catalysts at low temperature (650 °C) is herein put forward. Using solid Co catalysts, near-armchair (10, 9) tubes horizontal array with ≈75% selectivity and (12, 6) tubes array with ≈82% are realized by adopting a small amount of ethanol and large amount of CO respectively. (10, 9) tubes are enriched for thermodynamic stability and (12, 6) tubes for kinetics growth rate. Both kinds of tubes show a similar symmetry to the Co (1 1 1) face with threefold symmetry for the symmetry matching nucleation mechanism proposed earlier. This method provides a new strategy to study the nucleation mechanism and more possibilities for preparing new solid catalysts to control the structure of SWNTs.

Single-walled carbon nanotubes (SWNTs), since reported in 1993,^[1] have been regarded as a promising material owing to unique structure-dependent properties, especially in nanoelectronics applications.^[2,3] Therefore, tremendous efforts have been made to pursue the specific-chirality growth of SWNTs, including designing various catalysts^[4–9] and growth process controlling.^[10–12] Despite of some progresses made in chirality selective synthesis of SWNTs, the mechanism for the experiment successes is far from clarification.

Currently, epitaxial growth from well-defined seeds, such as solid catalysts^[13–17] and segments of carbon nanotubes,^[18–21] has been thought to be the most promising strategy to realize this goal. At present, mainly high temperature solid catalysts were developed to realize structure-controlled growth of SWNTs. For example, using Mo₂C and WC solid catalysts, a few (2*m*, *m*) SWNTs, such as (12, 6) and (8, 4), have been

synthesized respectively with symmetry-matching mechanism.^[13] Moreover, using W₆Co₇ solid catalysts, recent progresses enable the synthesis of (12, 6),^[14] (16, 0),^[15] and (14, 4)^[16] tubes with structure-matching growth mechanism. Both two mechanisms imply the thermodynamic nucleation mechanism for SWNTs on solid catalysts. In addition, by adopting extreme dilute carbon feeding, another SWNT family, (*n*, *n*–1) tubes, with sub-stable structure, could be enriched by using large solid Co catalysts at high temperature.^[17] However, it is challenging to design new solid catalysts at high growth temperature and species of SWNTs obtained are always limited in single chirality or one family for one catalyst.

In fact, most metal nanoparticles could keep solid state at low temperature and their structures could be tuned easily by treating in different ways. Some of these catalysts have been proved to grow SWNTs with different morphologies, such as Co/Mo, Fe, and Ni for powder SWNTs samples,^[4,22] and Fe/Al₂O₃ for CNTs vertical array.^[23] However, the complex growth condition makes it impossible to grow SWNTs in uniform structure. Therefore, developing solid catalysts at low temperature is necessary to directly obtain SWNTs horizontal array with chirality controlling and helpful for further exploration of growth mechanism.

Herein, we put forward a rational approach to grow SWNTs horizontal array with different chiralities on same solid Co catalysts at low temperature (650 °C). In our work, growth of SWNTs horizontal array at low temperature was first realized on quartz substrate by introducing much more etching agents, which can inhibit the high activity of solid catalysts with low carbon solubility. Then (1 1 1) face of Co nanoparticles are identified as the direct template to grow SWNTs, and near-armchair (10, 9) tubes with ≈75% selectivity and (12, 6) tubes with ≈82% were realized using a few ethanol and large amount of CO to reduce or increase growth tube's growth rate respectively. (10, 9) Tubes were enriched for thermodynamics stability and (12, 6) tubes for fastest kinetics growth rate. Both their symmetries show a similar symmetry to the Co (1 1 1) face for the symmetry matching nucleation mechanism proposed earlier. This opens up a new avenue for controlling chirality of SWNTs and developing further electronic applications.

Previous theoretical calculations^[24] demonstrate that (2*m*, *m*) tubes on flat Co (1 1 1) face have the largest growth rate than other tubes with similar diameter. While our previous studies^[17]

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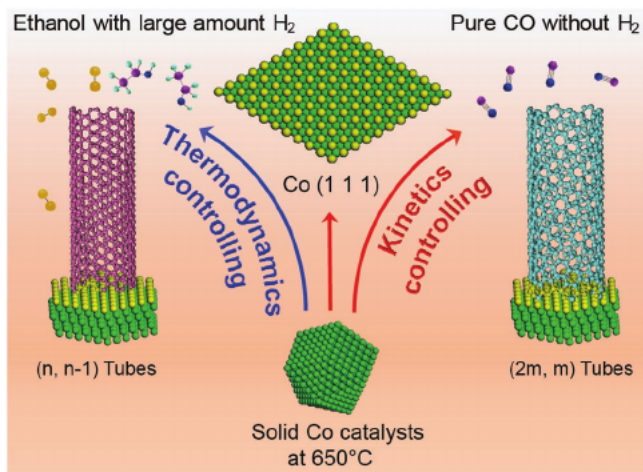


Figure 1. Schematic illustration of the strategy to realize thermodynamics and kinetics selectivity of SWNTs using solid Co catalysts at low growth temperature (650 °C).

show that armchair tubes own the most stable edge structure on Co (1 1 1) face. But for absent of kinks, armchair tubes are inhibited in kinetic and this leads to the enriched growth of near-armchair tubes, $(n, n-1)$, as thermodynamics selective results. According to these analyses, we put forward our design shown in **Figure 1** to realize thermodynamics and kinetics selectivity of SWNTs using same solid Co catalysts. To realize this goal, solid Co catalysts are first assured and two methods could be adopted, one is using large Co nanoparticles at high growth temperature, and the other one is reducing growth

temperature to ensure the stability of small Co nanoparticles. In the former, large Co nanoparticles always present low efficiency to grow SWNTs with large diameter as we know. Therefore, the latter is preferred and experiments are explored to realize the growth of SWNTs horizontal array at low temperature. When using direct disperse Co catalysts and a ratio of 50/400 for C/H at 650 °C, amorphous carbon was obtained shown in **Figure 2a**. Through introducing much more hydrogen during growth process, such as C/H ratio is 20/400, a few SWNTs would appear as shown in **Figure 2b**.

Further growth difference for high and low temperature was compared. As shown in **Figure 2c**, the density of SWNTs horizontal array obtained at low growth temperature is much lower than those obtained at high growth temperature. Another fact is high growth temperature shows a greater tolerance on C/H ratios to grow SWNTs than low growth temperature, also proved in **Figure 2d**. In addition, statistics on length of SWNTs with different growth temperature in **Figure 2d** reveals SWNTs obtained at low growth temperature own much shorter length than those at high growth temperature. Narrow growth window, low density, and short length of SWNTs at low temperature indicate catalysts are very different in terms of state and activity.

Compared the SEM images in **Figure 2a** (**Figure S1**, Supporting Information), catalysts at low temperature produce much more amorphous carbon than equivalent amount of those at high temperature under the same growth condition. The main reasons lie in the difference of activity and carbon dissolving capacity, which both are affected by catalysts state. At low growth temperature, Co catalysts are solid (**Figure S6**, Supporting Information), while most of Co nanoparticles will tend to be liquid at high growth temperature. Solid catalysts

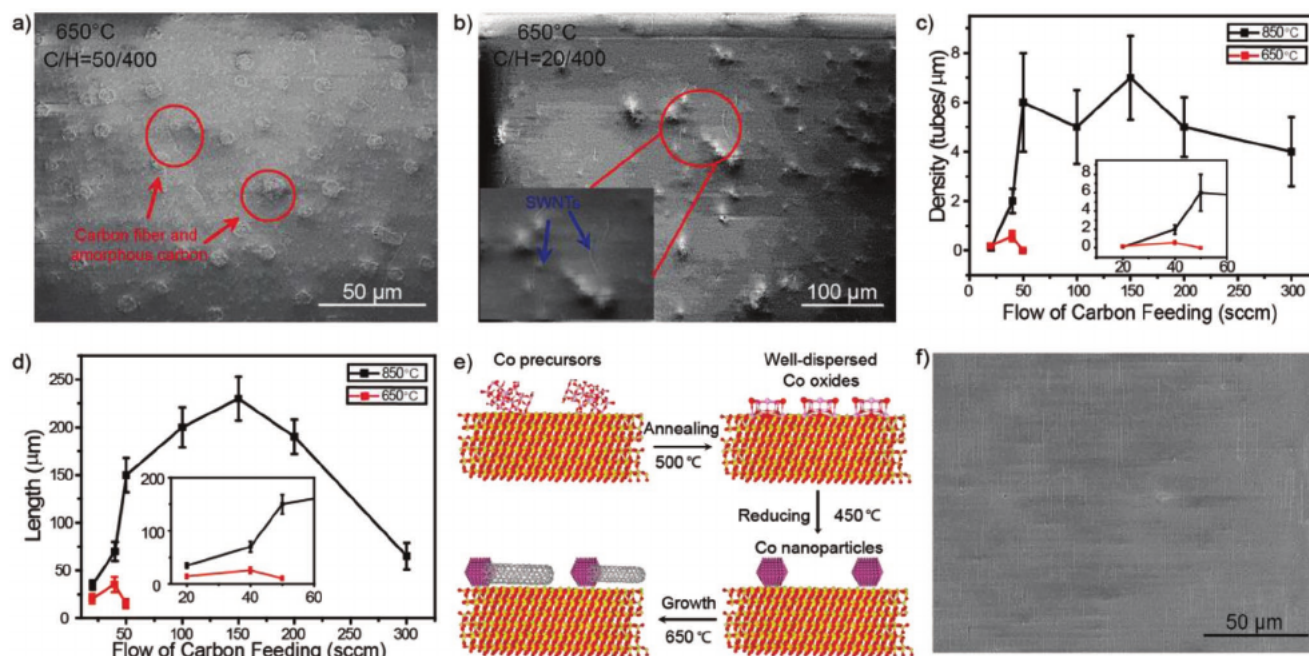


Figure 2. Realizing Growth of SWNTs horizontal array at low temperature. Using different C/H ratios, a) 50/400 and b) 20/400, to grow SWNTs on substrate with Co catalysts. The red circles in insets (a) and (b) represent the amorphous carbon and SWNTs respectively. Statistics on the c) density and d) length of SWNTs obtained at different growth temperature with different amounts of carbon source. e) The strategy to obtain well dispersed Co catalysts for growing SWNTs at low temperature. f) SEM image of SWNTs horizontal array obtained using the strategy in inset (e) with C/H ratio, 30/400.

show better and stable catalysts activity, but lower carbon solubility than liquid catalysts. But for the higher carbon solubility of liquid catalysts at high growth temperature, carbon atoms produced by carbon feedings will have access to inside of catalysts and are not easy to aggregate on the catalysts surface, which leads the high tolerance of carbon source based on vapor–liquid–solid (VLS) mechanism. Correspondingly, growth of SWNTs at low temperature need much more etching agents, such as hydrogen, to inhibit catalysts activity and surface aggregation of carbon atoms, which proved in our experiments.

On the other hand, for the lifetime of the catalyst is limited and low temperature will decrease the growth rate of SWNTs, the length of SWNTs is hard to be improved, but the density of SWNTs at low growth temperature could be improved by tuning the density of Co catalysts. Figure 2b, showing some large nanoparticles except amorphous carbon around SWNTs, indicates that the catalysts are not well dispersed, which also proved by the atomic force microscopy (AFM) image (Figure S3, Supporting Information). To better disperse catalysts, an extra annealing for the catalysts precursors is introduced as shown in Figure 2e. After annealing at 450 °C, AFM images (Figure S4a, Supporting Information) imply the catalysts precursors are well dispersed. Using hydrogen to reduce the precursors, monodispersed solid Co catalysts with proper size were obtained (Figure S4b, Supporting Information). Then, at 650 °C, with a proper C/H ratio,

clean SWNTs horizontal array shown in Figure 2f with mean length of 35 μm and density of ≈ 0.3 tubes per μm and without any amorphous carbon were finally acquired.

Based on the above experiments, the specific template was explored. First, SWNTs were grown on SiN grid with 10 nm thickness at 650 °C and the result was characterized by transmission electron microscopy (TEM), as shown in Figure 3a, in which a SWNT grew from a nanoparticle evidently. High resolution transmission electron microscopy (HRTEM) in Figure 3b indicates the size of catalyst is 5.3 nm and the diameter of SWNT is 4.1 nm, which fits the perpendicular growth mode.^[25] The lattice spacing of this catalyst in Figure 3b is 0.206 nm, which presents the Co (1 1 1) face. The tube is vertical to the Co (1 1 1) face and catalysts, captured in situ TEM with heating, is also further proved to be solid (Figure S6, Supporting Information). Further elements analysis was done based on the STEM images shown in Figure 3c,d, and the corresponding results were shown in Figure 3e (Figure S8b, Supporting Information), which indicate the catalyst was mainly consisted of cobalt and almost no carbon. In addition, X-ray photoelectron spectroscopy (XPS) was done for the SWNTs with catalysts on quartz substrate and SiN grid, and as shown in Figure 3f, there is no Co–C peak that also is proved in analysis of C peak in XPS (Figure S11, Supporting Information). On the other hand, oxidized cobalt was formed for the direct exposure to air after

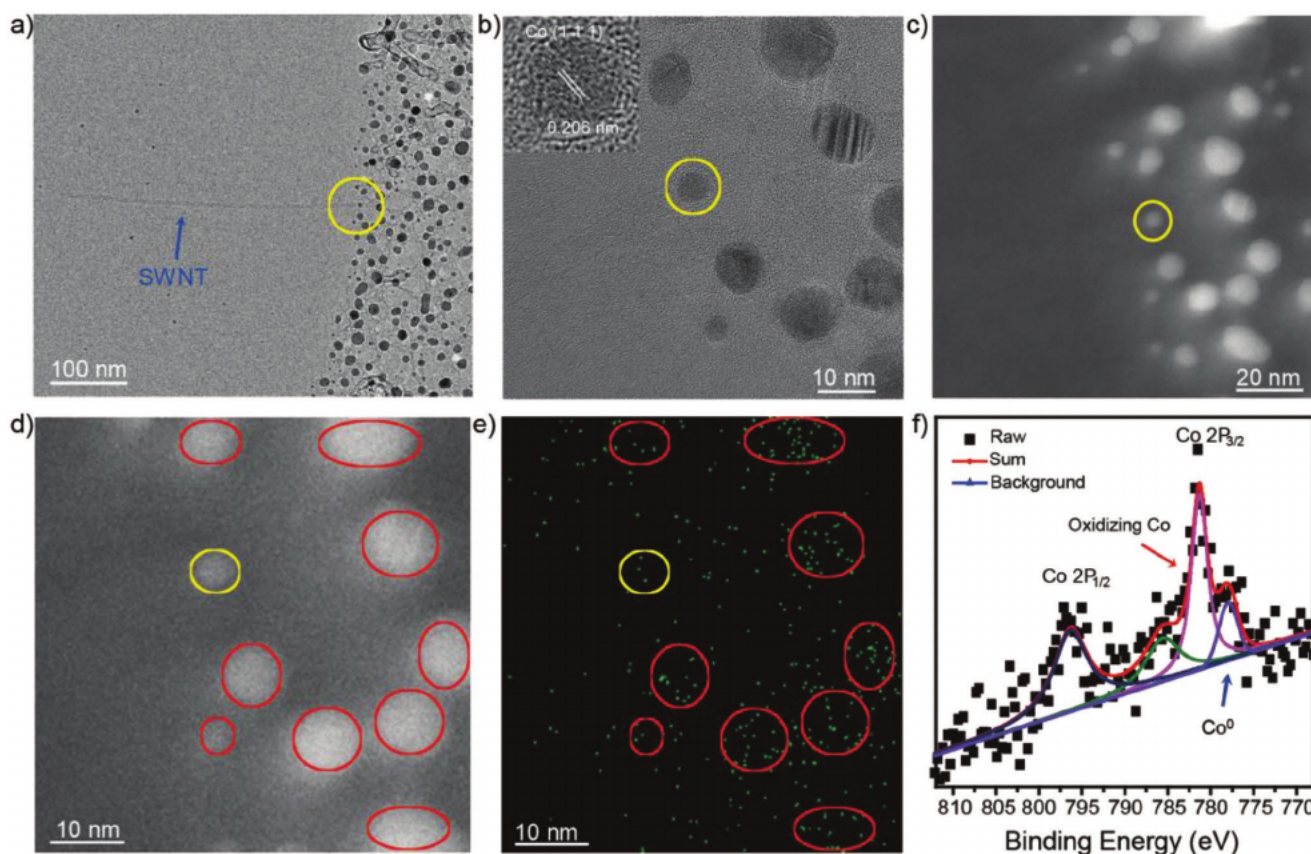


Figure 3. a) TEM images of a SWNT grown from a nanoparticle in the yellow circle on SiN grid at 650 °C and C/H ratio, 30/400. b) HRTEM was used to characterize the catalysts in inset (a) and it shows a perpendicular growth mode at low temperature. The inset is HRTEM image of the Co catalysts. c,d) STEM images with different magnifications and e) element mapping to show the distribution of Co. And all the yellow circles represent the same catalyst. f) XPS for catalysts on quartz substrate after SWNTs growth at 650 °C and it indicates no cobalt carbides are formed.

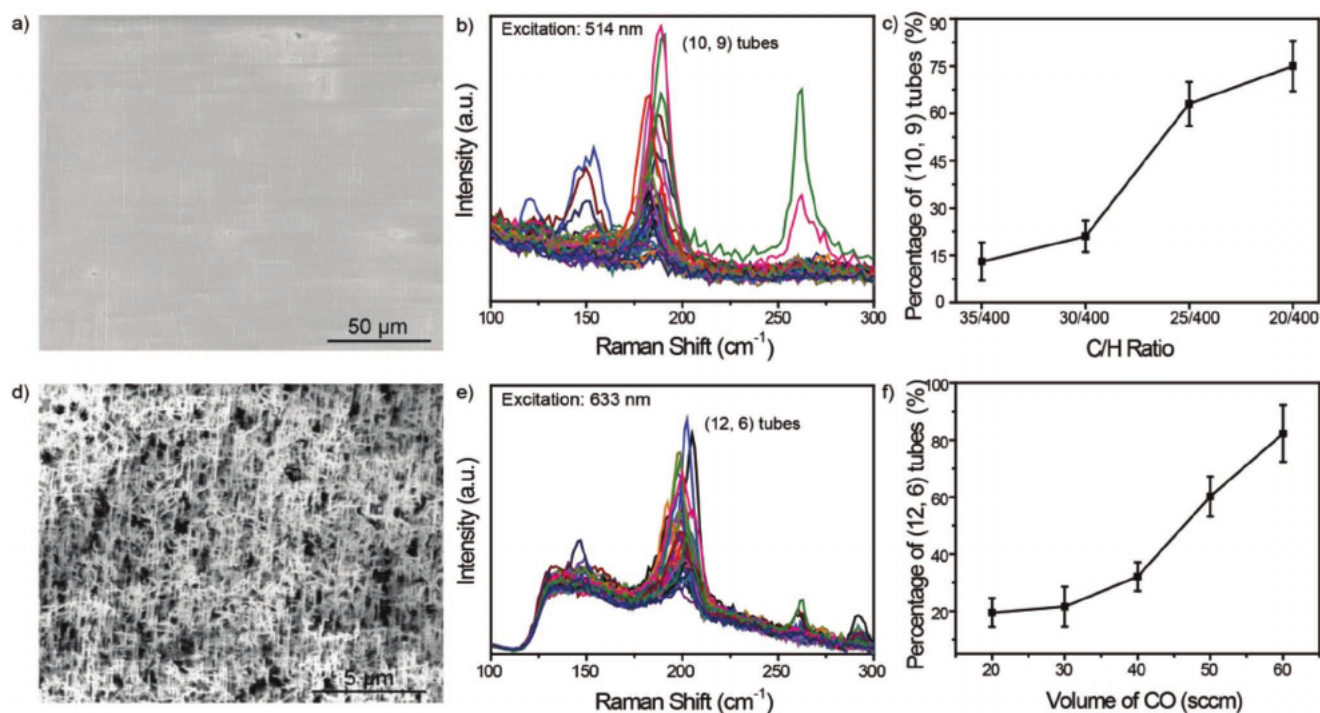


Figure 4. a,d) The SEM images of SWNTs with thermodynamic and kinetic selectivity obtained using ethanol and CO as carbon feeding respectively at 650 °C. For ethanol, the C/H ratio is 20/400, but for CO, in the growth of SWNTs, only 60 sccm CO with 300 sccm Ar and without any hydrogen. b,e) The Raman mapping results for SWNTs in insets (a) and (c) with different lasers, 514 and 633 nm. c,f) The evolution trend of (10, 9) tubes and (12, 6) tubes with the change of C/H ratios and volume of CO respectively. And the C/H ratio was defined as the flow ratio of Argon through ethanol tank and hydrogen.

SWNTs growth and therefore, Co⁰ is the main element for the catalysts. Moreover, X-ray diffraction (XRD) is applied to prove this fact by comparing the samples treated with different atmospheres on quartz sand, and the result (Figure S12, Supporting Information) reveals that after growth of SWNTs, there is still no cobalt carbides formed but exists the peak presenting Co nanoparticles. Therefore, Co nanoparticle is the direct template for the SWNTs growth, during which it adopts (1 1 1) face as the epitaxy template.

Using solid Co catalysts, different chirality selective growth of SWNTs could be realized successfully. Considered hard decomposition of CH₄, and high percentage carbon atoms of C₂H₄ or C₂H₂, ethanol was the best choice to tune the thermodynamics selective growth of SWNTs firstly. Thermodynamics selectivity requires a slower growth rate and therefore, the concentration of ethanol is provided as low as possible. In the experiments, when adopted 20 sccm ethanol bubbled by Ar with 400 sccm H₂, SWNTs, as shown in Figure 4a, obtained the lowest growth rate and if further reducing the concentration of ethanol, SWNTs will not appear in our system. Raman spectra with different lasers were used to characterize the sample and the results were shown in Figure 4b (Figure S13, Supporting Information), which indicate an obvious enrichment with the peak at 190 cm⁻¹ as the thermodynamic selective result. According to Kataura-plot and literatures, this peak is assigned to (10, 9) tubes and statistics on RBM peaks showed about 75% selectivity of (10, 9) tubes. Figure 4c shows the enrichment tendency of (10, 9) tubes, which seriously depends on the concentration of ethanol. On the other hand, to pursue the kinetic selectivity

growth of SWNTs, growth rate should be maximized through introducing carbon feeding with the highest concentration possible. In the experiments, we found C₂H₅OH, C₂H₄, and C₂H₂ with excessive concentration would produce much amorphous carbon because they are easy to be decomposed. Further screened, CO was chosen to realize kinetic selectivity in that disproportionation reaction of CO produces not only carbon, but also CO₂ or O_{ads}, which could be used as etching agents to remove the excess carbon on the surface of catalysts. Especially O_{ads} can react with amorphous carbon to reproduce CO₂ or CO, and therefore it maintains the better activity of catalysts. Using CO as carbon feeding, it is also Co nanoparticle that is direct template to grow SWNTs proved by TEM (Figure S9, Supporting Information). Based on this, different amounts of CO were used to explore the kinetic selective growth of SWNTs and when used 60 sccm CO, (12, 6) tubes at 193 cm⁻¹, detected by Raman spectra with 633 nm, were enriched evidently, as shown in Figure 4d,e. In the Figure 4f, it shows the enrichment tendency of (12, 6) tubes and it is the kinetic selective result on solid Co catalysts. Statistics on RBM peaks showed about 82% selectivity of (12, 6) tubes. Finally, both (10, 9) tubes with near threefold symmetry and (12, 6) tubes with threefold symmetry show a similar symmetry to the Co (1 1 1) face, which further prove our symmetry matching nucleation mechanism proposed earlier.^[13]

We found that the key point to realize the growth of SWNTs horizontal array at low temperature is to introduce much more etching agents, such as H₂, to remove excess carbon on the catalysts surface, because of the high activity and low

carbon solubility of solid Co catalysts. Based on solid Co catalysts, thermodynamic and kinetic selective growth of SWNTs was explored respectively. Because of low C/H ratio and easy cracking, ethanol with large amounts of hydrogen was chosen to realize thermodynamic selectivity and in this system, it is near-armchair tubes, such as (10, 9) tubes, that is the final products. Adopting CO as carbon feeding, (12, 6) tubes will be enriched as the kinetic selective products for their large kinetic growth rate. (10, 9) Tubes with near threefold symmetry and (12, 6) tubes with threefold symmetry show a similar symmetry to the Co (1 1 1) face, which further proves our symmetry matching nucleation mechanism proposed earlier.

Experimental Section

Methods and Synthesis: In the general growth of SWNTs, the Co precursors, usually $\text{Co}(\text{NO}_3)_2$ ethanol solution with the concentration $0.1 \times 10^{-3} \text{ M L}^{-1}$, were spinning coated with 2000 rpm or direct coated with 4 μL on quartz substrates. The quartz substrates containing catalysts were placed into a 1 inch tube and heated in air to 850 °C or 650 °C for 30 min and after the system was purged with 300 sccm argon for 5 min, a flow of hydrogen (200 sccm) and argon (300 sccm) was introduced to reduce the catalyst precursors for 10 min to form catalysts. Then the designed flows of hydrogen and extra argon through an ethanol bubbler were introduced to grow SWNTs at different temperature for 30–50 min, as shown in Figure 2c,d. Finally, the system was cooled to room temperature with the protection of H_2 and Ar.

Measurements on Mean Length and Density of SWNTs Horizontal Array at Low Temperature: To obtain the mean length, every tubes were amplified and determined according to the scale bar, and 100 tubes have been measured. And for the density, statistics of tubes density was done in every 10 μm and about twenty different places have been adopted to decide the final mean density.

Extra Dispersing Co Precursors to Improve Density of SWNTs at Low Growth Temperature: Co precursors, usually $\text{Co}(\text{NO}_3)_2$ ethanol solution with the concentration $0.1 \times 10^{-3} \text{ M L}^{-1}$, were spinning coated with 2000 rpm or direct coated with 4 μL on quartz substrates. Then, the quartz substrates containing catalysts were placed into muffle furnace and annealed in the air as shown in Figure 2e. The substrates were heated in air to 450 °C in 4 h and kept at 450 °C for 1 h. Finally, the substrates were cooled to room temperature in the air naturally.

The quartz substrates containing well-dispersed catalysts were placed into a 1 inch tube and heated in air to 450 °C in 20 min and after the system was purged with 300 sccm argon for 5 min, a flow of hydrogen (200 sccm) and argon (300 sccm) was introduced to reduce the catalyst precursors for 10 min at 450 °C. Then the substrates were heated to 650 °C in 15 min with the flow of hydrogen (200 sccm) and argon (300 sccm). When the temperature rose to 650 °C, the designed flows of hydrogen and extra argon through an ethanol bubbler were introduced to grow SWNTs for 30–50 min, as shown in Figure 2e. Finally, the system was cooled to room temperature with the protection of H_2 and Ar.

Enriched Growth of (10, 9) Tubes and (12, 6) Tubes: The quartz substrates containing well-dispersed catalysts were placed into a 1 inch tube and heated in air to 450 °C in 20 min and after the system was purged with 300 sccm argon for 5 min, a flow of hydrogen (200 sccm) and argon (300 sccm) was introduced to reduce the catalyst precursors for 10 min at 450 °C. Then the substrates were heated to 650 °C in 15 min with the flow of hydrogen (200 sccm) and argon (300 sccm). When the temperature rose to 650 °C, the flows of hydrogen (400 sccm) and extra argon (10 sccm) through an ethanol bubbler were introduced to grow (10, 9) tubes for 30–50 min to realize thermodynamic selectivity. But when the temperature rose to 650 °C, only the flows of Argon (300 sccm) and CO (60 sccm) were introduced to grow (12, 6) tubes for 15–20 min to realize kinetic selectivity.

TEM Characterizations for the Catalysts: To obtain the exact structure and state of catalyst in our system, catalysts were deposited on the SiN grid with $\approx 10 \text{ nm}$ film to grow SWNTs in the same CVD system and then the grid was used to do the TEM (JEM-2100F, 200 kV) observation. And the in situ TEM was also done based on JEM-2100F with heating sample rod.

XPS and XRD Characterizations for the Catalysts: XPS was done for the sample after SWNTs growth on the quartz substrate and parallel experiments were done to further confirm XPS results. But for XRD, the catalysts on the quartz substrate are hard to be detected and quartz sand was adopted to load the same catalysts with similar annealing process. Then, XRD characterizations were done for the samples before and after SWNTs growth, and the results were shown in Figure S12 in the Supporting Information.

Raman and AFM Characterizations for the Thermodynamic and Kinetic Selectivity of SWNTs Growth: Both the (10, 9) and (12, 6) tubes were transferred on the SiO_2 (300 nm)/Si substrates for Raman detection. Because they are horizontal arrays, Raman line mapping was adopted with 1 μm step size. And AFM was directly done on the quartz substrates to characterize the morphology and diameter distribution of SWNTs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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