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Environmental Transmission Electron Microscopy Investigations of Pt-Fe₂O₃ Nanoparticles for Nucleating Carbon Nanotubes

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Abstract:

Elucidating the evolution of bimetallic catalyst for nucleating carbon nanotube has been challenging. In this work, acorn-like Pt-Fe₂O₃ nanoparticles are developed for the growth of single-walled carbon nanotubes (SWCNTs) by chemical vapor deposition. Using *in situ* environmental transmission electron microscopy, restructuring of the acorn-like Pt-Fe₂O₃ nanoparticles at reaction conditions is investigated. Upon heating to reaction temperature, ϵ -Fe₂O₃ is converted to β -Fe₂O₃, which can be subsequently reduced to metallic Fe once introducing CO. As Pt promotes the carburization of Fe, part of the metallic Fe reacts with active carbon atoms to form Fe_{2.5}C instead of Fe₃C, catalyzing the nucleation of carbon nanotubes. Nanobeam electron diffraction characterizations on SWCNTs grown under ambient pressure at 800 °C demonstrate that their chiral angle and diameter distributions are similar to those of SWCNTs grown on monometallic Fe. The results further indicate that the active components in both the catalysts, determining the chirality distribution of SWCNTs, are similar. In addition, Pt facilitates the reduction of Fe₂O₃, rendering SWCNT growth at a relatively low temperature of 700 °C. This work provides a profound understanding of the structural reconstruction in bimetallic catalyst, shedding more light on designing novel catalysts for the growth of SWCNTs.

Keywords: single-walled carbon nanotube, Pt-Fe bimetallic catalyst, chirality, structural evolution, *in situ* environmental transmission electron microscopy

1. Introduction

Since the landmark work on the synthesis of single-walled carbon nanotubes (SWCNTs) by electric arc technique using Fe-containing cathode,[1] the search for better catalysts has been one of the main tasks in controlled synthesis of SWCNTs. Of numerous catalysts studied, bimetallic catalysts have attracted particular interests due to their high activity and better control over SWCNT structures by

chemical vapor deposition (CVD) technique. As the result of adding a second metal, catalysts, such as CoMo,[2] CuFe,[3] RuFe,[4] PtCo[5] and WCo,[6, 7] lead to higher carbon nanotube yields and narrower chirality distributions compared to their monometallic counterparts. In spite of these progresses, secret behinds the successful growth is far from being clarified. For example, a mysterious WCo bimetallic system has been reported by two research groups to selectively grow (12, 6) SWCNTs.[6, 7] Yang *et al.*[6] proposed that the fabrication of stable W_6Co_7 alloy is responsible for the preferential synthesis of (12, 6) SWCNT. While recent work by An *et al.*[7] identified an intermediate structure of Co_6W_6C , where most of W atoms disappear after 5 min CVD growth, indicating the complexity in determining the active catalyst components for SWCNT synthesis.

Pt-based bimetallic particles have long been applied as excellent catalysts for generating carbonaceous deposits, such as carbon filaments and SWCNTs.[5, 8, 9] Pioneer work by Bark *et al.*, [8] reported the formation of filaments when heating Pt-Fe particles in acetylene. It was discovered that, with the addition of Pt into Fe catalyst, the growth rate of filament increased two orders of magnitude.[8] Using PtCo catalyst, Liu *et al.*[5] achieved a narrow SWCNT chirality distribution at a relatively high temperature of 800 °C. Recently, Ohashi *et al.*[9] prepared half-buried FePt between deposited MgO for growing vertically aligned SWCNTs with metallic chirality.

Besides the achievements in carbon nanotube synthesis using Pt-based catalyst, uncovering the structure of catalyst particles under reaction conditions is of fundamental importance in understanding SWCNT nucleation mechanisms and establishing structure correlations between catalysts and SWCNTs. Although alloy formation was observed after CVD growth by *ex situ* characterizations,[5, 9] some works suggest that separation of the alloy components could occur under certain conditions.[8, 10] In order to address the detailed structural change and track the evolution of catalyst nanoparticles, it is necessary to

map the atomic structure in reactive environments using *in situ* environmental transmission electron microscopy (TEM).[11]

In the work reported here, we present an acorn-like Pt-Fe₂O₃ catalyst for the growth of carbon nanotubes. Combined with *ex situ* TEM characterizations on catalyst nanoparticles before and after CVD growth, *in situ* environmental TEM was carried out to clarify the structural dynamics of such hybrid nanoparticles in nucleating carbon nanotubes. In addition, SWCNTs grown at different temperatures will be characterized and compared with those synthesized on monometallic Fe.

2. Materials and methods

2.1 Formation of acorn-like Pt-Fe₂O₃ catalyst

Similar to the previously reported Fe-Ti-O catalyst,[12] the Pt-Fe₂O₃ catalyst was prepared by combining Pt layer deposition onto premade Fe nanoparticles with subsequent high-temperature air calcination. Briefly, FeO_x nanoparticles generated by hydrolysis of ferric chloride[13] were first casted onto Si₃N₄ TEM grids, a thin layer of Pt was then sputtered onto the grids with a current of 10 mA for 1 min in an Emitech K100X glow discharge unit. The catalyst was finally annealed at 800 °C for 20 h in a muffle furnace.

2.2 Growth of carbon nanotube with Pt-Fe₂O₃ catalyst

Carbon nanotubes were grown by CVD. Pt-Fe₂O₃ catalyst supported by Si₃N₄ TEM grid was loaded into a horizontal CVD reactor followed by flushing with 200 cm³/min helium. After reaching the desired temperature, CO with a flow rate of 200 cm³/min was introduced to the CVD reactor, in place of helium stream. CO was turned off after 1h and the CVD reactor was cooled under helium environment.

2.3 Characterizations of Pt-Fe₂O₃ catalyst and carbon nanotubes

TEM observations of Pt-Fe₂O₃ nanoparticles were carried out on a JEOL-2200FS TEM and a Zeiss LIBRA 200FMC TEM. Elemental analysis was performed by energy dispersive X-ray (EDX) spectroscopy and electron energy-loss spectroscopy (EELS). The structure and morphology of carbon nanotubes were studied by a JEOL-2200FS TEM operated at 80 kV. Electron diffraction patterns of randomly distributed carbon nanotubes were taken to determine the chirality and diameter distributions of carbon nanotubes.

2.4. In situ environmental TEM studies on dynamics of Pt-Fe₂O₃ catalyst and nucleation of carbon nanotube

Pt-Fe₂O₃ catalyst supported by a Si₃N₄ TEM grid was mounted in a Gatan heating holder, which was then inserted in an FEI Titan 80-300ST environmental TEM and heated to 700 °C in vacuum. Subsequently, a flow of CO (6 cm³/min) was introduced into the TEM chamber to stabilize at a pressure of 8 mbar. The structural evolution of the catalyst particles was monitored in real time during the chemical reaction at 300 kV.

3. Results and Discussion

3.1. Characterizations of Pt-Fe₂O₃ catalyst before and after CVD growth

ESI **Figure S1a** presents a TEM close view image of nanoparticles prepared by Pt deposition onto iron oxide nanoparticles followed by high temperature calcination. A detailed examination shows that the acorn-like particles consist of a dark embryo partly enclosed by a light cupule. On the basis of the TEM image (**Figure 1a**) and its corresponding fast Fourier transform (FFT) pattern (**Figure 1b**), the dark embryo can be well assigned as face centered cubic (FCC) structured Pt with a lattice parameter of 0.393

nm (pdf card: 04-0802). The lattice spacing measured from the TEM image is 0.23 nm (**Figure 1a**), resembling its (111) plane spacing (0.227 nm). Similarly, the cupule in light contrast is indexed as orthorhombic Fe_2O_3 ($a = 0.509$ nm, $b = 0.878$ nm, $c = 0.943$ nm, pdf card: 52-1449) based on the structural analysis of particle shown in **Figure 1c** and its FFT pattern (**Figure 1d**).

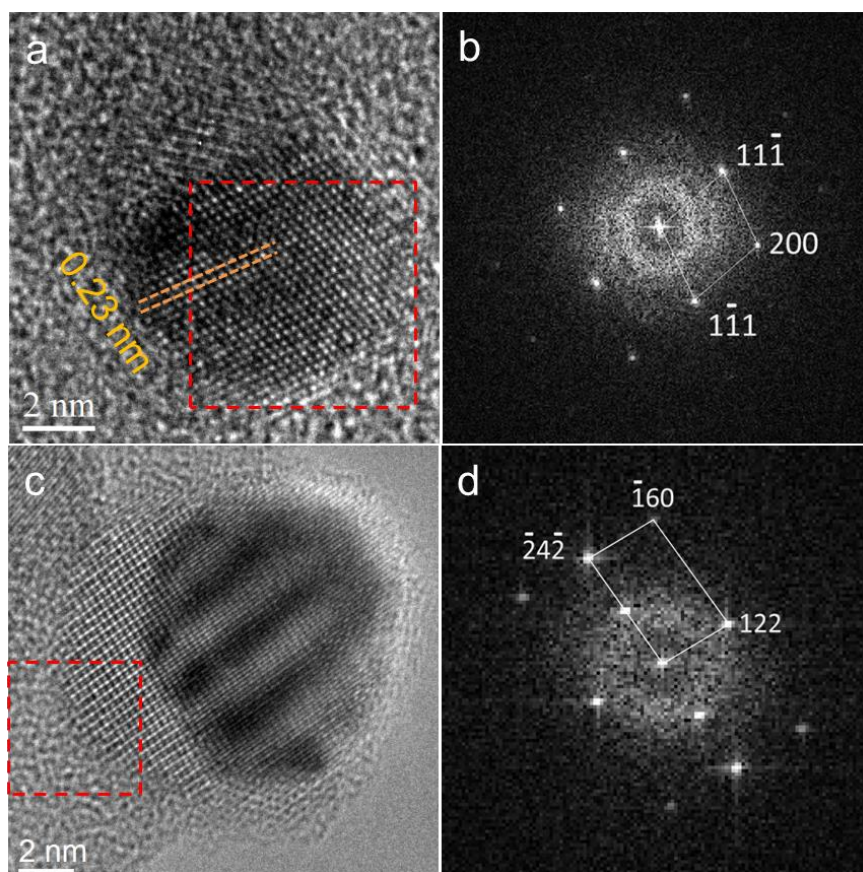


Figure 1. (a) A high resolution TEM image of an acorn-like Pt- Fe_2O_3 hybrid nanoparticle and (b) the FFT pattern of the dark part of the hybrid structure. (c) A high resolution TEM image of another Pt- Fe_2O_3 hybrid nanoparticle and (d) the FFT pattern of the square part of the particle.

In addition, moiré pattern is observed in **Figure 1c**, suggesting that at least part of Pt is covered by Fe_2O_3 layer. Such an assignment is further confirmed by EELS on the hybrid nanoparticles. As shown in Supporting Information **Figure S1b**, the EELS spectrum from the cupule part exhibits the L_3 and L_2

peaks of Fe at 710 eV and 722 eV, respectively, in agreement with the L_3 and L_2 edges of Fe in Fe_2O_3 . In contrast, Fe signals on the dark embryo of the particle became negligible. The above characterization results suggest that the catalyst is a two-phase hybrid of Fe_2O_3 and Pt. The driving force for the hybrid Pt- Fe_2O_3 catalyst formation could be the high temperature calcination. As Pt is a noble metal, therefore metallic Pt is the most stable phase.[14] In the case of Fe, it tends to be oxidized to Fe_2O_3 which mainly has four crystalline polymorphs: α - Fe_2O_3 , β - Fe_2O_3 , γ - Fe_2O_3 and ϵ - Fe_2O_3 . [15] Although the observed orthorhombic Fe_2O_3 (ϵ - Fe_2O_3) is thermodynamically metastable, it can exist in the form of nanostructures. [15, 16]

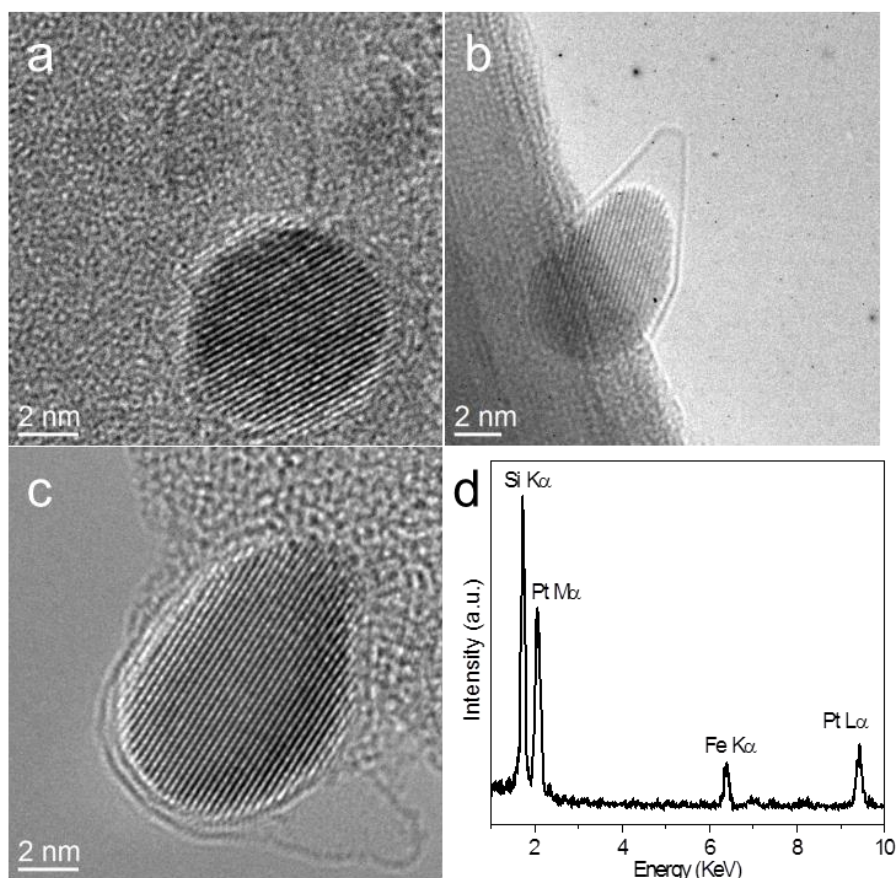


Figure 2. (a)(b)(c) TEM images of active PtFe nanoparticles after CVD process. (d) A typical EDX spectrum of an individual nanoparticle after CVD, showing the presence of both Fe and Pt.

Carbon nanotubes were grown on the Pt-Fe₂O₃ catalyst using CO as the carbon precursor at different temperatures. A TEM overview of SWCNTs produced after CVD reaction at 800 °C is presented in ESI **Figure S2**. **Figure 2a-2c** present TEM images typifying three nanoparticles which nucleate short carbon nanotubes after CVD reaction at 800 °C. In contrast to the two-phase hybrid before reaction, all the particles display a single phase only. Further considering the presence of both Pt and Fe in the catalyst, as evidenced by the EDX spectrum (**Figure 2d**), it is concluded that PtFe alloy forms during CVD. Systematic EDX characterizations were performed on a number of PtFe particles after CVD. ESI **Figure S3a** depicts the histogram of Pt atomic percentages, which shows that most particles have near-equal atomic percentages of Pt and Fe. From their binary phase diagram (ESI **Figure S3b**), it can be seen that in a wide composition range (Pt atomic percentage of 32% ~ 60%) these particles tend to adopt a chemically disordered FCC structure, where Pt atoms are randomly substituted by Fe atoms in the lattice. The FCC structure of PtFe nanoparticles is also confirmed by their FFT patterns (ESI **Figure S4**). Overall, after CVD reaction, most hybrid Pt-Fe₂O₃ nanoparticles transformed into FCC PtFe alloy nanoparticles.

3.2. Investigations of dynamics of Pt-Fe₂O₃ catalyst and nucleation of carbon nanotube by environmental TEM

As indicated by TEM investigations of WCo catalysts,[6, 7] it is complicated to assign the active components for SWCNT growth, the structure and the composition of which could change with prolonged reaction time. In CO hydrogenation, the addition of Pt substantially improves the reducibility of Fe₂O₃, [17] which can be ascribed to the spillover effect of reductive species on Pt. Similarly, the improved reducibility of Fe₂O₃ in the presence of Pt is of great importance for nucleation and growth of carbon nanotubes, as reduction of Fe₂O₃ is a prerequisite for catalytic dissociation of carbon source and dissolution of carbon atoms. In order to further study evolutions of Pt-Fe₂O₃ hybrid nanoparticles during

CVD and identify the active components for carbon nanotube nucleation, *in situ* environmental TEM was performed.

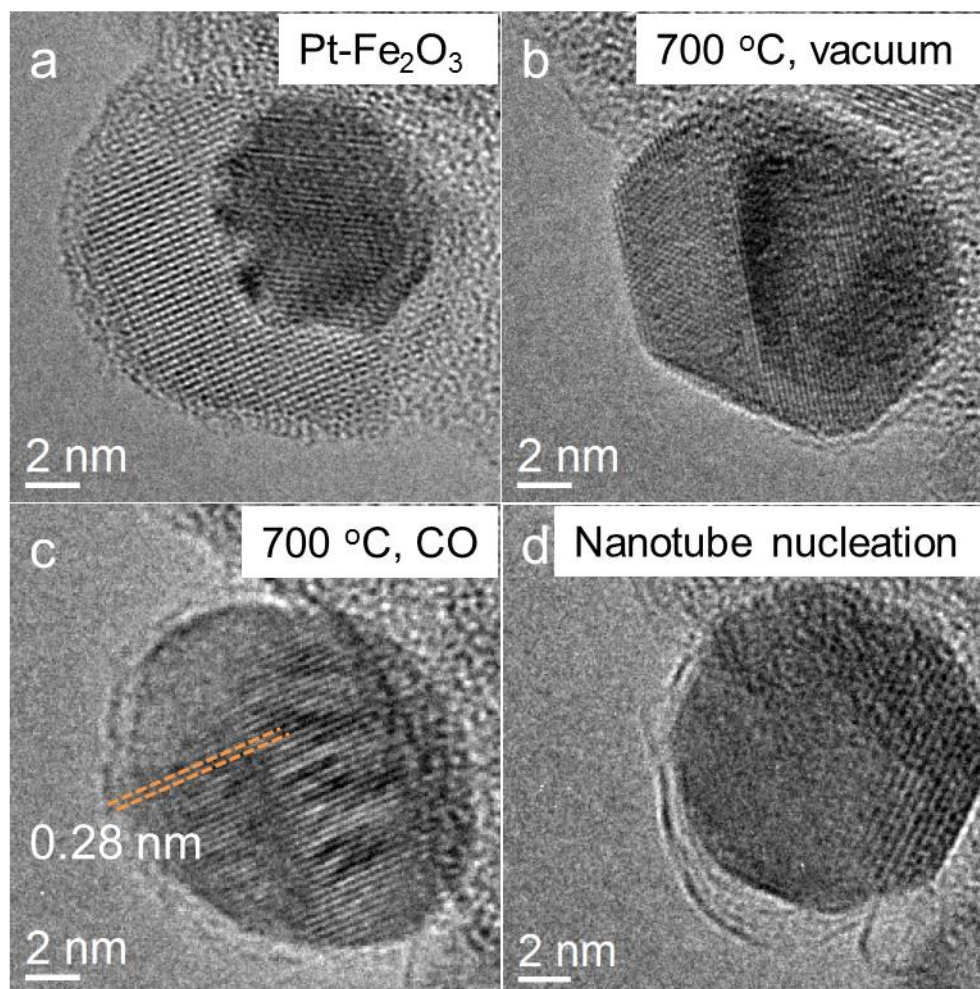


Figure 3. Evolutions of a Pt- Fe_2O_3 hybrid particle monitored by environmental TEM: (a) as-prepared particle; (b) Heated to 700 °C in vacuum; (c) Introduction of CO at 700 °C; (d) Nucleation of a carbon nanotube.

Figure 3 shows a sequence of TEM images taken by following the same isolated Pt- Fe_2O_3 particle. **Figure 3a** presents the acorn-like Pt- Fe_2O_3 particle at room temperature which contains a dark Pt embryo and a light Fe_2O_3 cupule. Based on the FFT pattern of the Fe_2O_3 cupule (ESI **Figure S5**), the Fe_2O_3 can be well assigned as $\epsilon\text{-Fe}_2\text{O}_3$, in agreement with the assignments of other Fe_2O_3 cupules shown in **Figure**

1. With the increase of the temperature, the morphology of the Pt-Fe₂O₃ changes, as indicated by **Figure 3b**. The morphology change could be related to the phase transformation from ϵ -Fe₂O₃ to β -Fe₂O₃, with a cubic structure and a lattice parameter of 0.939 nm (ESI **Figure S6**). With the introduction of CO, Fe₂O₃ is reduced to metallic Fe and the particle is thus transformed into a spherical-like shape (**Figure 3c**). In the middle of the catalyst, there is a boundary region. The left part of the particle is assigned as metallic Fe, with a plane spacing of 0.28 nm, corresponding to that of the Fe (001) interplanar spacings (pdf card: 06-0696). While in the right of the boundary region, moiré fringes were observed, suggesting that the Pt is overlaid by the reduced Fe.

With prolonged exposure to CO at 700 °C, carbon nanotube cap was observed to form from the left part of the particle (**Figure 3d**). Clearly, the left part of the particle differs greatly from its right part. The measured one-dimensional fringe-spacing (0.38 nm), visible for the right part, is consistent with (100) spacing of PtFe alloy structure (pdf card: 29-0718). Analyzing the FFT pattern of the left part (ESI **Figure S7**) gives an assignment of Fe_{2.5}C, the Hägg carbide. Such metastable Hägg carbide phase has been widely observed in Fischer-Tropsch process, especially at a high carbon chemical potential.[18] Besides Fe_{2.5}C, cementite (Fe₃C) is another carbide that usually formed when exposing Fe catalyst to CO.[18, 19] In previously reported *in situ* environmental TEM experiments on monometallic Fe catalysts, Fe₃C formation occurs more readily and catalyzes the subsequent carbon nanotube growth.[20-22] Different from monometallic Fe catalyst, in our PtFe catalyst, Fe tends to form Hägg carbide (Fe_{2.5}C) phase in the presence of CO, which could be related to the presence of Pt.[8, 17] As discussed by Wei *et al.*, [18] Fe_{2.5}C can be stabilized under high carbon chemical potential at temperatures resembling our reaction conditions. The Pt promotes the reduction and carburization of Fe₂O₃ by a spillover effect, facilitating the formation of carbon-rich Fe_{2.5}C.[8, 17] The finding is consistent with that of Yu *et al.*[17] who studied the effect of Pt on a Fe-based Fischer-Tropsch catalyst. However, it is noted that with long enough

reaction time (1 h), the catalyst evolved into single-crystalline PtFe alloy phase (ESI **Figure S8**), in agreement with *ex situ* TEM investigations (**Figure 2**). Schematic illustration of carbon nanotube nucleation from the acorn-like Pt-Fe₂O₃ catalyst is presented in **Figure 4**.

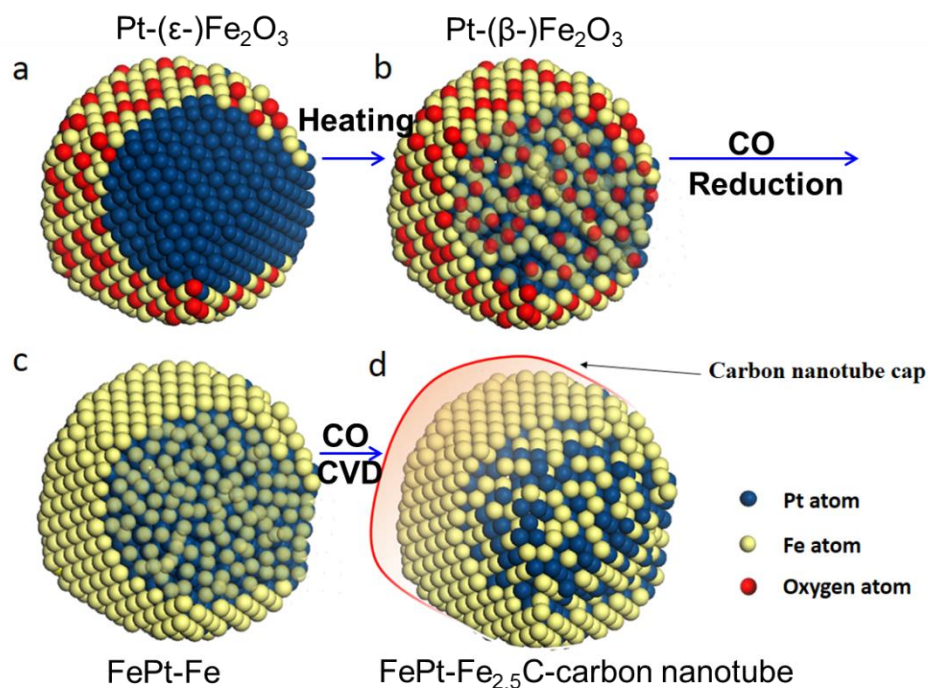


Figure 4. Schematic illustration of carbon nanotube nucleation from the Pt-Fe₂O₃ hybrid catalyst.

3.3. Characterizations of SWCNTs grown by CVD

In general, the chirality of an SWCNT is determined by the tube cap, which is formed at the beginning of SWCNT nucleation.[23, 24] Therefore, under certain CVD conditions, the catalyst structure, which is related to the composition and carbon solubility of the nanoparticle, [24-27] could determine the chirality distribution of the SWCNT product. As revealed by *in situ* environmental TEM, in the reduced PtFe catalyst, it is the Hägg carbide instead of PtFe alloy that catalyzes the nucleation of carbon nanotubes. Therefore, in order to further clarify the SWCNT nucleation mechanisms, nanobeam electron diffraction was performed to study SWCNTs grown at different temperatures.

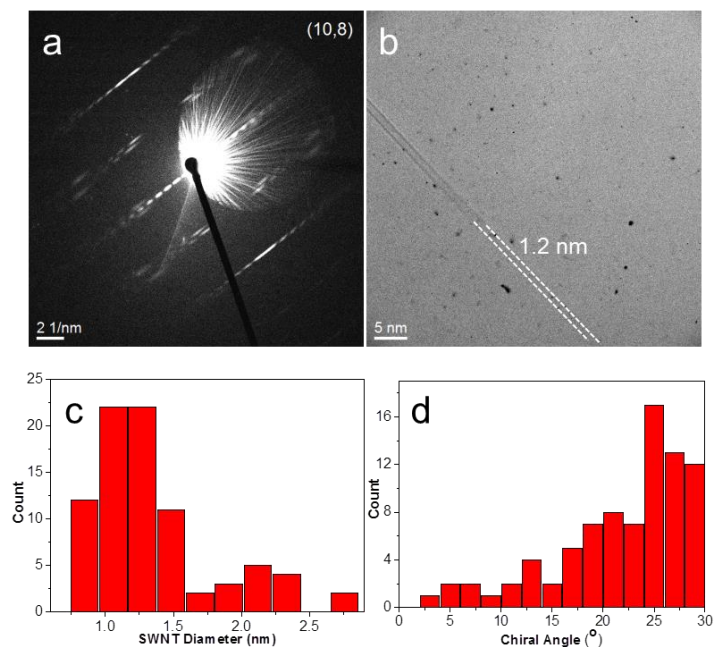


Figure 5. (a) A nanobeam electron diffraction pattern of the individual SWCNT shown in (b), the chirality of the SWCNT is identified as (10, 8). (c) Diameter distribution and (d) chirality distribution of SWCNTs grown on Pt- Fe_2O_3 catalyst at 800 °C using CO as the carbon source.

Figure 5a and **5b** present a diffraction pattern of a suspended SWCNT grown at 800 °C and its TEM image. The sharp diffraction spots appear smeared because of radial curvature, forming a series of layer lines. The chiral angle and diameter of the SWCNT can be calculated respectively from the axial distances of the layer lines from the equatorial line and the pseudo-period of the equatorial oscillation.[28, 29] Accordingly, the tube with the diffraction pattern shown in **Figure 5a** is identified as having the chiral indices of (10, 8), a semiconducting tube with a diameter of 1.2 nm, which is in agreement with the diameter determined from the real space measurement (**Figure 5b**). The histograms of tube diameter and chiral angle are shown in **Figure 5c** and **5d**. The mean diameter of SWCNTs grown at 800 °C is 1.35 nm. The formation of small-diameter SWCNTs from large-size catalyst particle is attributed to selective nucleation on small-diameter particles and the perpendicular growth mode when using CO as the carbon source, [25, 30] as demonstrated in **Figure 2**. Similar to Fe-grown SWCNTs synthesized under similar

growth conditions, [31, 32] the PtFe-grown SWCNTs are biased at large chiral angles, 57 out of 83 (68%) have chiral angle larger than 20° . Meanwhile, the observed semiconducting SWCNTs have a fraction of 71%, suggesting no selection to the conductivity of SWCNTs. The similar chirality distributions between PtFe-grown SWCNTs and Fe-grown SWCNTs further indicates that the active component for SWCNT nucleation could be similar. The chirality of an SWCNT is defined either by epitaxial relationship with the catalyst [24] or by specific growth mode. [30]

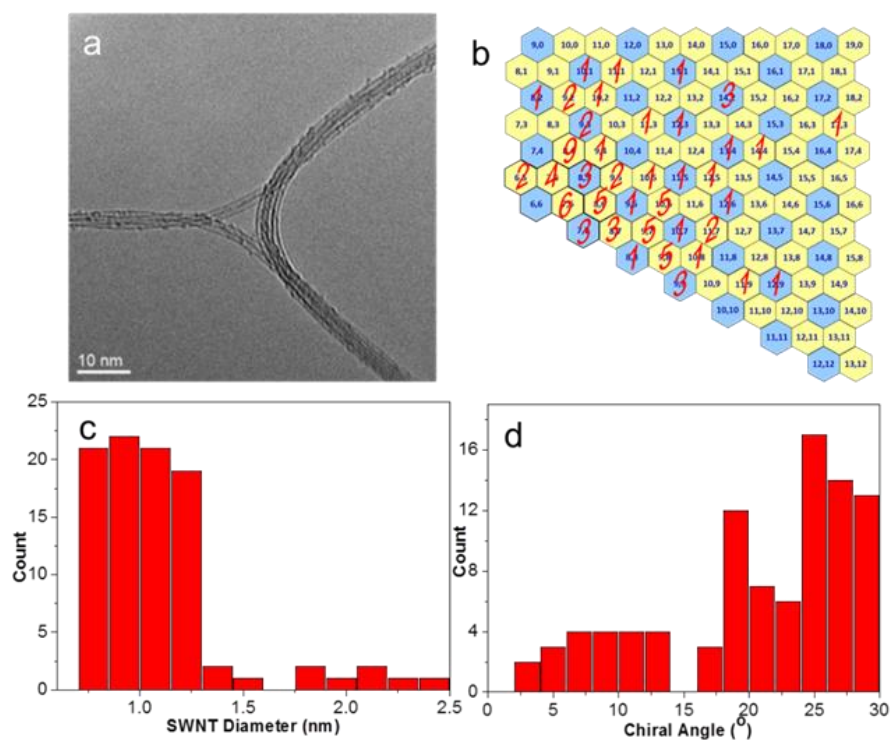


Figure 6. (a) A TEM overview of SWCNTs grown at 700 °C by catalytic decomposition of CO; (b) Chiral map of SWCNTs without 7 large diameter ones, namely, (24,6), (17,15), (14,13), (28,6), (16,12), (23,2) and (21,11). (c) Diameter distribution and (d) chirality distribution of SWCNTs grown on Pt-Fe₂O₃ catalyst at 700 °C.

Nevertheless, different from monometallic Fe supported by Si₄N₃ grid, which can only afford the growth of carbon nanotubes at temperatures over ~800 °C, the Pt-Fe₂O₃ catalyst could grow SWCNTs at

a lower temperature because of the spillover effect of Pt. [17] **Figure 6a** depicts a TEM image of carbon nanotubes, showing that single-walled nanotubes with small diameter were produced. The chirality map, the diameter distribution and chirality distribution of SWCNTs are presented in **Figure 6b-6d**. The SWCNTs exhibit a small mean diameter of 1.09 nm and most of the tubes are in the diameter range from 0.7 to 1.2 nm. Similar to 800 °C-grown SWCNTs, the SWCNTs synthesized at 700 °C also show a preference to large chiral angles (20°–30°). There is no high selectivity to certain (n, m) species, but (8, 4), (7, 6), (8, 6), (9, 7), (9, 8) and (10, 6) tubes occupy more than 37% of the total.

4. Conclusions

To summarize, we have described an acorn-like Pt-Fe₂O₃ hybrid catalyst for growing SWCNTs by catalytic decomposition of CO. *In situ* environmental TEM studies reveal that the presence of Pt promotes the carburization of reduced Fe, leading to the formation of Hägg carbide which catalyzes the nucleation of SWCNTs. Prolonged exposure of the hybrid catalyst to CO at reaction temperature leads to the formation of single-crystalline PtFe alloy, as also revealed by *ex situ* TEM characterizations. Meanwhile, the chirality distribution of SWCNTs grown at 800 °C is similar to that of SWCNTs grown on monometallic Fe nanoparticles, as the active components in both cases are quite similar. In addition, Pt facilitates the reduction of Fe₂O₃, accounting for SWCNT growth at a relatively low temperature of 700 °C. This work not only helps understand the structure evolution of Pt-Fe₂O₃ bimetallic system and opens the way to a profound understanding of the heterogeneous catalysis, but also guides the design of bimetallic catalyst for the growth of SWCNTs.

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Supplementary data: More characterization and analysis results of Pt-Fe₂O₃ nanoparticles and carbon nanotubes grown on them by CVD.

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