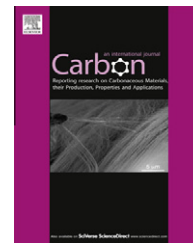


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Review

Controlling the growth of single-walled carbon nanotubes on surfaces using metal and non-metal catalysts

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ABSTRACT

Thanks to the development of controlled synthesis techniques, carbon nanotubes, a 20-year-old material, are doing better at finding practical applications. The history of carbon nanotube growth with controlled structure is reviewed. There have been two main categories of catalysts used for carbon nanotube growth, metal and non-metal. For the metal catalysts, the growth process and the mechanism involved have been adequately discussed, with a widely accepted vapor–liquid–solid growth mechanism. The strategies for preparing single-walled carbon nanotube samples with well-defined structures such as geometry, length and diameter, electronic property, and chirality have been well developed based on the proposed mechanism. However, a clear mechanism is still being explored for non-metal catalysts with a hypothesis of a vapor–solid growth mechanism. Accordingly, the controlled growth of carbon nanotubes with a non-metal catalyst is still in its infancy. This review highlights the structure-control growth approach for carbon nanotubes using both metal and non-metal catalysts, and tries to give a full understanding of the possible growth mechanisms.

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1. Introduction

As a famous one dimensional nano-material, carbon nanotubes are effectively 20 years old this year. Since Iijima's landmark studies [1,2], people started to focus on the structure control of carbon nanotubes. As shown in Fig. 1a, the number of reports has increased dramatically in the past 20 years. Briefly, the history of carbon nanotube research can be divided into five stages (Fig. 1b). At its earliest stage, people mainly focused on how to grow carbon nanotubes and many metal particles were tried for this purpose. When carbon nanotube fabrication was no longer a key problem, structure control at the mesoscopic level took its place as the second stage. There were two kinds of growth methods to control carbon nanotube orientation. The first was the gas-flow directed mode, with the advantage of growing ultra-long carbon nanotubes. The second was the surface directed mode, which was good at growing well aligned carbon nanotubes. The third stage for the growth control of carbon nanotubes was structure control at the microscopic level, such as length and tube diameter. People also focused on the yield of single-walled carbon nanotubes (SWCNTs) and a huge number of results were reported during that time. Nevertheless, there was a dramatic gap between material fabrication and device application, because of the co-existence of metallic and semiconducting SWCNTs in the current growth methods. In order to conquer this huge barrier on the way to success, SWCNTs must be separated either during or after growth which was another hot research topic and served as the fourth stage. The final stage was the control of single chirality with the expectation of a uniform band gap. However, this might not be possible for metal catalysts, since they were

melted at high temperatures, according to the well accepted vapor–liquid–solid (VLS) mechanism. In recent years, people also turned to investigate the possibility of non-metallic catalysts for carbon nanotube growth. With a hypothesis of vapor–solid (VS) or vapor–solid–solid (VSS) mechanism, in which non-metallic catalysts were not melted, there might be a possibility to control the chirality of carbon nanotubes. Nowadays, it has been confirmed that plenty of non-metal nanoparticles can be used to grow carbon nanotubes. Although still at the early stage of structure control, the achievement of single chirality does not seem far away.

Generally speaking, the synthesis methods of SWCNTs can be divided into two categories: physical methods like laser vaporization and arc discharge, and chemical methods like catalytic chemical vapor deposition (CVD) on various surfaces and floating catalyst or aerosol method. In this paper, we will provide a review of the history of structure control in carbon nanotubes and attempts at a full understanding of the growth mechanism of carbon nanotubes for both metal and non-metal catalysts on various surfaces. Since we mainly focus on the growth control, any post treatment methods involved [3,4], such as in the separation and chirality control, will not be discussed.

2. Growing single-walled carbon nanotubes on a surface with controlled structures using metal catalysts

2.1. Metal catalysts for carbon nanotube growth

At the very beginning, it was well accepted that only iron-family elements such as Fe, Co, Ni had the catalytic function

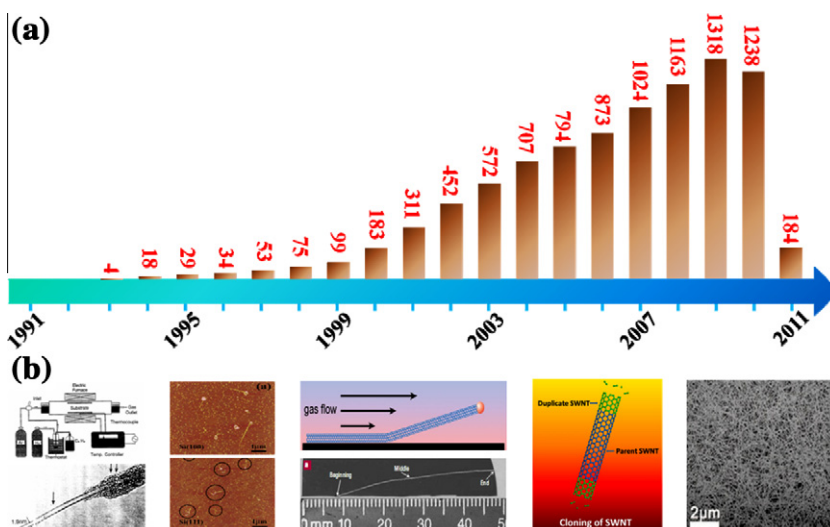


Fig. 1 – Research history of carbon nanotube growth in the past 20 years. (a) The number of papers relative to carbon nanotubes in the past 20 years. (b) Typical reports of the five stages in the carbon nanotube evolution [5–10].

1 H																	2 He																														
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne																														
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar																														
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr																														
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe																														
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn																														
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq		116 Uuh		118 Uuo																														
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57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu																																	
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr																																	

Fig. 2 – Metal nanoparticles which have been confirmed to be suitable for carbon nanotube growth.

of graphite formation and thus for carbon nanotube growth [11–13], due to the large bonding energy of carbon [14]. However, an exciting discovery confirmed that noble metals, such as Au, Ag, Pt and Pd can also be used as catalysts to grow carbon nanotubes [15,16]. The essential role of these metal particles was thought to be their ability to provide a platform on which carbon atoms can form a hemispherical cap, and then a carbon nanotube can grow in a self-assembled fashion. This was a breakthrough in the catalyst choice for carbon nanotube growth, which expanded the method of carbon nanotube growth using traditional catalysts. Since this work was reported, plenty of metal nanoparticles were tested and confirmed to be suitable for carbon nanotube growth. One systematic report concluded that a large variety of metals including Fe, Co, Ni, Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, and Al can successfully catalyze the growth of carbon nanotubes [16]. This revolution of catalyst discovery totally destroyed the former hypothesis. So far, the tested metal nanoparticles which have been confirmed to be suitable for carbon nanotube growth are summarized in Fig. 2. Nowadays, it is well

accepted that almost any metal nanoparticles can be used as catalysts for the growth of carbon nanotubes.

2.2. Geometry control of carbon nanotubes

During the attempts to find different catalysts, it was found that carbon nanotubes behaved quite different under various growth conditions, and this resulted in the proposal of two main growth mechanisms. In brief, the first one was called the gas-flow directed mode [7] while the second one was the surface directed mode [6]. As mentioned above, each mode had its own advantages in the orientation control of growing carbon nanotubes. Some other ways were also developed to control the orientation of carbon nanotubes, such as electrical field orientation [17].

Typical work using the gas-flow directed mode was the fabrication of long and aligned carbon nanotubes using a “fast heating” CVD method [7]. It was demonstrated that a change in heating speed can alter the growth of carbon nanotubes and a “kite-mechanism” was proposed to explain the

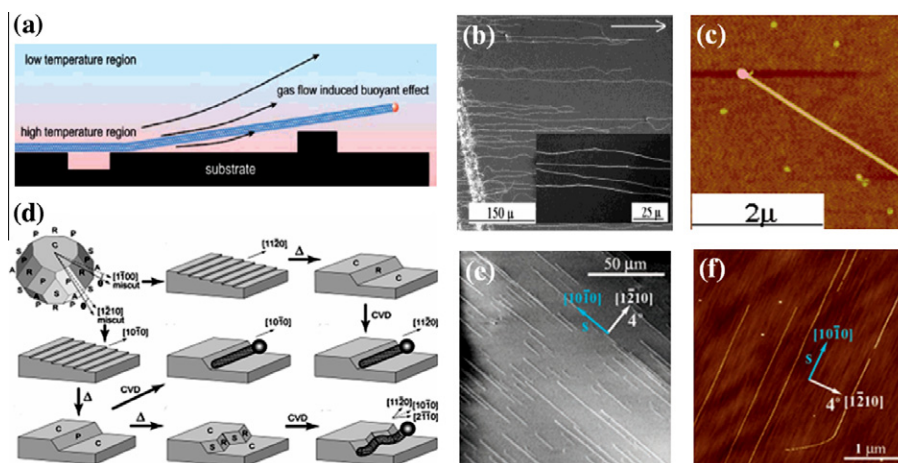


Fig. 3 – Schematics of carbon nanotube growth in (a) gas-flow directed [18] and (d) surface directed modes [22]. (b) SEM and (c) AFM images of carbon nanotubes following the gas-flow directed mode [7]. (e) SEM and (f) AFM images of carbon nanotubes following the surface directed mode [22].

process (Fig. 3a). Fig. 3b and c is the typical scanning electron microscope (SEM) and atomic force microscope (AFM) images of the growth results under the gas-flow directed mode. Since carbon nanotubes were kept “flying” during growth, the growth result was further improved in an ultraslow gas flow [18]. It was confirmed that carbon nanotube arrays could be obtained under an extremely low CH_4 feeding flow of 1.5 sccm in a 1 in. quartz tube reactor. The tubes grew in a floating manner and could cross micro-trenches or climb over micro-obstacles. Besides these, carbon nanotube arrays could be formed no matter whether the substrate was placed vertically or upside down. In a word, the advantage of the gas-flow directed mode was its suitability for very long carbon nanotube production, but the alignment was not so perfect.

The surface directed growth mode [19,20] is more complicated and there is much controversy about its mechanism. Using this mode, carbon nanotubes were synthesized on silicon surfaces for the first time as early as 2000 [6]. It was found that carbon nanotubes grown on Si (100)-based surfaces were aligned in two perpendicular directions, while those grown on Si (111)-based surfaces were in three preferred directions separated by 60° . Simulations indicated that the observed orientation locking was the result of interactions between carbon nanotubes and the surface lattices. Similar growth results were also realized on a-plane and r-plane sapphire substrates, using ferritin as the catalyst [21]. In contrast, no orientation was achieved on the c-plane and m-plane sapphire substrates. Thus, these results were also believed due to the surface lattice. However, another explanation was proposed for this mode. One typical work reported that carbon nanotubes can grow along self-assembled nanosteps of annealed miscut C-plane sapphire (Fig. 3d) [22]. Depending on the miscut orientation and annealing conditions, graphoepitaxy led to the formation of either unprecedentedly straight and parallel nanotubes, with angular deviations as small as $\pm 0.5^\circ$, or to wavy nanotubes loosely conformed to sawtooth-shaped faceted nanosteps. Fig. 3e and f is the typical SEM and AFM images of the growth results under the surface-directed mode.

Besides the controversy of “lattice” and “nanostep” directed growth, the growth process for the surface directed mode was also unclear. During carbon nanotube growth, it was frequently found that some of the nanotubes bent to form a “sickle”-shaped structure which can be explained with a hypothesis of a “tip-growth” mechanism where the catalyst nanoparticles slid on the substrate [23]. However, we used carbon nanotubes as nanobarrriers to terminate the growth of carbon nanotubes on a quartz surface, in which a base-growth mechanism was indicated [24]. Furthermore, people found that the growth mode would change even with the catalyst size [25]. In this work, carbon nanotube growth was investigated using cobalt, nickel and iron catalyst particles of different sizes. For the three catalysts examined, it was shown that the growth mode switched from “tip-growth” for large particles ($\gg 5$ nm) to “base-growth” for smaller ones (< 5 nm). While SWCNTs and those with few walls (typically < 7 walls) grow from their base, larger multi-walled carbon nanotubes (MWCNTs) were fed with C atoms via their tips which supported the catalyst particles.

Although the mechanism was quite unclear, a combination of the two modes has been used to achieve special carbon nanotube-based structures. One study demonstrated that the combination enabled the controlled formation of uniquely complex and coherent geometries of carbon nanotubes, including highly oriented and periodic serpentine and coils [26]. A mechanism of non-equilibrium self-organization, in which competing dissipative forces of adhesion and aerodynamic drag induce oscillations in the nanotubes as they adsorb on the surface, was proposed. We further improved this method to controllably crinkle carbon nanotubes into serpentine geometries (Fig. 4a) [27]. Based on this improvement, the yield of serpentine carbon nanotubes exceeded 96%, with the amplitude and density (Fig. 4b) over 100 mm and 2 tubes/mm. Moreover, the serpentine carbon nanotubes were also introduced into ultrahigh-current carbon nanotube-based devices. Without losing the high $I_{\text{ON}}/I_{\text{OFF}}$ ratio that a single carbon nanotube exhibited, the current can be easily scaled up if more parallel segments were fabricated into the devices. Besides this, we also developed another method to prepare large area, well-aligned carbon nanotube crossbar (Fig. 4c) with a node density up to $10^7/\text{cm}^2$ by a convenient one-step process (Fig. 4d), where the direction of gas flow and lattice direction of the substrate (quartz) were perpendicular to each other [28].

2.3. Length and diameter control of carbon nanotubes

After several years' experiences, the research frontier turned to focus on the structure control of carbon nanotubes, mainly on the length and tube diameter. As a typical one dimensional material, there had been a great interest in creating long, continuous nanotubes for applications [29,30]. For quite a long time, the maximum length of carbon nanotubes was around several millimeters, until the synthesis of 4-cm-long individual single-walled carbon nanotubes at a high growth rate of $11 \mu\text{m/s}$ was reported (Fig. 5a) [8]. After that, the record was frequently increased from 10 cm [31] to 20 cm (Fig. 5b) [32]. Nowadays, the world record is as long as 40 cm [33].

On the other hand, people also focused on the cutting of carbon nanotubes. Initially, most methods were based on selective destruction [34–36]. We have developed a direct growth method using carbon nanotubes as nanobarrriers (Fig. 5c) [24]. The length of carbon nanotubes can be controlled by the nanobarrriers and most importantly, the form of the array can be controlled at the same time.

For the case of carbon nanotube diameter control, many parameters had been taken into consideration. It was reported that discrete catalytic nanoparticles with different diameters were obtained by placing controllable numbers of metal atoms into the cores of apoferritin, and used for the growth of single-walled carbon nanotubes [37]. Transmission electron microscopy (TEM) images show that the diameters of the nanotubes are determined by the diameters of the catalytic nanoparticles (Fig. 6a). Besides this, temperature is another crucial parameter to control carbon nanotube diameter. A higher temperature will lead to a larger carbon nanotube diameter in the case of a large amount of catalyst, since catalyst nanoparticles would aggregate at high temperatures. However, the opposite is true in the case of

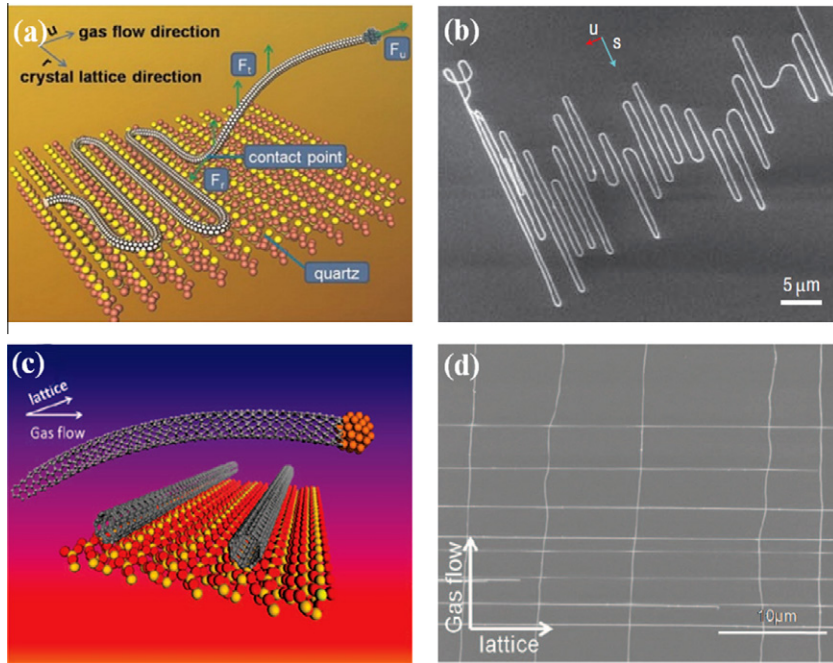


Fig. 4 – Schematics of special formations by combining both gas-flow directed and surface directed modes. (a) Schematic and (b) SEM images of serpentine geometries [27]. (c) Schematic and (d) SEM images of cross-bar structures [28].

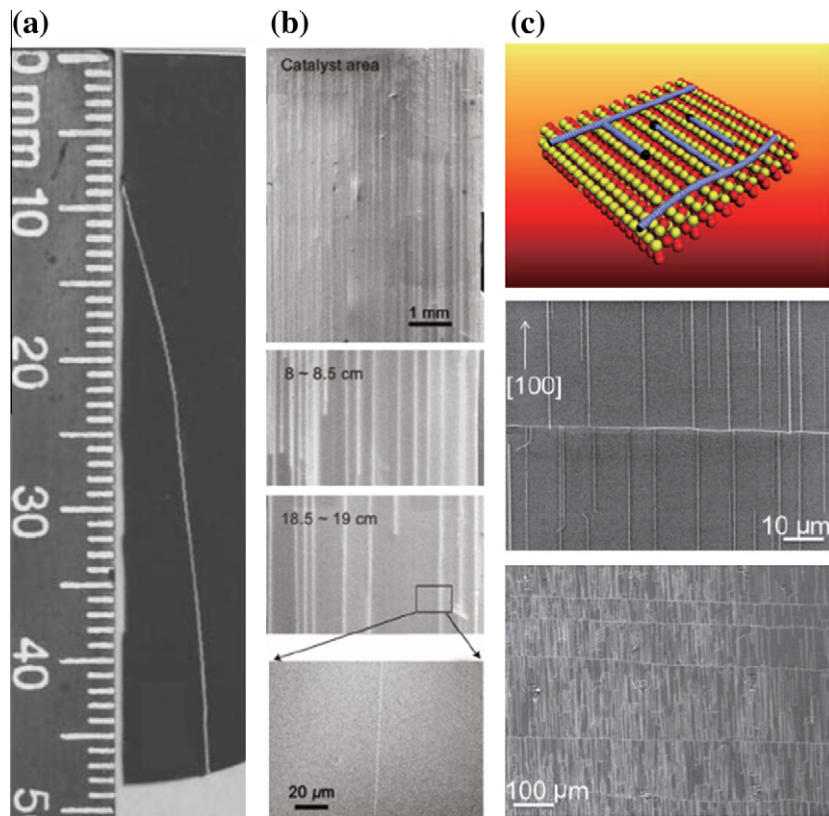


Fig. 5 – Length controlled growth of carbon nanotubes. (a) SEM image of 4 cm carbon nanotubes [8]. (b) SEM images of 20 cm carbon nanotubes [32]. (c) Schematic and SEM images of carbon nanotubes with controlled length using carbon nanotubes as nanobarriers [24].

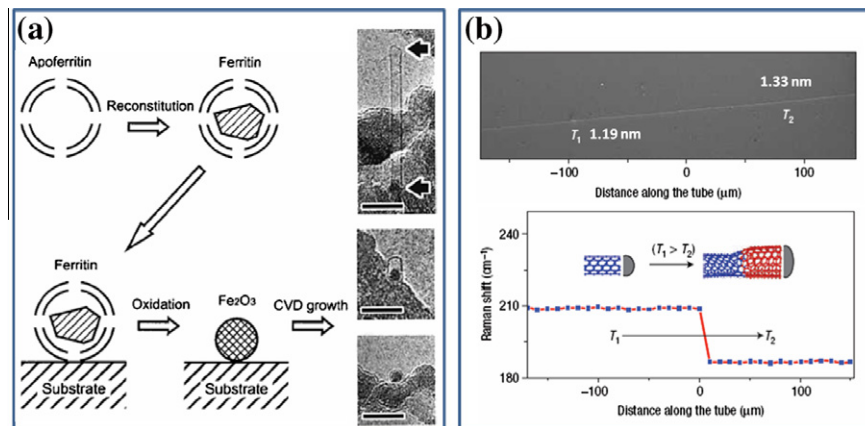


Fig. 6 – Diameter control of carbon nanotubes. (a) Diameter control by tuning nanoparticle size [37]. (b) Temperature-mediated growth of SWCNT intramolecular junctions [38].

single catalyst nanoparticles. We developed well-controlled temperature-mediated growth of intramolecular junctions in SWCNTs [38]. This was achieved by a consistent variation in the SWCNT diameter and chirality with the changing growth temperature with the same catalyst nanoparticle. As a result, the diameter became larger at a lower temperature while it was smaller at a higher temperature (Fig. 6b). Besides this, the gas pressure was also very important in controlling the diameter [39].

2.4. Controlled growth of metallic and semiconducting single-walled carbon nanotubes

Using the common growth methods for carbon nanotubes, the coexistence of metallic (m-) and semiconducting (s-) SWCNTs cannot be avoided. However, the separation of different types of SWCNTs can be realized after or during growth, which are conventionally named as post treatment

and direct growth methods, respectively. Initially, almost all approaches belonged to the post treatment method, which can be further divided into selective destruction [40–43] and solution based methods [3,44,45].

Post treatment methods can realize a high effective separation of SWCNTs [46,47], but contamination adhering to SWCNTs cannot be avoided. In order to solve this problem, people started to investigate the direct growth of SWCNTs, which can be further divided into selective destruction and catalyst modification methods [48]. For the case of the selective destruction method, the first work reported was the growth of SWCNTs by a plasma enhanced chemical vapor deposition (PECVD) method (Fig. 7a) which also established the standard of characterization for selectively grown carbon nanotubes [49]. Electrical characterization revealed that nearly 90% of the nanotubes were semiconducting. Control experiments with other carbon nanotube materials found that high-pressure CO (HiPco) [50] nanotubes consist of about

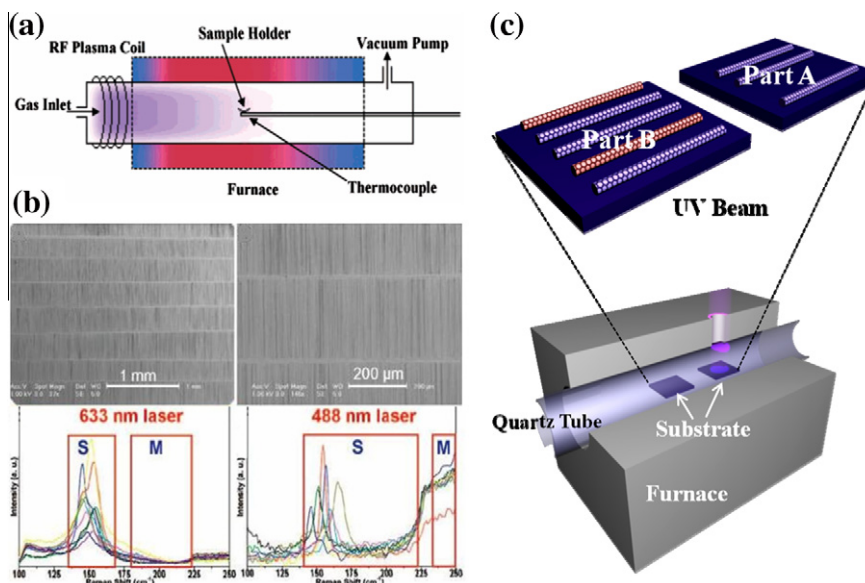


Fig. 7 – Growth of carbon nanotubes with controlled electrical properties. (a) Direct growth of s-SWCNTs in a PECVD system [49]. (b) Direct growth of s-SWCNTs by carbon source modification [52]. (c) Direct growth of s-SWCNTs using UV irradiation [53].

61% s-SWCNTs, while laser ablation [51] preferentially grows m-SWCNTs (about 70%). After that, carbon source modification was confirmed to be available for the fabrication of aligned s-SWCNTs on ST-cut quartz substrates (Fig. 7b) [52]. Raman spectroscopy together with electrical measurements from the as-grown samples showed that over 95% of the nanotubes in the arrays were semiconducting. It was proposed that introducing methanol in the growth process, combined with the interaction between the SWCNTs and the quartz lattice, led to the selective growth of aligned s-SWCNTs. We presented another way to directly grow s-SWCNT arrays with the assistance of ultraviolet (UV) irradiation (Fig. 7c) [53]. It was confirmed that UV irradiation can introduce radicals into the reaction chamber of CVD system, which can selectively destroy m-SWCNTs and leave the s-SWCNTs on the substrate. Control experiments also demonstrated that the separation process happened at the very beginning of carbon nanotube growth. While all the characterization methods above were used after growth, the first *in situ* work was reported on a gas phase oxidation approach for the selective removal of m-SWCNTs [54]. It was performed by introducing a small amount of oxygen during the synthesis of SWCNTs.

Because a m-SWCNT is more reactive than its counterpart under common physical or chemical conditions, there were few reports about the direct growth of m-SWCNTs. Alcohols with different ratios of carbon atoms to oxygen atoms (RCO) (methanol, ethanol, propanol, butanol, and pentanol) were selected as carbon feedstocks for the growth of SWCNTs [55]. The growth results suggested that the overall m-SWCNT content can be enriched with an increase of the RCO. The selective etching effect of hydroxyl radicals from the alcohol molecules and the protection of amorphous carbon were believed to be responsible for the enrichment.

Because the selective destruction method depends on the different reaction activities of m-SWCNTs and s-SWCNTs, damage to the desired material cannot be avoided. The only way to avoid this is the catalyst modification method. However, this is the most difficult aspect toward carbon

nanotube growth and only a few results have been reported. By varying the noble gas ambient during thermal annealing of the catalyst, and in combination with oxidative and reductive species, the fraction of tubes with metallic conductivity changed from 33% of the population to a maximum of 91% [56]. *In situ* TEM studies revealed that this change led to differences in both the morphology and coarsening behavior of the nanoparticles which were used to nucleate the nanotubes. These catalyst rearrangements demonstrated that there were correlations between catalyst morphology and resulting nanotube electronic structure and indicated that the chirality-selective growth may be possible. Besides this, europium oxide (Eu_2O_3) was also confirmed to be a new type of active catalyst for s-SWCNT growth [57].

2.5. Narrowing the chirality distribution of single-walled carbon nanotubes

After separation according to their electrical properties, carbon nanotubes have been used in plenty of electronic devices [58]. However, because separated s-SWCNTs consist of many SWCNTs with different chiralities, the differences in band gap hamper the performance of integrated devices. Catalyst modification was the first attempt to solve this problem. CoMoCAT was confirmed to selectively grow (6,5) and (7,5) SWCNTs [59]. It was suggested that, in the CoMoCAT method, interactions between Mo oxides and Co stabilized the Co catalyst against aggregation through high-temperature sintering. At low ratios, catalyst particles contained highly dispersed molybdenum oxide covered by a Co molybdate layer. With exposure to CO, the Mo oxide was converted into Mo carbide. This disrupted the molybdate layer, allowing the Co to be reduced by CO and migrate on the surface to form small, growing catalytic clusters of metallic Co. Carbon accumulated on these nanoclusters through CO disproportionation, leading to the formation of correspondingly small diameter SWCNTs. After that, a bimetallic FeRu catalyst was confirmed to produce SWCNT growth with a narrow diameter and chirality distribution in methane CVD, which produced predominantly

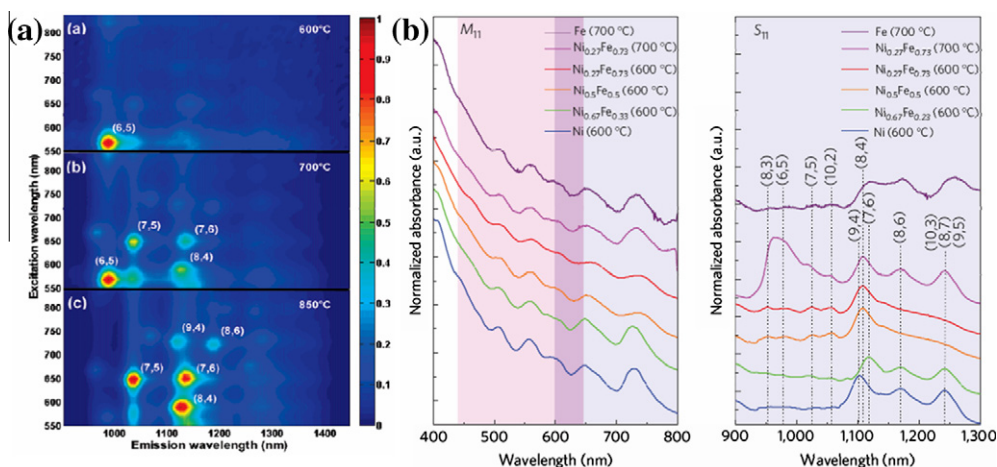


Fig. 8 – Chirality controlled growth of carbon nanotubes using an alloy catalyst. (a) Contour plots of normalized photoluminescence emission intensities under various excitations for the Fe–Ru SWCNTs grown at various temperatures [60]. (b) Absorbance spectra of SWCNTs grown with compositionally tuned $\text{Ni}_x\text{Fe}_{1-x}$ nanocatalysts at the indicated furnace temperatures [61].

(6,5) SWCNTs [60]. The intimate alloying of FeRu and strong Fe–Ru interactions produced small catalytic nanoparticles that were stable against high-temperature sintering for producing small diameter SWCNTs (Fig. 8a). The composition of $\text{Ni}_x\text{Fe}_{1-x}$ nanocatalysts can also alter the chirality distribution of as-grown SWCNTs [61]. Precise tuning of the nanocatalyst composition at constant size was achieved by a new gas-phase synthesis route based on atmospheric-pressure microplasma. The growth of specific SWCNT chiralities may be determined by their epitaxial relationship with the solid catalyst surface. It was believed that perturbations to the crystal structure, as a result of compositional tuning, affected the lattice match of the catalyst with certain chiralities and led to the observed shifts in the chirality distributions (Fig. 8b). Finally, a magnesia (MgO)-supported iron-copper (FeCu) catalyst was developed to accomplish the growth of SWCNTs using CO as the carbon source at ambient pressure [62]. The FeCu catalyst system facilitated the growth of small-diameter SWCNTs with predominantly of (6,5) SWCNTs. The role of Cu was to enhance the reducibility of Fe and inhibit the aggregation of Fe clusters. The reductive CO and H_2 , which first reduced CuO to metallic Cu and then adsorbed on it, could “spill over” to the adjacent Fe phases and facilitate the reduction of Fe. The reduced Fe then formed subnanometer clusters that could be stabilized in the Cu matrix. Consequently, the SWCNT growth that occurred on Fe clusters at Fe–Cu interfaces can be envisaged as the growth of thin carbon filaments. The reduced metallic Fe clusters

were thus supposed to act as the catalyst, leading to the high yield of SWCNTs.

Along with different catalyst components, different carbon sources can also lead to changes in the chirality distribution [63]. Four different carbon precursors, CO, $\text{C}_2\text{H}_5\text{OH}$, CH_3OH , and C_2H_2 , on Co–Mo catalysts were used to synthesize SWCNTs. However, narrowly (n,m) distributed SWCNTs can only be obtained under HiPco or vacuum $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH . The majority of these nanotubes were predominately in the same higher chiral-angle region. Besides catalysts, the pressure of the carbon precursor (Fig. 9) was also a key factor in the chirality control and SWCNT samples enriched with three dominant tubes at (6,5), (7,5), and (7,6) were obtained by increasing the pressure of CO on Co–Mo catalysts from 2 to 18 bar [64]. A detailed summary of the actual (n,m) distributions as determined based on optical (absorption, photoluminescence or Raman spectroscopy) methods [63] has been made by some work, which is shown in Fig. 10 [59] as examples.

There were also other special methods to control the chirality distribution. The continued growth of SWCNTs from ordered arrays of open-ended SWCNTs is analogous to epitaxy [65]. In this technique nanometer-sized metal catalysts were docked to the SWCNT open ends and subsequently activated to restart growth. The SWCNTs thus grown inherit the diameters and chirality from the seed SWCNTs, as indicated by the closely matched frequencies of Raman radial breathing modes before and after the growth. Instead of the

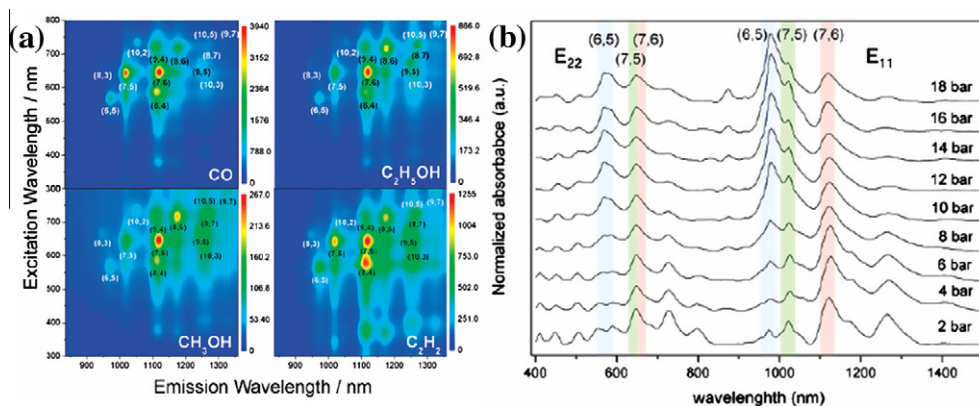


Fig. 9 – Chirality control growth of carbon nanotubes using (a) carbon source [63] and (b) pressure of the carbon precursor [64].

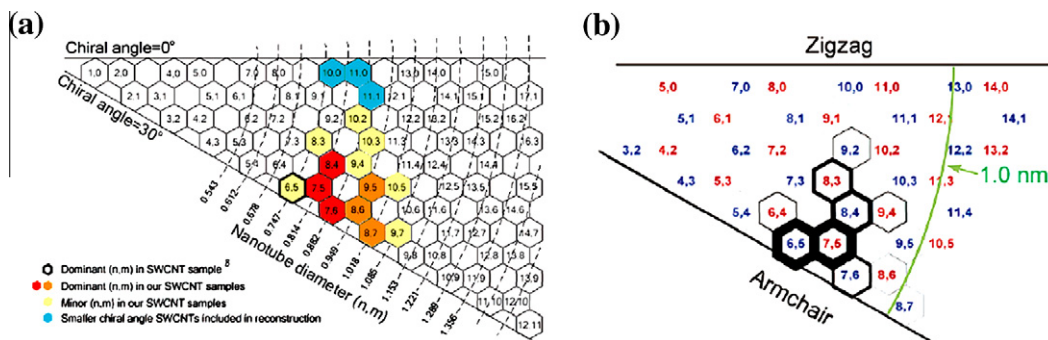


Fig. 10 – (n,m) Plots of SWCNT samples produced by using different carbon precursors (a) or CoMoCAT (b).

usual growth with the nanotube nucleation step, SWCNTs restarted the growth as an extension of the seeded SWCNTs and therefore inherited the same diameter and chirality from the starting SWCNTs. Another report indicated that not only the orientation, but also the diameter and chirality of the SWCNTs were affected by the crystal plane of the sapphire substrate [66]. The aligned SWCNTs grown on the A- and R-planes of sapphire have narrower diameter distributions than those of randomly oriented tubes produced on the C-plane sapphire and amorphous SiO₂. Photoluminescence measurements revealed a striking difference between the aligned SWCNTs: near-zigzag tubes were observed on the A-plane and near-armchair tubes on the R-plane. It was reasonable to suggest that the dissimilar atomic structures of the A- and R-plane sapphire surfaces induced differences in the particle morphology and orientation thereby affecting the SWCNT chirality. Another possible explanation was the formation of specific cap structures during the initial growth due to the direct interaction with the different atomic arrangements of the sapphire surfaces. In other words, an epitaxial relationship due to the matching of the lattice constants of sapphire and a specific SWCNT may lead to the crystal plane-dependent growth.

Generally speaking, the factors found to affect the efficiency of chiral-selective growth include temperature, the composition of bimetallic nanocatalysts, carbon sources, the pressure of the carbon precursor, micro-structure of the substrate, etc. Among those factors mentioned, a relatively low growth temperature is always essential for the effective selective growth. Some theory calculation results predict that the

chiral-selective growth of SWCNTs is more likely to be achieved on (n, m) species with low energy barriers of growth reactions such as (6, 5) and (7, 5) [67]. However, considering the thermal distortion by the temperature during the growth, the growth energies' difference of only a couple of eV is not significant. Further findings imply that the structure of catalytic metal clusters strongly correlates with chiral nanotubes through charge transfer (or redistribution) from metal atoms to edge carbon atoms on growing SWCNTs, which enhances the reactivity of edge carbon atoms [68]. Different chiral nanotubes exhibit distinct reaction active sites. Therefore, enabling (n, m) selective growth by engineering charge transfer between metal clusters and growing carbon structures is quite promising.

3. Growth mechanism of carbon nanotubes with metal catalysts

Many researchers have investigated SWCNT growth and several mechanisms have been proposed. The most well accepted one is the VLS mechanism, which was first proposed as a growth model for silicon nanowires (Fig. 11a) [69]. Fig. 11b is a typical TEM image of a silicon nanowire following the VLS mechanism. Considering the comparability between a silicon nanowire and a carbon nanotube, the VLS mechanism was adopted to explain carbon nanotube growth [70]. It was assumed that the formation of a SWCNT started with co-condensation of carbon and metal atoms from the vapor to form liquid metal carbide. Once the liquid reached super saturation, the solid phase carbon nanotubes began to grow.

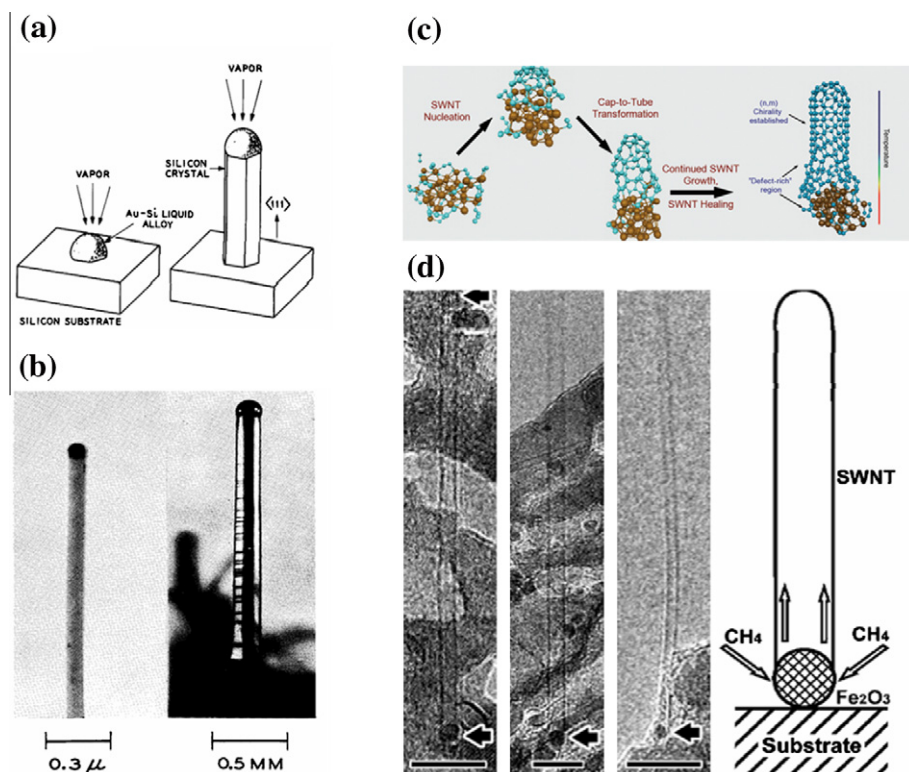


Fig. 11 – (a) The VLS mechanism of silicon nanowire growth [69]. (b) TEM images of silicon nanowire [69]. (c) The VLS mechanism of carbon nanotube growth [70]. (d) TEM images of carbon nanotubes [37].

The growth process was divided into three distinct stages: nucleation of a carbon “cap-precursor”, “cap-to-tube” transformation, and continued SWCNT growth (Fig. 11c). It was reported that particles in the liquid state were the active sites in the process of catalytic carbon nanotube growth from the observed catalyst particle shapes [71]. It was inferred that a VLS growth mechanism was operative in the catalytic process. The interfacial energy contribution to the total free energy of nanoparticles was assumed to be responsible for the significant lowering of the melting temperature of the catalyst particles. The variety of carbon forms was explained in terms of a periodic instability in the VLS growth process. Some modifications of this mode were also proposed. In the beginning, the VLS model often included a temperature gradient (TG) across the catalytic metal particle [72]. Later, it was confirmed that a TG was only important for the growth of carbon species from large metal particles. Molecular dynamics (MD) simulations showed that it was not required for SWCNT growth from small catalytic particles [72]. Quantum mechanical molecular dynamics (QM/MD) methods were also used to simulate SWCNT nucleation, growth, and healing phenomena on transition-metal catalysts [70]. With respect to the nucleation of a SWCNT cap-precursor, it was shown that the presence of a transition-metal carbide particle was not a necessary prerequisite for SWCNT nucleation, contrary to conventional experimental assumptions. The formation and coalescence of polyene chains on the metal surface occur first, followed by the formation of the SWCNT cap-precursor, “ring condensation”, and the creation of a sp^2 -hybridized carbon structure. In this simulation, the nucleation process took approximately 400 ps. This first step occurred over a much longer time scale than the second stage of SWCNT condensation (approximately 50 ps). Therefore, SWCNT nucleation akin to the rate-limiting step of the SWCNT formation process was observed.

In situ TEM studies on CNT are able to tell a lot about mechanisms on SWCNT growth. Experimental study of the catalyst-support and catalyst-carbon interactions during the CVD growth of SWCNT has been done by Prof. Hofmann [73,74]. They found that the interplay of catalyst facets guiding carbon diffusion and network formation. They observe that transition metal catalyst nanoparticles on SiO_x support show crystalline lattice fringe contrast and high deformability before and during nanotube formation. A SWCNT nucleates by liftoff of a carbon cap. The carbon cap stabilization is guided by dynamic shape changes of the catalyst particle. In terms of a matching carbon cap, that is a good support for the SWCNT chirality selective growth by careful catalyst engineering. The understanding of the growth dynamics of SWCNT can also get hints from the study of the knot formation process of bamboo-like multi-walled carbon nanotubes (BCNTs) observed in real time using an *in situ* ultrahigh vacuum transmission electron microscope [73]. During BCNT growth, graphene sheets (bamboo knots) within the nanotube preferentially nucleate on the multistep Ni-graphite edges at the point where the graphene joins the catalyst particle, where it is stabilized by both the graphene walls and the Ni catalyst surface.

Besides the supported catalyst method which we focused in this review, the floating catalyst method is another kind

of important CVD growth method, the reader is referred to Ref. [75] for the detailed introduction of the method. Parametric analysis of the production of SWCNTs by the floating catalyst method performed by Cruden et al. gives a deeper understanding on the diameter and chiral family distribution of the synthesized SWCNTs [76]. Their work showed that larger residence time greater ferrocene percentage in the precursor solution both result in larger catalyst particles and hence larger diameter tubes, and higher temperature benefits the formation of smaller diameter tubes.

If the VLS mechanism is adequate to describe the process of carbon nanotube growth, it is quite pessimistic in predicting the control of the chirality of carbon nanotubes, since metal catalyst nanoparticles have to undergo melting state. In this case, the catalysts have no control toward cap formation of carbon nanotube growth at the initial stage. The precipitation of carbon from saturated metal carbide becomes a totally random process. As a result, if we want to control the initial cap formation, the dissolution and precipitation processes should be avoided. Based on this hypothesis, people turned to investigate the possibility of growing carbon nanotubes using non-metal nanoparticles.

4. Growing single-walled carbon nanotubes with controlled structures using non-metal catalysts

4.1. Non-metal catalysts for carbon nanotube growth

The first report using a non-metallic catalyst was the catalyst-free horizontal growth of carbon nanotubes on the Si face of hexagonal silicon carbide (6H-SiC) at temperatures above 1500 °C [77]. These nanotubes were single walled with a very narrow distribution of diameters. Nanotubes tended to follow the atomic structure of the surface, leading to preferential orientation and the development of ordered networks of tubes. Manipulation of nanotubes using AFM indicated that the tubes moved on the surface at high temperatures and were stabilized in the directions parallel and perpendicular to the step edges. Carbon nanotube formation was also reported using CVD with ethanol on semiconductor nanoparticles of SiC, Ge, and Si, with which no catalytic activity was expected [78]. Grown carbon nanotubes were single-walled or double-walled, with a diameter of 5 nm or smaller. The yield was much lower for SiC, Ge, and Si than for iron group metals. The difference in the carbon nanotube yield might reflect the catalytic activity of ethanol decomposition. SiC, Ge, and Si should have little activity of ethanol decomposition. Thus, a higher growth temperature was essential to induce the pyrolysis of ethanol. This implied that nanosize structures might act as a template for the formation of CNT caps composed of five- and six-membered rings. Providing a template for cap formation was the essential role of the catalysts. Isolated, two-dimensionally packed and three-dimensionally accumulated nano-diamond particles were also used for carbon nanotube growth [79]. After heat treatment in air, carbon nanotubes were grown at 850 °C by CVD using ethanol as a carbon source. Carbon nanotube growth from nano-diamond particles must be promoted by the

surface diffusion of carbon, and this was called the “vapor-solid surface–solid” (VSSS) mechanism. The VSSS mechanism of carbon nanotube growth on the nano-diamond surface was analogous to the mechanism of homoepitaxial diamond growth. Besides these techniques, the metal-free synthesis of high-quality MWCNTs by using new-diamond (n-diamond) as a catalyst was achieved by the heat fuse chemical vapor deposition (HFCVD) process [80]. In the growth of MWCNTs, the hexagonal planes of the n-diamond particles play a key role. It was proposed that the decomposition of CH_4 resulted in free activated carbon atoms that adsorbed on the hexagonal-ring-planes on the surface of n-diamond, and the continuous carbon deposition on the n-diamond surface formed hexagonal rings one after another, finally leading to the formation of MWCNTs. In the growth procedure, the n-diamond particle behaved like a Bucky shuttle seed, and was gradually stripped off with the upward growth of the nanotube. Similar to the metal-catalyst model for MWCNTs, the n-diamond catalyst particle kept the nanotube open and integrated the activated carbon atoms to form hexagons while lengthening the straight tube continuously, until the CVD process was terminated by closing the working gas inlet. Therefore, high purity and high graphitized MWCNTs were produced on an n-diamond film. It was also reported that a 30-nm-thick SiO_2 film deposited onto a Si wafer could serve as a substrate for carbon nanotube growth [10]. Dense and uniform SWCNT networks were reproducibly obtained on the surface of the substrate. A metal-catalyst-free “scratching growth” approach was also developed for the patterned growth of SWCNTs. Within the same principle, a clean Si wafer with a $1\ \mu$ layer of SiO_2 scratched by a diamond blade was used as the substrate for carbon nanotube growth [81]. From SEM observations, nanotubes can be found around the edge of the scratched areas. The fact that no carbon nanotubes can be found on the nanoscopically smooth surfaces, while

growth occurred on the scratched Si wafer/quartz plate under the same CVD conditions, indicated the growth of SWCNTs can only come from nanosized SiO_2 domains which were produced by scratching. It was proposed that the nanosized SiO_2 was in a molten state at the growth temperature and in the liquid-like structure allows Si and O atoms to move around quickly, thus creating a space hole or dislocation that might be able to catalytically decompose the hydrocarbon or ethanol molecules, and the high curvature of the SiO_2 nanoparticles could act as templates for the formation of a hemispherical cap with a graphitic structure for further SWCNT growth.

4.2. Length and diameter control of carbon nanotubes using non-metal catalysts

As with metal catalysts, people started to focus on structure control after succeeding in growing carbon nanotubes using non-metal catalysts. The direct length-sorted growth of SWCNTs was realized using SiO_2 as a catalyst [82]. It was found that the growth velocity of SWCNTs from a SiO_2 catalyst was only 8.3 nm/s, which was about 300 times slower than that of the commonly used iron group catalysts. Such slow growth allowed direct length-sorted growth of SWCNTs, especially for short SWCNTs, with hundreds of nanometers in length (Fig. 12a). As mentioned above, the diameter of carbon nanotubes can be altered by the size of metal catalyst particles. Even with this different growth mechanism, we confirmed that SiO_2 nanoparticles of various sizes can be used as nucleation centers realizing the growth of SWCNTs with controlled diameters [83]. It was found that the SiO_2 nanoparticles ranging from 1.22 to 1.98 nm could be obtained by the thermal oxidation of 3-aminopropyltriethoxysilane with different numbers of assembled layers. Using these nanoparticles as nucleation centers, SWCNTs with diameters from 0.90 to 1.82 nm could be grown by ethanol-CVD, which

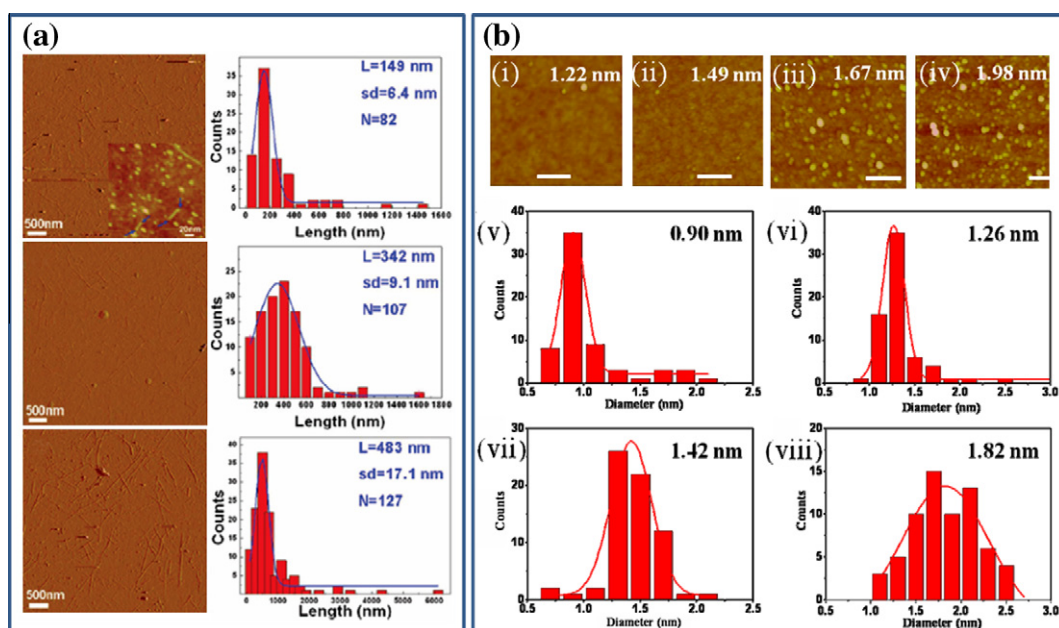


Fig. 12 – (a) Length [82] and (b) diameter [83] control of carbon nanotubes using non-metallic catalyst. (i–iv) AFM images of SiO_2 nanoparticles. Corresponding histograms of SWCNT diameter were plotted in (v–viii), respectively.

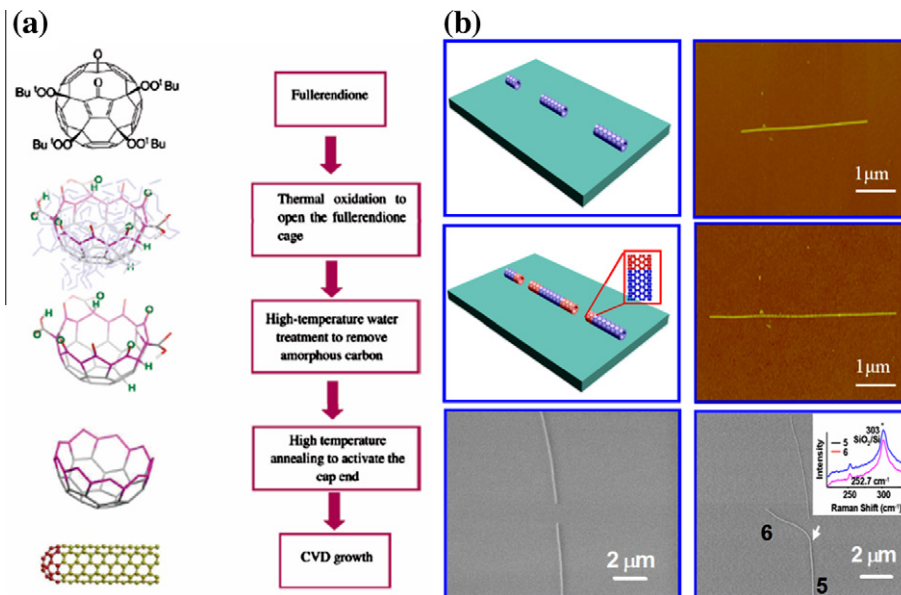


Fig. 13 – (a) Carbon nanotube growth from opened C₆₀ [84] and (b) an opened carbon nanotube [9].

indicated a direct relationship between SWCNT diameter and SiO₂ nanoparticle size (Fig. 12b). *In situ* resonance Raman spectroscopy and X-ray photoelectron spectroscopy proved that spherical SiO₂ nanoparticles did not transform into SiC but just played a role of nucleation centers during SWCNT growth. In this way, it was suggested that the SWCNT growth process in our system follows the VS mechanism with a lower growth velocity.

4.3. Cap-engineering for chirality control of single-walled carbon nanotubes

In the past decade, it has been confirmed that many non-metallic nanoparticles, such as SiO₂, diamond, and even C₆₀, can be used as catalysts for carbon nanotube growth. However, all these catalysts are still not able to control carbon nanotube chirality.

For this purpose, we developed a new SWCNT growth method using opened C₆₀ as a cap [84]. Several pretreatment procedures were used to obtain hemispherical fullerene (Fig. 13a). The fullerendione first underwent thermal oxidation in air at various temperatures to open the carbon cage. After thermal oxidation treatment, the furnace temperature was increased to 900 °C and the thermally-opened C₆₀ was treated in the presence of water to remove amorphous carbon. Lastly, the sample was annealed at 900 °C for 3 min to activate the carbon cap by removing carboxyl groups at the open end of the cap. The growth of SWCNTs from thermally opened C₆₀ followed a VS mechanism, for which the opened C₆₀ served as a carbon cap for growing SWCNTs by an open-end growth mode. The results indicated that the cage opening temperature directly affects the diameter distribution of SWCNTs. Higher cage opening temperatures were favorable for growing small-diameter SWCNTs, while lower cage opening temperatures were favorable for growing large diameter SWCNTs. In addition, the as-grown SWCNTs from

thermally-opened C₆₀ showed a steplike diameter distribution compared to SWCNTs grown by the Fe catalyst. Since C₆₀ can only influence the diameter of carbon nanotubes, we also developed a SWCNT clone method using SWCNT as seed [9]. A possible open-end growth mechanism of SWCNT cloning was proposed (Fig. 13b). Initially, SWCNTs with a predetermined chirality and open ends were prepared as seeds. When the temperature was higher than the decomposition temperature of the carbon source, C_x (mainly C₂ and C₃) radicals can be released, and then directly added to the open-ended SWCNT seeds. Thus duplicate SWCNTs can be continuously grown from the parent seed SWCNTs. It was reported that more than 600 short seed segments were measured and the cloning yield was relatively low (around 9%). This yield can be greatly improved up to 40% by growing SWCNTs on a quartz substrate. AFM and Raman spectroscopy characterization indicated that the parent nanotube and the duplicate nanotube had the same structure.

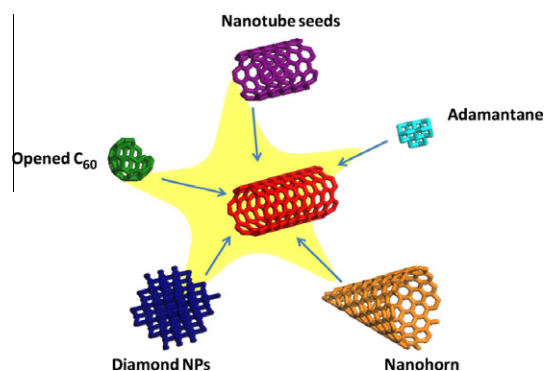


Fig. 14 – Schematics of carbon nanotube growth from carbon based catalysts [9,79,84,85].

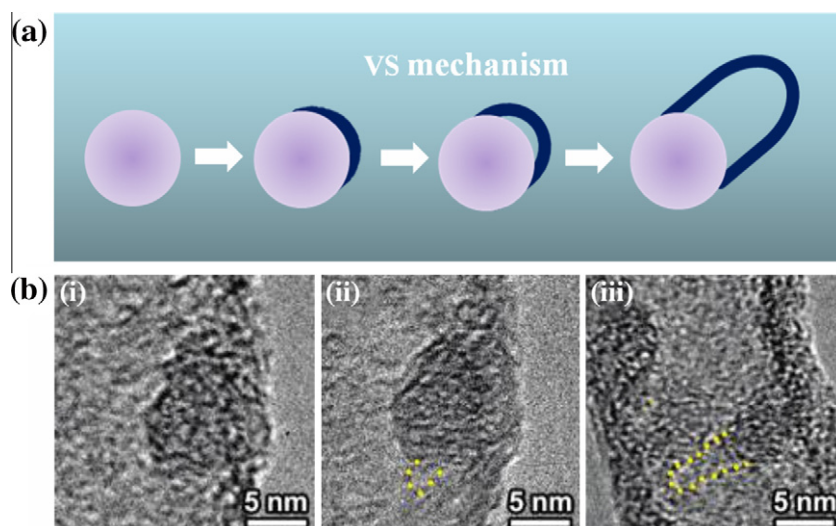


Fig. 15 – (a) Schematic growth of SWCNT on a non-metal solid surface [87]. (b) *In situ* TEM observations of the growth of SWCNTs from SiO_x [86]: (i) an original SiO_x nanoparticle; (ii) the same SiO_x nanoparticle with nucleation of an SWCNT after continuous heating for 2 min; (iii) an SWCNT grown from a small SiO_x nanoparticle.

Nowadays, many carbon nanostructures have been tried in attempts to control the chirality of carbon nanotubes using the cap-engineering hypothesis (Fig. 14) [9,79,84,85]. Moreover, this can introduce a total-carbon system without the contamination of metal species.

5. Growth mechanism of carbon nanotubes with non-metal catalysts

To understand the growth mechanism of carbon nanotubes using a non-metal catalyst, both experimental and theoretical studies were performed using SiO_x nanoparticles as catalysts [86]. *In situ* TEM observations revealed that the active catalyst for the carbon nanotube growth was solid and amorphous SiO_x nanoparticles, suggesting a VSS growth mechanism. From *in situ* TEM and CVD growth experiments, it was found that oxygen played a crucial role in the carbon nanotube growth in addition to the well-known catalyst size effect. Density functional theory calculations showed that oxygen atoms can increase the capture of $-\text{CH}_x$ and consequently facilitate the growth of SWCNTs on oxygen-containing SiO_x nanoparticles (Fig. 15).

Homma's group reviewed recent studies of SWCNT growth with these non-metallic materials and highlighted the mechanisms involved [87]. It was concluded that the ability of diamond, Si, SiC, and alumina to act as solid "catalysts" can be explained in terms of becoming carbon-coated nanoparticles. On these carbon-saturated surfaces, a graphene island with five-membered rings is formed as the nucleus of a SWCNT [88]. A nano-scale curved surface thus provides a template for carbon nanotube-cap formation. It is noteworthy that, in the cases of SWCNT growth using opened C_{60} as a cap and SWCNT cloning, along with performing as the solid "catalysts", the C_{60} and the parent seed SWCNTs also provide an existed cap or a predetermined open end for the following guided addition of carbon species.

6. Conclusion

The history of carbon nanotube research can be divided into five stages: catalyst choice, geometry control, conductivity separation and chirality control. Most researches have focused on metallic catalysts. Many difficulties have been conquered on the way to electronic applications. However, the key problem for metallic catalysts is that it is hard to control the carbon nanotube chirality since a metallic catalyst would pass through a melting state during growth at high temperatures which is called the VLS mode. In order to solve this problem, people have turned to investigate possibilities of using a non-metallic catalyst with the hypothesis of VS or VSS mode. Nowadays, plenty of non-metallic particles have been confirmed to be suitable for carbon nanotube growth. Although the catalyzing efficiency remains to be improved, some exciting attempts, such as clones of carbon nanotubes have been made. With so many promising results being obtained, the clear mechanism involved and more convincing evidence of the hypothesis are still required. This will benefit the bulk production of SWCNTs with well defined structures as well as the exploration of carbon nanotube-based applications. At present, the path to carbon nanotube-based electronic devices appears quite optimistic, if precise single chirality characterization can be realized in the near future.

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