

Catalysts for the growth of carbon nanotube “forests” and superaligned arrays

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When the size and spacing of catalyst nanoparticles are well controlled on a substrate, carbon nanotubes (CNTs) can grow and assemble into a unique, vertically aligned structure frequently called a “forest.” Long, aligned, and pure CNTs can easily be synthesized in simple or highly complex configurations. First reported in 1996, CNT forests have been shown to be unique and useful forms of CNTs, as they have spurred the development of novel processes and applications and in addition, served as test beds for investigations into CNT growth mechanisms. This article provides an overview of two decades of research in this area.

Introduction

A carbon nanotube (CNT) is a unique pseudo-one-dimensional structure composed of one or more layers of graphitic sp^2 -hybridized carbon and is a representative material for nanotechnology. The initial report of the discovery and elucidation of the structure of CNTs by S. Iijima has been cited more than 28,000 times (as of September 2017, according to the Web of Science), and was ranked among the top 100 (at #36) most highly cited scientific papers in 2014.^{1,2} CNTs possess diameters less than 100 nm for multiwall CNTs (MWCNTs) and generally less than ~3 nm for single-wall CNTs (SWCNTs) and can have exceptionally high-aspect ratios as their lengths extend into the centimeter scale.³ Importantly, being completely composed of carbon where the location of each atom is precisely defined, CNTs have exceptionally low density (e.g., 1.3 g/cm³, one-half that of aluminum) and possess a Young’s modulus as high as 3.7 TPa, which is about 5× that of carbon fibers.⁴

Vertically aligned CNT arrays (**Figure 1a**),⁵ called “VANTAs” for short or “forests,” or “carpets” are unique and interesting CNT assemblies, grown from well-defined arrays of catalyst nanoparticles on substrates by chemical vapor deposition (CVD). The alignment stems from crowding among CNTs, which then vertically orients the growth.^{6–8} CNT forests possess a number of merits. First, since the growth is carried

out from surface-bound catalysts, the catalysts can remain in the growth-step of the CVD process for arbitrarily long periods (up to ~30 h)⁹ to increase the CNT length, in contrast to other synthesis methods, such as arc discharge¹⁰ and laser ablation,¹¹ where the growth time is fundamentally limited. Second, in many cases, the catalysts remain anchored to the surface during growth (called “root growth”),^{12–15} and the CNT forest can be separated from the catalyst and substrate to yield high-purity, catalyst-free CNT material.¹⁶ These features have proven important for applications.

The growth process for CNT forests is scalable and industrial processes have been developed to mass produce CNT forests leading to numerous CNT applications, some of which have been commercialized, spanning CNT touch screens,¹⁷ thermal interface materials (TIMs),¹⁸ field emitters,^{19,20} planar incandescent light sources,²¹ flexible charge collectors,²² high-power and high-density supercapacitors,^{23,24} gecko-foot-mimetic dry adhesives,²⁵ bristles/brushes,^{26,27} through-silicon vertical interconnect access (vias),²⁸ and high current-carrying capacity CNT-Cu composites.²⁹

For example, Foxconn Electronics, in collaboration with Tsinghua University, China, fabricated ultrathin and aligned CNT sheets from superaligned MWCNT forests on 8-in. (200-mm) silicon wafers. These sheets have been used for transparent conducting films in smartphone touch screens.^{17,30,31}

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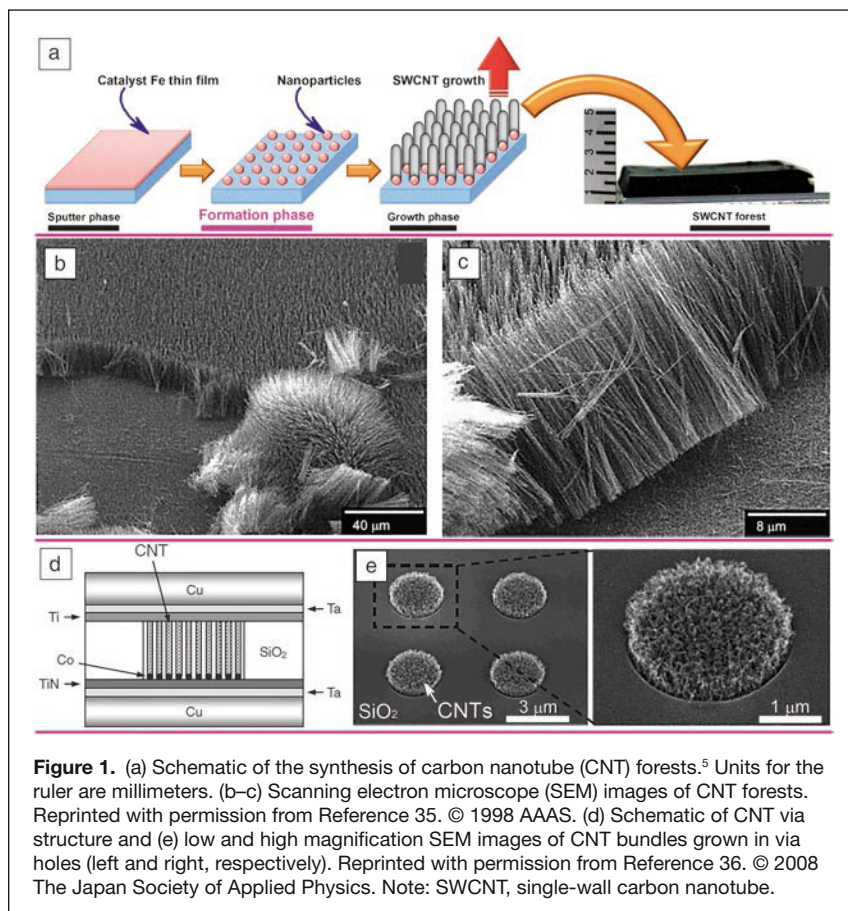


Figure 1. (a) Schematic of the synthesis of carbon nanotube (CNT) forests.⁵ Units for the ruler are millimeters. (b–c) Scanning electron microscope (SEM) images of CNT forests. Reprinted with permission from Reference 35. © 1998 AAAS. (d) Schematic of CNT via structure and (e) low and high magnification SEM images of CNT bundles grown in via holes (left and right, respectively). Reprinted with permission from Reference 36. © 2008 The Japan Society of Applied Physics. Note: SWCNT, single-wall carbon nanotube.

In addition, the National Institute of Advanced Industrial Science and Technology (AIST), Japan, in collaboration with Zeon Corporation, developed a continuous, belt conveyor process to synthesize aligned SWCNTs on flat 50 cm × 50 cm metal substrates and realized metric ton-level production of a high surface area material composed of long and pure SWCNTs.³² These SWCNTs have been used to produce TIM sheets with excellent thermal resistance (0.05°C/W), lower than that of thermal grease (0.10°C/W).³³ Further, the growth of forests is not limited to flat substrates and can be extended to three dimensions. Wei et al. demonstrated a potentially unlimited production capacity by growing forests on bead substrates using the fluidized bed CVD process.³⁴

This article presents a general picture of the development of CNT forest research, drawing on groundbreaking milestones, aspects of controlled synthesis, advances in material processing, and the essential requirements for CNT forest synthesis.

Overview of CNT forest research Inception

Li et al. first reported the synthesis of a vertically aligned CNT forest in 1996, where a 50- μm -tall forest of 30-nm dia. MWCNTs was grown by CVD using acetylene at 700°C from iron catalyst nanoparticles embedded in a mesoporous silica

substrate.⁶ This pioneering work marked an impetus for researchers to investigate challenges surrounding the synthesis as well as application potential of this material.

Low-temperature synthesis

One of the initial challenges was to reduce the CVD temperatures to enable synthesis directly onto devices. Ren et al. used plasma-enhanced hot filament CVD in 1998 to synthesize MWCNT forests with heights from 0.1–50 μm and controllable diameters (20–400 nm) on glass substrates at temperatures below 666°C (Figure 1b–c).³⁵ Research groups led by Awano at Fujitsu Laboratories Ltd. and Robertson at the University of Cambridge demonstrated further advancements in growing CNT forests below 400°C to integrate forests into the back-end-of-line of large-scale integration (LSI) for use in CNT vias (Figure 1d–e).^{36,37} Conventional copper LSI vias made by the dual-damascene process were expected to fail after miniaturization to the 22-nm node due to fundamental electromigration limitations. Awano et al. used remote plasma CVD and demonstrated forest growth in vias at temperatures as low as 430°C to overcome this obstacle.³⁶ Robertson et al. demonstrated the synthesis of SWCNT forests with narrow diameter distribution at 350°C by a cold-wall CVD process using NH_3 and H_2 to facilitate catalyst nanostructuring and activation.³⁷ Hart et al. later demonstrated an alternative approach to reduce the process temperature to 500°C by preheating the reactive gases.³⁸ Recent research has shown that low-temperature synthesis leads to defective CNTs, and therefore, the integration of highly crystalline CNTs into devices remains a challenge.^{39,40}

CNT forest patterning

Dai et al. demonstrated in 1999 that regular arrays of CNT forests (10–250 μm in size at pitches of 50–200 μm) could be synthesized using thermal CVD at 700°C by simply patterning the catalyst (Figure 2a–b).⁷ Additionally, they showed that these arrays could function as low-operating-voltage field emitters. Nilsson et al. later reported the relationship between emitter (CNT) spacing and field-emission properties.⁴¹ These pioneering studies sparked an enormous research effort to develop CNT field-emission displays led by two companies, Samsung and Noritake Co., Ltd.^{19,42,43} Currently, work on field emission from CNTs is ongoing, but significantly less for display applications as it has given way to the fast development of competing technology (e.g., organic light-emitting diodes). In fact, many companies have slowed or completely halted field-emission display development.⁴⁴

Dai et al. showed in their initial work that the synthesis of high-aspect-ratio and self-oriented arrays grown normal

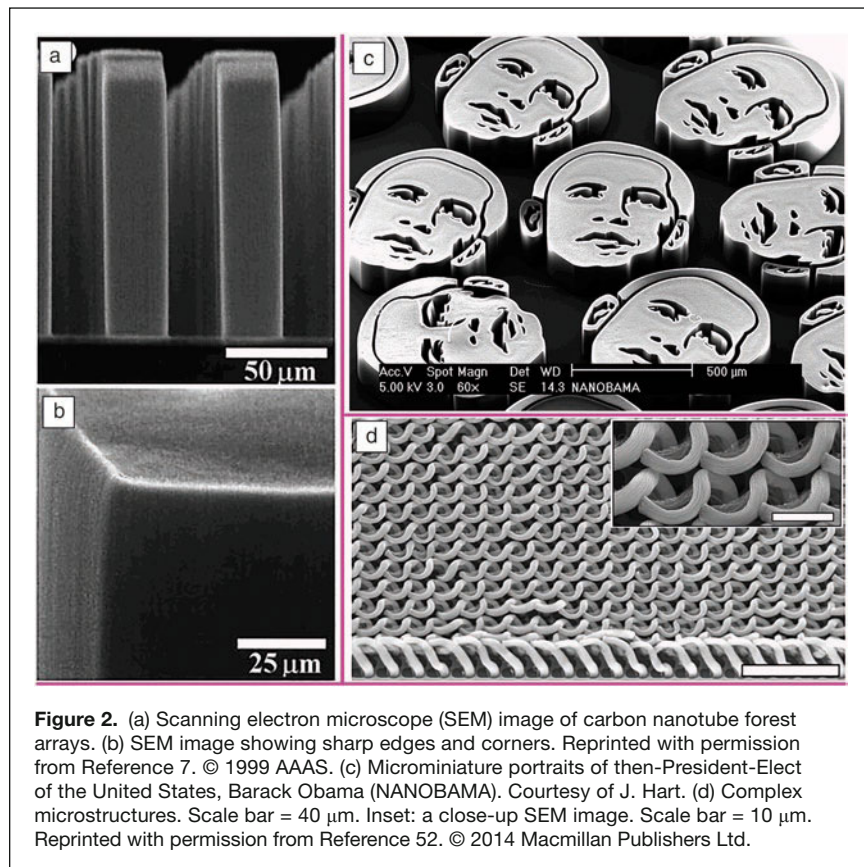


Figure 2. (a) Scanning electron microscope (SEM) image of carbon nanotube forest arrays. (b) SEM image showing sharp edges and corners. Reprinted with permission from Reference 7. © 1999 AAAS. (c) Microminiature portraits of then-President-Elect of the United States, Barack Obama (NANOBAAMA). Courtesy of J. Hart. (d) Complex microstructures. Scale bar = 40 μm . Inset: a close-up SEM image. Scale bar = 10 μm . Reprinted with permission from Reference 52. © 2014 Macmillan Publishers Ltd.

to the substrate by the self-assembly of CNTs was possible. Furthermore, these structures could be uniform in shape with sharp, well-defined edges, precisely matching the catalyst pattern throughout its length.⁷ Beautiful and complex structures could also be fabricated by utilizing lithography. Ajayan et al. pursued this aspect of making complex structures by simultaneously synthesizing laterally and vertically oriented forests from the sides and top, respectively, of trenches and demonstrating a flower-like structure grown from a silica pole.⁴⁵ J. Hart famously drew a 500- μm -wide image (NANOBAAMA) in 2008 of the then-president-elect of the United States (Figure 2c).⁴⁶

Engineering complex CNT forest structures

The structure of a CNT forest can also be engineered to control its density, orientation, and shape, opening up new application areas, such as supercapacitors and microelectromechanical systems. As grown, the CNT forests have a low mass density (0.037 g/cm^3) and high porosity (~96%).⁴⁷ Futaba et al. found that the CNT forest could form a packed, highly dense (0.57 g/cm^3), and aligned solid by immersing the forest into a liquid and allowing capillary forces to draw the CNTs together.⁴⁸ In addition, by applying external forces, the forests could be reoriented into a laterally aligned sheet for supercapacitor electrodes. This approach has been expanded by various methods, such as controlling the capillary force, multistep lithography, and controlling the strain during growth to

fabricate diverse three-dimensional (3D) structures (Figure 2d), spanning supercapacitors, cantilevers, relays, switches, and field-effect transistors.^{49–52} The state of the art of this technique is exemplified by an all-CNT 3D relay composed of a suspended cantilever, gate, and drain electrodes.⁴⁹

Drawing fibers and sheets

CNTs within a forest are not isolated, but rather, are interconnected through intermittent contact with adjacent CNTs, due to the self-assembly necessary for vertical alignment. This interconnection allows for a unique structural transformation of the forest into a fiber or aligned sheet. Jiang et al. were pioneers in this field where, in 2002, they reported that one could continuously draw bundles of CNTs into a fiber from a superaligned MWCNT forest (Figure 3a–b), analogous to drawing a thread from silk.⁵³ Baughman et al. further improved this drawing process by adding a simultaneous twist and demonstrated mechanically robust CNT yarn that did not degrade in strength when knotted, such as conventional fibers (Figure 3c).⁵⁴ He later demonstrated that CNTs could be drawn out one-dimensionally from the side of the forest to fabricate transparent, freestanding MWCNT

sheets (Figure 3d–e).²¹ These thin sheets (~50-nm-thick, sheet resistance of ~700 Ω/\square in the draw direction; transmittance of >85%) could therefore potentially serve as transparent conductors as touchscreens require sheet resistance of less than 500 Ω/\square and a transmittance greater than 85%. Jiang et al. developed this technique into a roll-to-roll process to produce transparent conducting films adequate for touch panels (sheet resistance of 208 Ω/\square with a transmittance of 90%) (Figure 3f).^{17,55} Foxconn Electronics (Hon Hai Precision Industry, China) uses this technology in some smartphones.⁵⁶

An alternative approach to fabricate CNT thin films from forests is to grow them vertically from catalyst lines, lay them horizontally onto a substrate, and solidify them through liquid-induced densification. When strained, these thin and aligned CNT films fractured into islands, however, they remained interconnected through CNT bundles in a manner similar to peeled string cheese. This phenomenon was used to develop a band-aid-type strain sensor suitable for monitoring a wide range of human motions by affixing the sensor onto skin.⁵⁷

SWCNT forests

All of the early studies on CNT forests involved MWCNTs. Almost a decade passed before a process was developed that could grow a forest of SWCNTs. To achieve this, it was necessary to develop a method to prepare an array of small catalyst nanoparticles and a special CVD process, both suited for

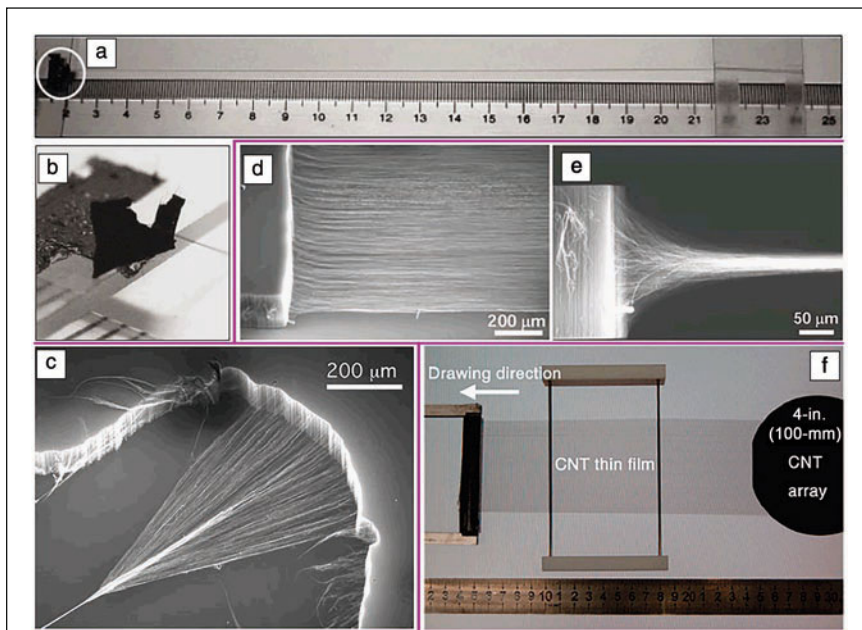


Figure 3. (a) 30-cm long carbon nanotube (CNT) yarn drawn from a 100- μm -tall, freestanding CNT forest. Units for the ruler are centimeters. (b) Enlarged photograph of the forest. Reprinted with permission from Reference 53. © 2002 Macmillan Publishers Ltd. (c) Scanning electron microscope (SEM) image of the draw and twist process from a CNT forest. Reprinted with permission from Reference 54. © 2004 AAAS. SEM images of a multiwall CNT (MWCNT) forest transformation into sheets viewed (d) at 35° angle with respect to the forest plane and (e) from the side. Reprinted with permission from Reference 21. © 2005 AAAS. (f) Freestanding CNT film drawn out from a superaligned MWCNT array grown on a 4-in. (100-mm) silicon wafer. Units for the ruler are centimeters. Reprinted with permission from Reference 55. © 2008 American Chemical Society.

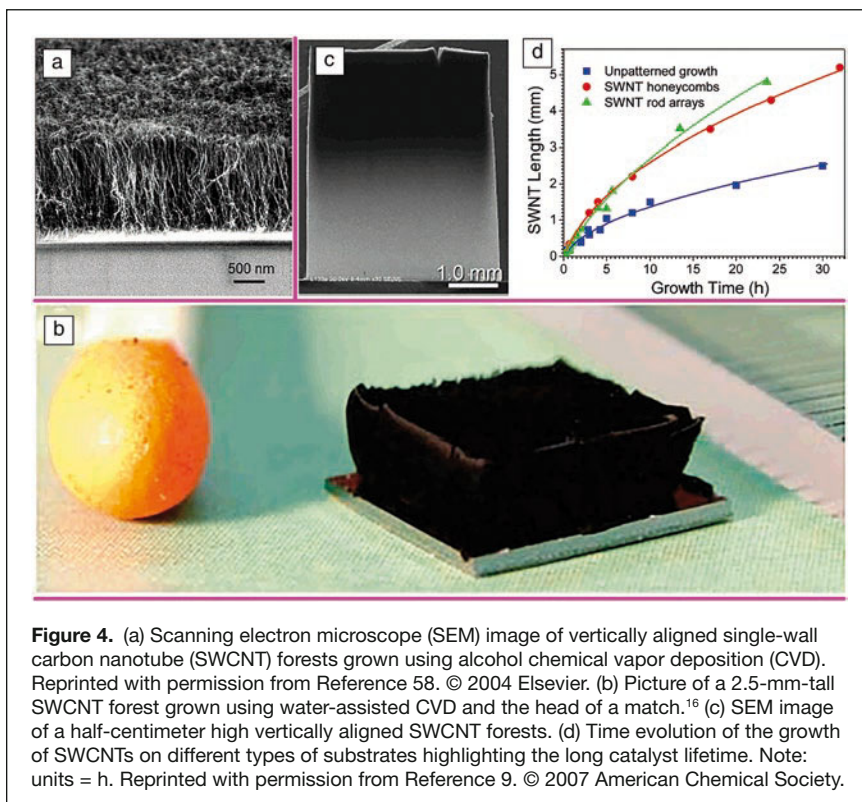


Figure 4. (a) Scanning electron microscope (SEM) image of vertically aligned single-wall carbon nanotube (SWCNT) forests grown using alcohol chemical vapor deposition (CVD). Reprinted with permission from Reference 58. © 2004 Elsevier. (b) Picture of a 2.5-mm-tall SWCNT forest grown using water-assisted CVD and the head of a match.¹⁶ (c) SEM image of a half-centimeter high vertically aligned SWCNT forests. (d) Time evolution of the growth of SWCNTs on different types of substrates highlighting the long catalyst lifetime. Note: units = h. Reprinted with permission from Reference 9. © 2007 American Chemical Society.

SWCNT growth. Maruyama et al. reported the first pioneering work using monodispersed Co-Mo catalyst nanoparticles on quartz substrates and alcohol as the carbon feedstock to grow a 1.5- μm -tall forest in 60 min (**Figure 4a**).⁵⁸ Alcohol was important for high catalyst activity and long lifetime. The long lifetime was attributed to the etching of carbon atoms with dangling bonds by the decomposed OH radical.⁵⁹ Hata and Futaba et al. reported a water-assisted CVD technique on an alumina-Fe catalyst system to grow mm-scale (2.5 mm, 10 min) SWCNT forests (**Figure 4b**).¹⁶ These SWCNT forests could be easily separated from the substrate and catalyst, providing an extremely pure SWCNT material (>99.98%)¹⁶ with high specific surface area (>1100 m²/g).^{60,61} The long length and high purity were crucial and significant advantages for the development of applications.^{62,63} Currently, Zeon Corporation is producing metric ton-scale SWCNT forests per year,⁶⁴ under the subsidiary Zeon Nano Technology Co., Ltd., based on this synthesis technique and is developing applications spanning energy storage (e.g., supercapacitor electrodes), electronics (e.g., thermal interface materials for the heat management of servers and power devices), and functional materials (e.g., high-temperature tolerant rubber composites, electrically conductive rubbers and paints, and antistatic plastics).^{33,62,63,65} Subsequent studies have shown that SWCNT forests can be grown with long lifetimes of up to ~30 h and forest heights beyond 0.5 cm (**Figure 4c–d**).⁹

Requirements for the synthesis of CNT forests

Catalyst size and spacing

The catalyst is one of the primary factors in CNT forest synthesis. Because the synthesis of a CNT forest requires an array of catalyst nanoparticles on a substrate, the catalyst size and spacing are important parameters. Many studies have proven that for most CVD conditions, the catalyst size determines the nanotube diameter and the number of walls, where a small catalyst produces a small diameter SWCNT and the number of walls increases with catalyst size.^{66–69} This relationship has been used to modulate the CNT diameter and its number of walls within the forest. In addition, the catalyst spacing determines the interaction between the CNTs and thus is strongly correlated to the ability to self-assemble.

This is particularly true for SWCNTs, as they cannot individually stand vertically and require the support of adjacent SWCNTs for vertical alignment.⁸

A systematic investigation of synthesis of CNT forests to determine relationships between catalyst size and the spacing, forest height, and number of walls in the CNTs was carried out and mapped (catalyst size: 1.3–8.0 nm; spacing: 5–80 nm).⁷⁰ This map revealed the existence of a “sweet spot” for the highly efficient growth of SWCNT forests (**Figure 5a**). SWCNT forests could only be grown efficiently within this region because (1) increased catalyst particle diameter would lead to MWCNTs growth (multiwall border); (2) decreased diameter would lead to low growth rates (low-efficiency border); (3) large catalyst spacing would lead to the inability to vertically align (lateral growth border);^{71,72} and (4) tightly

spaced catalysts are difficult to prepare (high catalyst density border).

Root growth or tip growth

Early on, debate began on the growth mechanism of CNT forests, in particular, whether or not CNT growth proceeded through a root growth mode (catalyst anchored to the substrate) or a tip growth mode (catalyst at the top of the CNTs). Through a number of studies, it is now known that both modes can occur depending on the strength of the catalyst–substrate interaction. Strong interaction resulted in root growth, while weak interaction resulted in tip growth. For CNT forest growth, small catalysts require a smaller spacing, as previously discussed; therefore, in order to survive the severe growth ambient (~800°C) with a minimum of catalyst aggregation,

a relatively strong catalyst–substrate interaction is required. Thus, most of the CNT forest synthesis techniques result in root growth.^{12–16} However, when the catalyst size is large, tip growth has been observed.^{73,74} Interestingly, the root growth mode affords sequential growth cycles from the same catalyst. Eight stacked multilayers have been successfully synthesized with each layer being physically disconnected to generate clean and identical forests.¹³ In addition, this phenomenon has been combined with *in situ* time-lapse photography and laser irradiation to investigate the growth kinetics of forests.¹⁵

Catalyst stability and growth termination mechanisms

Any mechanism that affects the density of the CNTs affects the vertical growth progression of the forest. Hart et al. reported that termination of the forest growth results from the reduction in the number of active catalyst nanoparticles (**Figure 5b**).⁷¹ In short, when the density of the CNTs, which is dependent on the number of active catalyst nanoparticles, is insufficient to maintain a self-supporting structure, the forest growth terminates. Therefore, the catalyst nanoparticle array must remain stable both morphologically (i.e., size and spacing) and chemically (able to grow CNTs) throughout the CVD process, which typically occurs at high temperature.

Of the many mechanisms triggering instability in the catalyst array, Ostwald ripening (coarsening) and subsurface diffusion are two often discussed mechanisms. Ostwald ripening is characterized by the increase in size of larger particles at the expense of smaller particles, which results in the overall reduction in the number of catalyst particles (i.e., increased spacing).

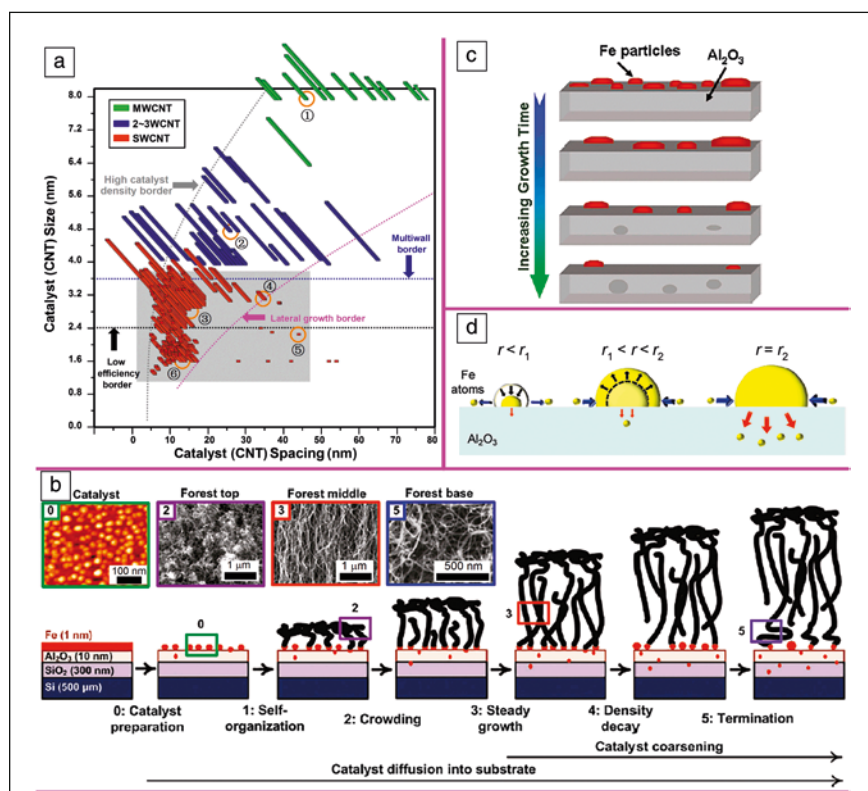


Figure 5. (a) Map showing the multiple borders and zones enclosing the high-efficiency single-wall carbon nanotube (SWCNT) region (3) as a function of catalyst (CNT) size and spacing. (1) Multiwall carbon nanotube (MWCNT) forest region; (2) two- to three-wall CNT forest region; (4) nonaligned (low-density) CNT forest region; (5) lateral SWCNT agglomerate region; and (6) low-efficiency short SWCNT forest region.⁷⁰ (b) Collective model of catalyst evolution and CNT population dynamics, showing five distinct stages of the forest growth process. Stage 1: lateral entanglement of CNTs at the onset of growth; Stage 2: beginning of vertical growth; Stage 3: continued vertical forest growth; Stage 4: forest growth rate decrease due to loss in active catalyst nanoparticles; Stage 5: forest growth stops. Reprinted with permission from Reference 71. © 2011 American Chemical Society. (c) Schematic diagram showing (top to bottom) the loss of Fe catalyst due to the combination of Ostwald ripening and subsurface diffusion. Reprinted with permission from Reference 76. © 2010 American Chemical Society. (d) Fe catalyst nanoparticle size stability driven by Ostwald ripening and subsurface diffusion competition. Left/middle: decrease/increase in particle size by Ostwald ripening. Right: stable particle size due to the balance between the two mechanisms.⁷⁷ Note: r , catalyst nanoparticle radius; r_1 , smaller, unstable equilibrium particle radius; r_2 , larger, stable equilibrium particle radius.

Maruyama et al. showed that the inclusion of trace amounts of water in the growth ambient reduced the diffusion rates of catalyst atoms.⁷⁵ Maruyama et al. first reported subsurface diffusion with respect to forest synthesis, a process whereby the catalyst nanoparticles diffuse into the bulk of the support layer and result in decreased catalyst size and, in some cases, complete disappearance (Figure 5c).⁷⁶

Sakurai et al. proposed that a balance between Ostwald ripening and subsurface diffusion would result in improved catalyst stability (Figure 5d).⁷⁷ Robertson et al. overcame both subsurface diffusion and Ostwald ripening through the use of TiSiN film substrates, which acted as a barrier toward subsurface diffusion and supported catalyst de-wetting due to its low surface energy.⁷⁸ In addition to morphological change in the catalyst nanoparticle array, chemical deactivation, either through carbon coating or by poisoning from reaction with the substrate or excessive additive gases, represents the other general mechanism to decrease the stability of the catalyst array.^{79,80} Stadermann et al. showed that excess water (>3000 ppm) resulted in a decreased growth rate and excess carbon resulted in growth termination due to the formation of an amorphous carbon coating on the catalysts.⁷⁹ Yamada et al. have shown that the inclusion of water was crucial in removing this carbon coating and increasing the catalyst activity significantly.⁸⁰

Summary and outlook

Remarkable progress has occurred in our understanding of the synthesis and application of CNT forests. We can now grow CNT forests with different numbers of tube walls, density, and height in the centimeter range. Further, we understand the limiting mechanisms and boundaries surrounding the synthesis. However, with all of these achievements and advancements, challenges remain as the landscape of the CNT field continues to evolve from that of scientific discovery toward industrial application. Further understanding of the synthesis for the development of low-cost mass production, scalable processing of the grown material, and identifying applications that highlight the unique and remarkable properties of CNTs are all continuing challenges representing the new frontier for CNT forests.

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