

Chemical Vapor Deposition Growth of Single-Walled Carbon Nanotubes with Controlled Structures for Nanodevice Applications

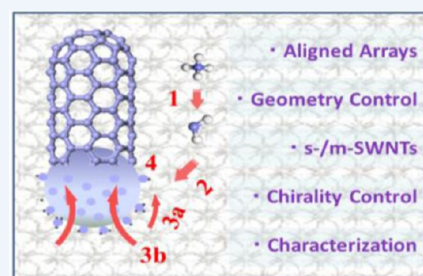
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CONSPECTUS: Single-walled carbon nanotubes (SWNTs), a promising substitute to engineer prospective nanoelectronics, have attracted much attention because of their superb structures and physical properties. The unique properties of SWNTs rely sensitively on their specific chiral structures, including the diameters, chiral angles, and handedness. Furthermore, high-performance and integrated circuits essentially require SWNT samples with well-aligned arrays, of single conductive type and of pure chirality. Although much effort has been devoted to chemical vapor deposition (CVD) growth of SWNTs, their structure control, growth mechanism, and structural characterizations are still the primary obstacles for the fabrication and application of SWNT-based nanodevices.

In this Account, we focus on our established CVD growth methodology to fulfill the requirements of nanodevice applications. A rational strategy was successfully exploited to construct complex architectures, selectively enrich semiconducting (s) or metallic (m) SWNTs, and control chirality. First, well-aligned and highly dense SWNT arrays are beneficial for nanodevice integration. For the directed growth mode, anisotropic interactions between the SWNTs and the crystallographic structure of substrate are crucial for their growth orientation. Just as crystals possess various symmetries, SWNTs with controlled geometries have the corresponding turning angles. Their complex architectures come from the synergetic effect of lattice and gas flow directed modes. Especially, the aligned orientations of SWNTs on graphite are chirality-selective, and their chiral angles, handedness, and (n,m) index have been conveniently and accurately determined. Second, UV irradiation and sodium dodecyl sulfate (SDS) washing-off methods have been explored to selectively remove m-SWNTs, leaving only s-SWNT arrays on the surface. Moreover, the UV-assisted technique takes the advantages of low cost and high efficiency and it directly produces a high ratio of s-SWNT arrays. We also designed a smart scotch tape to sort out the s-SWNTs and m-SWNTs from the as-grown mixture with 3-aminopropyl-triethoxysilane and triethoxyphenylsilane as glues, respectively. This is analogous to the mechanical exfoliation of a graphene sheet. Third, the obtained SWNT intramolecular junctions obtained by temperature-mediated CVD indicate that temperature can seriously affect the SWNT's chirality during its growth. Importantly, the cloning method can validate the chirality-controlled growth of SWNTs, and the cloning efficiency is significantly improved on a quartz surface.

Well-aligned SWNT arrays with a high density and controlled structures are highly desirable for carbon nanoelectronics. We hope that the advanced methodology used here will promote their controlled preparation and provide insights into the growth mechanism of SWNTs.



1. INTRODUCTION

Single-walled carbon nanotubes (SWNTs),¹ an allotrope of carbon with a cylindrical nanostructure, have been regarded as the potential building blocks for future carbon-based nanoelectronics.^{2,3} Due to their unique combination of extraordinary properties, plenty of functional nanodevices based on SWNTs have continuously emerged during the last two decades, from single p-type or doping free n-type field effect transistors (FETs)^{4,5} to the recently demonstrated nanotube computer.^{6–8} SWNT species for nanodevices should possess the following essential characteristics (Figure 1A): well-aligned arrays with controlled orientation to favor their large-scale integration, separated semiconducting and metallic properties with controlled conductivity type to enable efficient switching, and pure (n,m) index with controlled chirality to optimize the

performance.^{9,10} Obviously, these stringent requirements pose various intense challenges to the SWNT growth technique.

Among all available technologies for SWNT preparation, catalytic chemical vapor deposition (CVD) provides many distinct advantages, such as low-cost, wafer-scale, and repeated growth.^{11,12} Nevertheless, two daunting reasons preclude the CVD controlled preparation of SWNTs from satisfying the requirements of nanodevice fabrication. First is the diversity and similarity of SWNT chiral structures.¹³ Each SWNT can be uniquely defined with a chiral index (n,m) ; about 2/3 of SWNTs are semiconducting with a bandgap dependent on their diameters ($E_g = C/d$ (nm)), the constant C is approximately 0.7 eV/nm.¹⁴ The handedness of chiral SWNTs can be classified

Received: December 23, 2013

Published: June 13, 2014

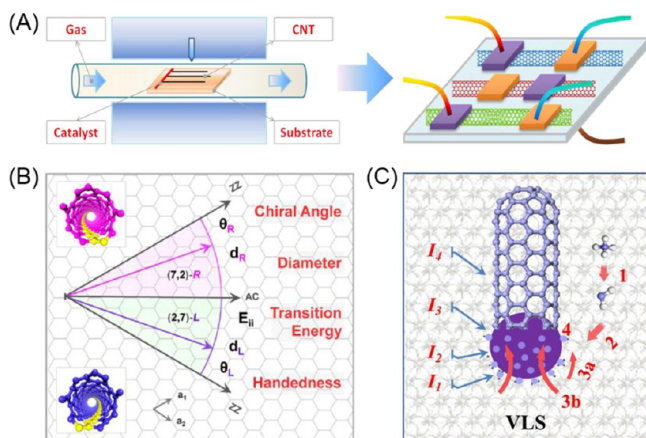


Figure 1. (A) CVD controlled growth of SWNTs for nanodevice applications. A typical growth process contains the catalyst, substrate, and carbon feedstock to prepare SWNTs. (B) Sketch showing SWNTs rolled from graphene sheets with different chiral angles, diameters, transition energies, and handednesses. (C) VLS growth mechanism of a SWNT from a metallic catalyst, including many important interfaces between the catalyst, gas molecules, the substrate, and the SWNT.

into right-handed ($n > m$, R) and left-handed ($n < m$, L). Moreover, SWNTs with similar diameters are endowed with different handednesses, chiral angles (θ), and conductive types, like (7,2)-R and (2,7)-L that belong to the $d \approx 0.6$ nm family (Figure 1B). Second, the growth mechanism is still controversial with several ambiguous hypotheses.^{15–17} Nucleation centers for SWNT growth can be divided into two categories: metallic catalysts involved in various transition metals and their alloys, and nonmetallic nanoparticles with many elements and their oxides.^{12,18} Although vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms have been proposed to illustrate the cap formation–elongation–termination process (Figure 1C), the detailed elemental reactions have still eluded scientists. These include the interactions between the carbon fragment and catalyst, the actual roles of the nanoparticles, and the key factor to chiral structures.¹⁹ A well established relationship among CVD conditions, the used catalysts, and the chiral structures of the grown SWNTs is still lacking.²⁰

In this Account, we will elaborate our recent progress on the CVD growth methodology of SWNTs with controlled structures. Many rational strategies, like surface induced growth, UV assisted CVD technique and cloning growth,

were established to control the aligned orientation, the conductivity type, and the chiralities of SWNTs toward their nanodevice applications. A novel characterization approach is introduced to promote the accurate and comprehensive determination of chiral structures.

2. WELL-ALIGNED SWNT ARRAYS FOR NANODEVICE INTEGRATION

The integration of SWNT-based nanodevices demands features such as large scale production, high density, and perfect alignment without any bundles.²¹ Well-aligned SWNT arrays can efficiently avoid the mis-orientations and tube–tube connections. Therefore, the fabricated FETs can show a remarkable on/off ratio and carrier mobility compared with the random networks.²² Directed growth methods for SWNT arrays can be classified into three categories: surface structures (atomic steps or lattices),^{23,24} gas flow,^{25,26} and external fields (like electrical fields).^{27,28} In general, SWNTs from lattice-directed growth are high density and wafer-scale, while the gas flow directed method gives ultralong SWNTs with a superior growth rate.

2.1. Lattice Directed Growth of SWNTs with Controlled Geometries

Lattice directed growth method has already been widely used to prepare SWNT arrays with controlled geometries, and it was first discovered on Si(100) and (111) surfaces in 2000.²⁹ The physical basis of this method originates from the anisotropic interactions between the elongated SWNTs and the substrate during CVD growth. Therefore, the superior surface structures, approximate temperature, and catalyst concentration are all critical parameters that determine the alignment quality of the SWNTs. Currently, various single crystals with flat surfaces are the predominant substrates, such as quartz and sapphire. The annealing process of substrate can reconstruct their surface structures and then significantly improve the alignment order of the obtained SWNTs. For instance, the optimized conditions for st-cut quartz are calcination at 900 °C for 8 h.²² The SWNT growth mostly occurs at 800–900 °C, because the higher temperature severely weakens the interactions between the catalyst/SWNT and substrate. Additionally, SWNT coverage can swiftly increase with catalyst concentration, while the growing SWNT will possibly change its growth direction if the concentration is too high due to Ostwald ripening.³⁰

In principle, the growth direction of SWNTs is dictated by the symmetries of the crystal surface. From the fundamental

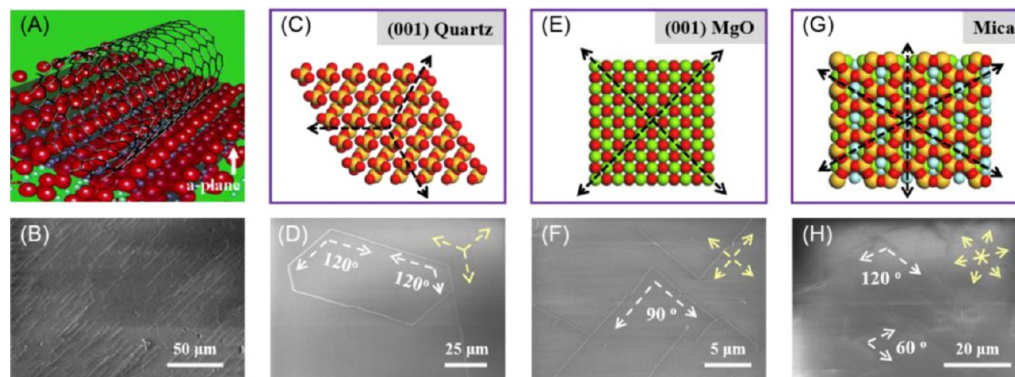


Figure 2. Lattice directed growth of SWNTs with various geometries. Surface structures of *a*-plane sapphire (A), quartz(001) (C), MgO(001) (E), and mica (G) with different symmetries. The obtained SWNTs with controlled geometries are shown in parts B, D, F, and H.

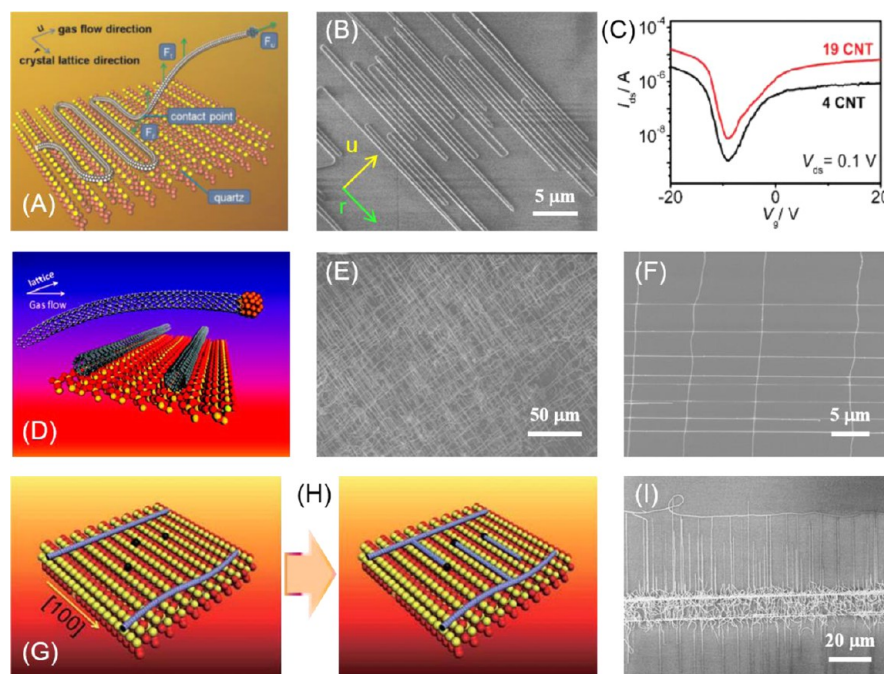


Figure 3. (A) Schematic of serpentine SWNT formation. (B) Typical scanning electron microscope (SEM) image of a serpentine SWNT. (C) Transport curves of nanodevice from serpentine SWNTs with different parallel segments. (D) Illustration of the growth mechanism of SWNT cross-bars and (E, F) their SEM images. (G, H) Schematic of SWNTs with controlled length and (I) the related SEM result.

crystallography, we know that there are five kinds of symmetries for all crystal substrates: 1-, 2-, 3-, 4-, and 6-fold. Amorphous SiO_x is a conventional substrate for the preparation of SWNT networks with arbitrary orientations. On *a*- and *c*-plane sapphire surfaces, SWNTs elongate along the linear oxygen-rich crystalline directions, and therefore, the obtained SWNTs are parallel arrays (Figures 2A,B).²⁴ Subsequently, Y-cut, st-cut, and R-cut quartz crystals have been successively developed to broaden the variety of 2-fold symmetrical substrates. We systematically exploited quartz(001), MgO(001), and layered mica with 3-, 4-, and 6-fold symmetry, respectively, to investigate the potential geometries of SWNTs.³¹ We found that the obtained SWNT arrays can be aligned along three directions at 120° , four directions at 90° , and six directions at 60° on their respective surfaces (Figures 2C–H). The appearance of these special angles mainly results from thermal perturbation or surface defects. Consequently, these SWNTs with controlled geometries can be utilized to fabricate and integrate multifunctional nanodevices.

2.2. Synergetic Effect of Lattice and Gas Flow Directed Modes for Complex SWNT Architectures

As described above, the van der Waals interaction between SWNTs and surface strongly depends on the growth temperature. The gas flow directed mode is undertaken at a higher temperature (normally $\geq 950^\circ\text{C}$) than the lattice directed mode. In this case, the thermal buoyancy is sufficient to lift the catalyst away from the substrate surface.²⁶ The alignment and growth direction of SWNTs is mainly determined by the gas flow. Additionally, fast-heating or ultralow gas flow can evidently prevent a turbulent state and this benefits the production of ultralong SWNTs. By synergetic effect of these two growth modes, complex architectures, such as the serpentine SWNTs,³² cross bars,³³ and SWNTs with specific lengths can be designed and constructed.³⁴

Serpentine SWNTs are essentially ultralong tubes that have been crinkled into many periodic parallel segments. This is suitable for SWNT arrays with identical chirality. We found that a controlled landing process during temperature decrease can adjust the competition of two crucial forces: the lattice-alignment force and the shear friction force. Additionally, the amplitude and period of the serpentine SWNTs (Figure 3A) are remarkably improved under a slow cooling speed.³² For example, from 975 to 775°C within 60 min, the yield of serpentine SWNTs on quartz was more than 96% and the amplitude and periodic density were $100\ \mu\text{m}$ and $2\ \text{tubes}/\mu\text{m}$, respectively. The measured curves showed that the fabricated devices can endure extraordinary current density with the remained on/off ratio (Figure 3C). Moreover, using multifold crystal substrates, we produced serpentine SWNTs along different directions.³¹ Lattice directed growth and gas flow directed growth methods can simultaneously result in growth of SWNT cross-bars in one CVD batch (Figure 3D).³³ Experimentally, it is critical that the lattice direction of quartz is perpendicular to the gas flow, and two perpendicular catalyst strips should be patterned. Additionally, we can arbitrarily terminate the growth of SWNTs with another SWNT as a nanobarrier (Figure 3G).³⁴ Ultralong SWNTs were initially grown or transferred onto quartz. Lattice directed SWNTs from the deposited catalysts will stop their growth when they meet the SWNT nanobarrier. In this way, SWNTs with controlled lengths can be achieved by defining the relative positions of the nanobarrier and the catalyst.

2.3. Chirality Dependent Alignment of SWNTs on Graphite

Although many growth methods or substrates have been exploited for the preparation of aligned SWNT arrays, the obtained SWNTs along each direction always present a mixture of chiral structures. Therefore, the alignment of SWNTs with selected chiralities remains a challenging issue. Graphene, a typical two-dimensional nanomaterial, possesses similar con-

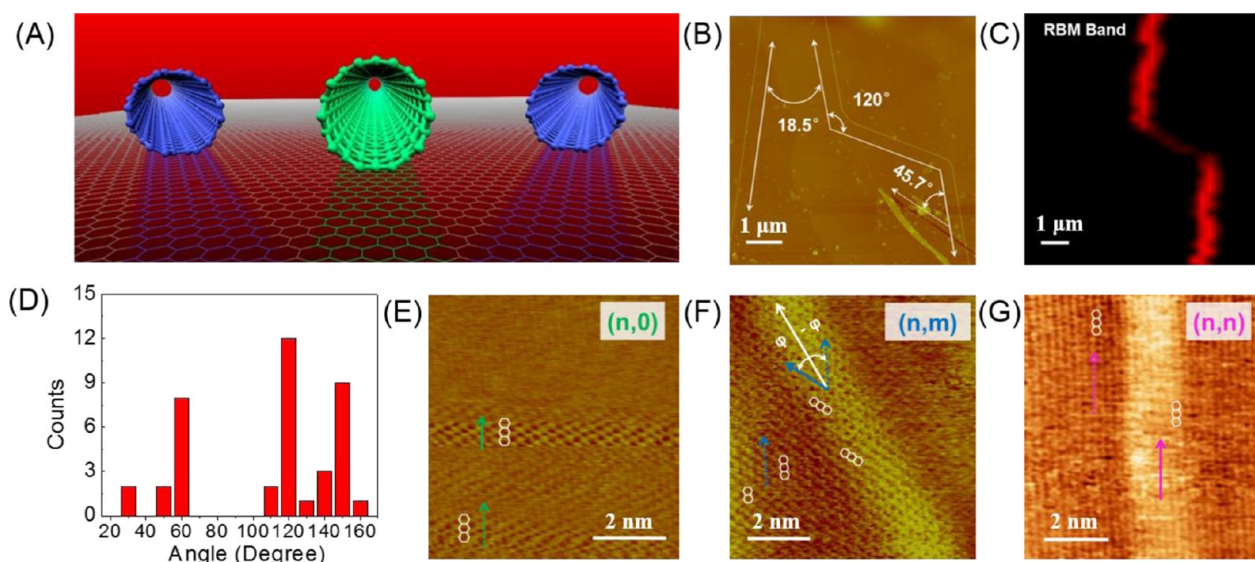


Figure 4. (A) Chirality dependent alignment of SWNTs on graphite. (B) AFM image of anchored SWNTs along the graphene lattice. The formed angle between the two SWNTs is 18.5°. (C) Raman mapping image of a SWNT at 120° in part B. (D) Turning angle distribution of the obtained SWNTs. (E–G) Atomically resolved STM images of $(n,0)$, (n,m) , and (n,n) SWNTs on graphene surfaces.

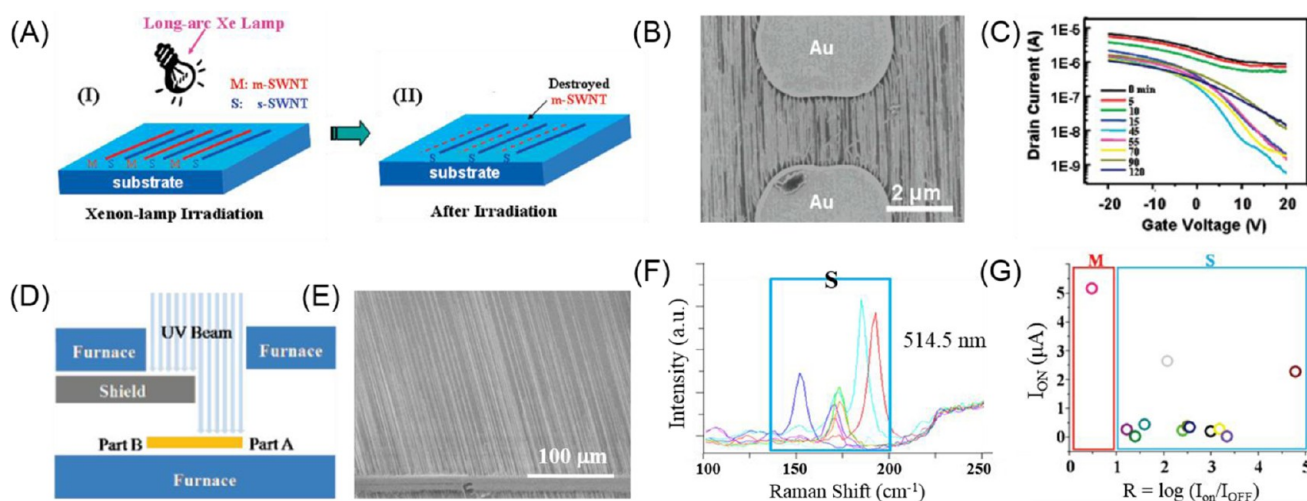


Figure 5. (A) UV irradiation to remove m-SWNTs from SWNT arrays. SEM image of the obtained s-SWNT arrays (B) and the corresponding in situ measurement (C). (D) Direct growth of s-SWNTs by the UV-assisted CVD technique. SEM image (E), Raman spectra (F), and electrical results (G) of the grown s-SWNT arrays. Laser wavelength was 514.5 nm.

jugated structures to SWNTs. It is well-known that AB stacking is the preferential configuration for two graphene layers.³⁵ When a SWNT is aligned by a graphene lattice, the strongest van der Waals interaction can be achieved when their interfaces have similar AB stacking (Figure 4).³⁶ Atomic force microscopy (AFM) and Raman results have revealed that the obtained SWNTs were anchored along six directions and further presented the special turning angles of 120°, 60°, and 150° because of the D_{6h} symmetry of the underlying graphene. Furthermore, we also performed scanning tunneling microscopy (STM) characterization to investigate the atomic structures of aligned SWNTs and graphene. As expected in Figure 4E–G, we speculated that $(n,0)$, (n,m) , and (n,n) SWNTs had identical benzene ring arrangements with their corresponding graphene substrates. So, it is confirmed that the growth orientation of SWNTs on graphene greatly depends on their chiral structures.

3. SEPARATED PREPARATION OF s-/m-SWNTs

Semiconducting SWNTs (s-SWNTs) are the functional building blocks for FET nanodevices and logical circuits. m-SWNTs can be used as essential device connectors or electrodes due to their ballistic transport behavior. The IBM Center, research leader in carbon nanoelectronics, claims that the impurity concentration of metallic SWNTs (m-SWNTs) should be less than 0.0001%.³⁷ However, conventional CVD SWNTs usually contain approximately 2/3 s-SWNTs and 1/3 m-SWNTs. Therefore, the separation or selective enrichment of s-SWNTs or their counterparts from naturally produced mixtures remains a challenge. Owing to their inherent electronic properties, the density of states of s-SWNTs presents a small energy band gap near Fermi level, which is inversely proportional to the tube diameter. m-SWNTs are therefore more reactive than s-SWNTs when their diameters are similar. All the current separation methods can be divided into two groups: postgrowth treatment and direct selective growth.³⁸ We

have developed a series of approaches for the preparation of SWNT arrays of a single conductive type, including a UV-assisted CVD technique,³⁹ a smart scotch tape separation method,⁴⁰ and SDS washing off m-SWNT method.⁴¹

3.1. UV-Assisted CVD Technique for s-SWNT Arrays

Directly selective growth methods are suitable for the production of clean, nondestructive, high density, and well-aligned SWNT arrays. This is compatible with the standard processes for nanodevice fabrication. UV beam irradiation can promote the decomposition of hydrocarbon gases, leading to concentration increase of oxidative chemicals (Figure 5A). In our case, SWNT arrays with a high density of 20/ μm were initially prepared on an *a*-plane sapphire surface.⁴² A long-arc Xe lamp was used to irradiate the naturally produced SWNT arrays. Both the resonant Raman spectra and the electrical measurements clearly revealed that m-SWNTs were preferentially destroyed, leaving s-SWNT arrays, 50–90% of which undergo radiation-induced modification. Furthermore, an in situ light treatment of FETs was performed to track the destructive process. The transport properties in Figure 5C show that the off-state current dramatically decreases after 15 min of irradiation and the on/off ratio exceeds 2000.

We have tentatively introduced this UV irradiation method for the direct CVD growth of SWNTs, named UV-assisted CVD technique (Figure 5D).³⁹ The effective wavelength of the used UV light ranged from 200 to 400 nm, and a manufactured hole on the top of furnace allows light to cover the quartz surface. The irradiation time and light intensity are critical to the density of SWNTs. A shorter irradiation time leads to longer and denser SWNTs by using Cu catalyst. In addition, we transferred the obtained samples under optimized conditions onto a SiO_x surface to examine the quality of the s-SWNTs. Raman data with different excitations showed amazing results without any m-SWNTs, which is in perfect agreement with the measured results from FET devices. We assumed that the separated growth of SWNTs under UV irradiation occurred at the stage of cap formation, so that the surviving s-SWNT arrays maintained a high density and intrinsic structures.

3.2. Smart Scotch Tape for s-/m-SWNT Separation

Reports on the direct preparation of m-SWNT arrays on surfaces are rare.⁴³ The postgrowth treatment method can successfully compensate for this inevitable drawback, which can be used to separate SWNT mixtures on a large scale. We designed a smart scotch tape mechanism to extract s-SWNTs or m-SWNTs from the array mixture (Figure 6A), analogous to the mechanical exfoliation of graphene.⁴⁰ The special scotch tape was composed of flexible polydimethylsiloxane (PDMS) films as the supporting materials and 3-aminopropyl-triethoxysilane ($\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$, APTES) and triethoxyphenylsilane ($\text{C}_{12}\text{H}_{20}\text{O}_3\text{Si}$, PTEOS) as the functional glues for s-SWNT and m-SWNT arrays, respectively. Theoretical simulation revealed that significant charge transfers from the $-\text{NH}_2$ of APTES to s-SWNTs and from m-SWNTs to the phenyl of PTEOS, played a pivotal role in selectively removing SWNTs. Numerous characterization results (Figure 6B–E) have confirmed that the purities of the obtained SWNTs are greater than 85% without any contamination on surfaces. Importantly, this rational approach favors the separated SWNT arrays for many attractive applications.

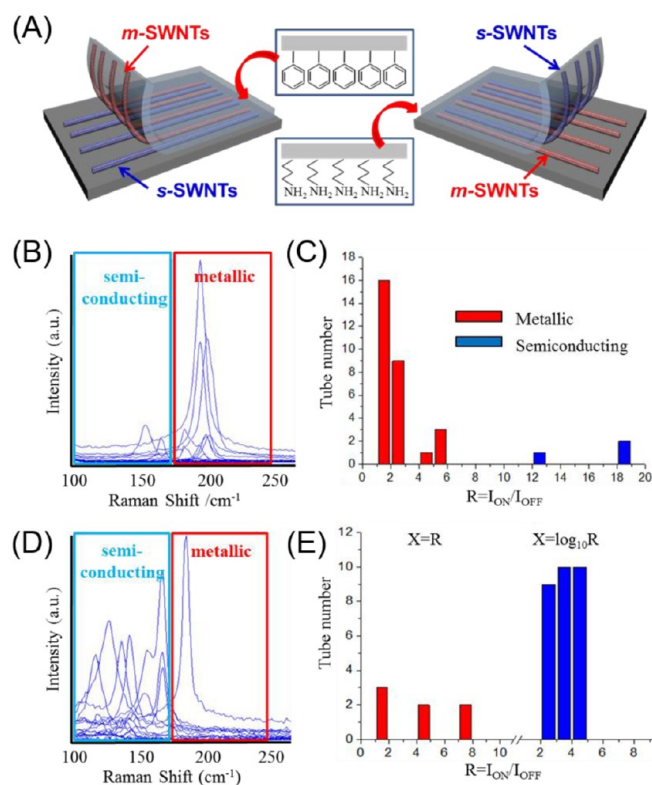


Figure 6. (A) Smart scotch tape for m-/s-SWNT separation. Raman results (B) and transport properties (C) of the obtained m-SWNTs. Raman results (D) and transport properties (E) of the obtained s-SWNTs.

3.3. SDS Washing off m-SWNTs

SDS washing off m-SWNTs is another practical method to sort out s-SWNTs from high density and horizontally aligned arrays. Surfactant-assisted decontamination is a popular method to remove various contaminants, owing to their stronger adsorption energy with surfactant molecules than that with surfaces. Using these facts, we produced similar systems with SDS and m-SWNTs as the crucial surfactant and contaminant, respectively (Figure 7).⁴¹ Briefly, the as-grown SWNT arrays on quartz were immersed into SDS aqueous solutions. Consequently, most SDS molecules preferred adsorption onto the circumference of the m-SWNTs, which dramatically weakened their interactions with the substrate surface. Ultrasonication was then used to selectively remove m-SWNTs, leaving the s-SWNTs with less SDS coverage on the surface. The obtained s-SWNT arrays retained their original aligned configurations and their ratio was as high as 90%.

4. CHIRALITY CONTROLLED GROWTH OF SWNTs

The superb electronic properties of SWNTs depend sensitively on their inherent chiral structures; therefore, SWNT nanodevices with controlled chiralities are required to optimize performance. Although much effort has been dedicated to this issue, the chirality controlled growth of SWNTs is regarded as the ultimate challenge.⁴⁴ Various reports indicate that almost all CVD parameters such as temperature, gas flow, and catalyst species, can influence chiral structures of the produced SWNTs.⁴⁵ Therefore, a CVD system seems like a mysterious black box that precludes us from investigating the elemental reactions during SWNT growth. Currently, catalyst nanoparticles with a narrow diameter distribution are normally used

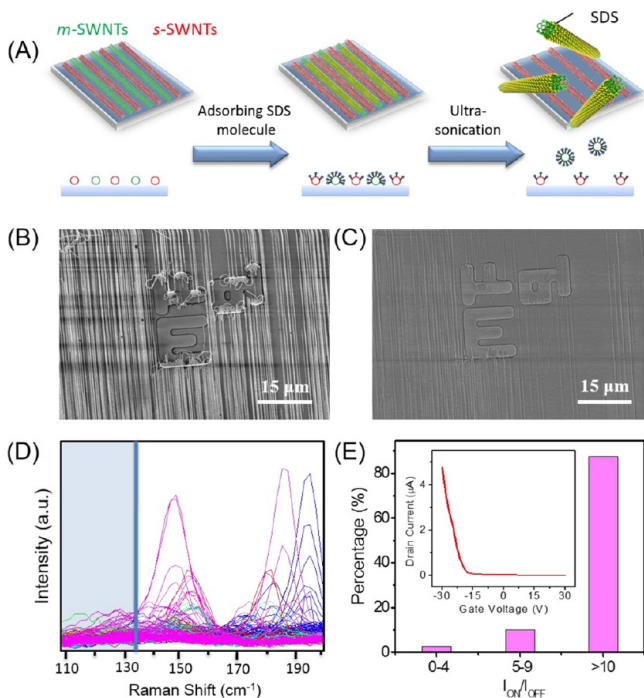


Figure 7. (A) SDS washing off m-SWNTs from SWNT arrays. (B) SEM image of the as-grown SWNT arrays. (C) SEM image of SWNTs after the washing process. The density decreased dramatically. Raman spectra (D) and electrical characterization (E) of the obtained s-SWNTs. Inset is a typical transport curve of the fabricated FET nanodevices.

to diminish the chirality ranges of grown SWNTs.⁴⁶ In situ preparation in a modified transmission electron microscopy (TEM) chamber can be used to continuously observe the growth process, while it is restricted under unusual pressures.⁴⁷ In addition, a convenient and accurate characterization method is not available that can easily determine the chiral structures of SWNTs on a large scale.⁴⁸ Resonant Raman spectroscopy based on Kataura plot is generally limited by the resonance window and environment effects. Although STM and TEM can

directly show the atomic structures of an individual SWNT, they require rigorous sample preparation and operating conditions.

4.1. Temperature-Mediated CVD Growth of SWNT Intramolecular Junctions

It is well accepted that the SWNT diameter is determined by catalyst size.⁴⁹ We first discovered that temperature, an essential CVD parameter, can modulate the diameter and chirality of an individual SWNT. Furthermore, this surprising phenomenon was successfully applied to produce SWNT intramolecular junctions.⁵⁰ Following the gas flow directed growth mode, Fe nanoparticles and ethanol were used as catalyst and carbon feedstock, respectively, to prepare ultralong SWNTs. During the growth process, a furnace tube with SiO_x substrate was artificially moved to vary the growth temperature. The significant shifts of the radial breathing mode (RBM) bands along one SWNT can conveniently reflect its diameter evolutions. Specifically, when the temperature increases from 900 to 950 °C, the SWNT diameter dramatically decreases with a red-shifted RBM peak and vice versa. In this way, the six intramolecular junctions induced by three temperature oscillations verified that this temperature-mediated growth method was rational and reliable. The clear rectifying behavior is easily observed from the fabricated FET nanodevices across the SWNT junctions, including S–S, S–M and M–M junctions.

4.2. Cap Formation Engineering of SWNTs from Opened C₆₀

The initially formed cap structures around the catalyst nanoparticles strongly relate to the final chirality of the obtained SWNTs. Therefore, each catalyst nanoparticle plays a template role during the chirality-controlled growth of SWNTs. Although the currently used catalysts extend to most transition metal elements, they remain liquid droplets at high temperature, and their original sizes and structures are certainly altered after the reaction with hydrocarbons. We exploited opened C₆₀ molecules with a desired size as the hemispherical caps to epitaxially control SWNT chirality, and the carbon source was ethanol (Figure 8A).⁵¹ A series of contrast

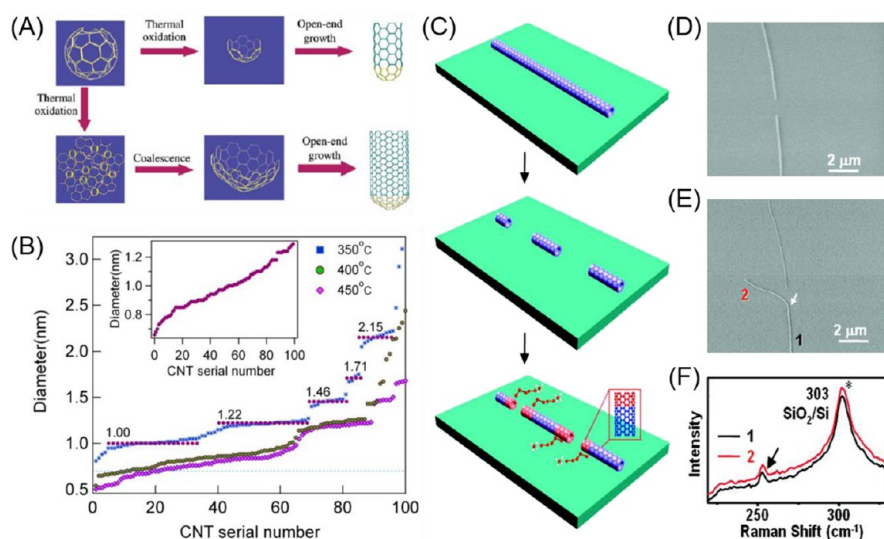


Figure 8. (A) Cap formation engineering of SWNTs from C₆₀ molecules. (B) The diameter distribution of the obtained SWNTs showed a step-like shape. Inset is the diameter distribution of SWNTs from Fe catalysts. (C) Cloning growth of SWNTs with controlled chirality. (D–E) SEM images of a SWNT before (D) and after (E) cloning growth. (F) Raman spectra of the cloned SWNTs in (E).

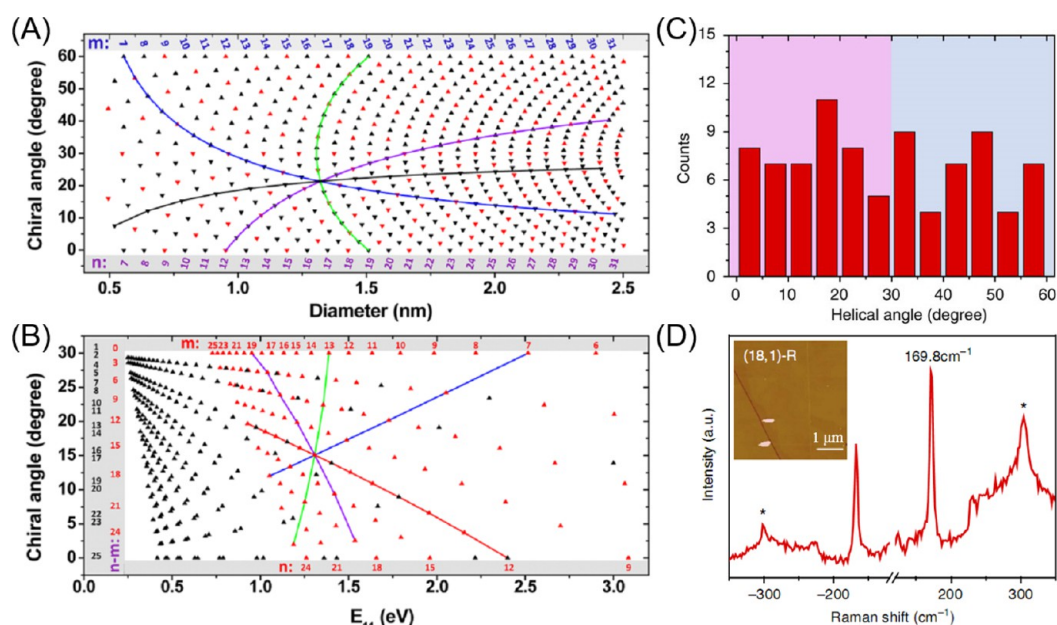


Figure 9. (θ, d) plot (A) and (θ, E_{ii}) plot (B) for the convenient assignment of the chiral index. The upward-pointing, downward-pointing, red, and black triangles represent the left-handed, right-handed, metallic, and semiconducting SWNTs, respectively. The SWNTs on the violet, blue, green, and black/red lines have the same n , m , $(n + m)$, and $(n - m)$ values, respectively. (C) The chiral angle distribution of the aligned SWNTs on graphite. (D) (18,1)-R SWNT to demonstrate the determination of the (n, m) index. AFM image of this SWNT is shown in the inset.

experiments indicated that the size and edge structure of C_{60} caps can be efficiently engineered by tuning the thermal treatment temperature. This determines the diameter distributions of the as-grown SWNTs. Generally, weaker oxidation is favorable for the production of SWNTs with a wider range. Moreover, the AFM-determined diameters in Figure 8B from numerous SWNT samples exhibited a step-like distribution, distinct from the SWNTs grown from normal metallic catalysts.

4.3. Cloning Growth of SWNTs with Controlled Chirality

Cloning growth of SWNTs is a rational strategy to completely control their chiral structures by an open-end mechanism without any additional catalysts (Figure 8C).⁵² Specifically, the parent SWNT segment etched by electron beam lithography and oxygen plasma can significantly increase its length with duplicated chirality. Both SEM and AFM images clearly show the length of the cloned SWNT obviously increased in contrast to the parent segment, and they had identical Raman shifts (Figure 8F). Moreover, it has been found that introducing a C_2H_4 source can efficiently accelerate the decomposition of CH_4 and promote growth rate. The substrate plays an important role on the cloning yield, and this greatly improved from 9% on SiO_x to 40% on quartz. This novel cloning method proves that the nanoparticle is not the essential template for SWNT growth. Recently, the cloning growth of the purified SWNTs with predefined chirality was successfully demonstrated, so this technique supplies an excellent platform for carbon nanoelectronics.

4.4. Chiral Structure Determination of SWNTs on Graphite Surfaces

The chiral structure characterization of SWNTs, including their chiral angle, handedness, and chiral index, is absolutely essential to both its fundamental research and practical applications. We developed an efficient and accurate approach to comprehensively determine SWNT chiral structures (Figure 9). As described above, the alignment of grown SWNTs on a graphite

surface is chirality dependent.³⁶ Many regular graphene trenches along the zigzag directions randomly emerge because of the etching effect of metallic nanoparticles.⁵³ Using the angles φ formed between the aligned SWNT and the graphite trench as a reference, we can conveniently characterize its handedness and chiral angle (Table 1).⁵⁴ By combining the

Table 1. Approach for the Determination of Chiral Structures of Aligned SWNTs on Graphite Surfaces

Handedness	$0^\circ < \varphi < 30^\circ$	$30^\circ < \varphi < 60^\circ$
R ($0^\circ < \theta < 30^\circ$)	$\theta = 30^\circ - \varphi$	$\theta = \varphi - 30^\circ$
L ($30^\circ < \theta < 60^\circ$)	$\theta = 30^\circ + \varphi$	$\theta = 90^\circ - \varphi$

^aThe dashed lines indicate the directions of the graphene trenches.

measured diameter or E_{ii} , the (n, m) index of SWNTs can be uniquely identified from the (θ, d) or (θ, E_{ii}) plots (Figure 9A,B), respectively. For example, the graphite trench in the counterclockwise direction of the SWNT and its formed angle was $\varphi = 27.3^\circ$; therefore, this aligned SWNT was right-handed with chiral angle $\theta = 2.7^\circ$ (Figure 9D). In addition, the diameter of approximately 1.46 nm can be extracted using its AFM profile or RBM band. The (n, m) index was thereof simply assigned to (18,1)-R from the (θ, d) plot. Compared with conventional Raman and STM techniques, this rational approach has advantages of low cost, high efficiency, and simplicity.

5. SUMMARY AND OUTLOOK

In conclusion, the future SWNT-based nanoelectronics with a high degree of integration and optimal performance rigorously demands specific SWNT structural and property characteristics

such as good alignment, high density, semiconducting nature, and single chirality. Toward solutions for this formidable challenge, we briefly summarize our exploited CVD growth methodology for the preparation of SWNTs with controlled structures, including surface directed growth, the UV-assisted CVD technique, smart scotch tape for s-/m-SWNT separation, cap formation engineering, and cloning growth. As discussed above, SWNT arrays with diverse architectures, s-/m-SWNTs with a purity of 90%, and SWNTs with defined chirality can be repeatedly obtained, and these methods are scalable.

The following obstacles toward CVD growth continue to attract our attention: (1) The absolute and subtle controlled growth of SWNTs. Rational approaches or concepts are necessary to amplify the inherent differences between s-SWNTs, m-SWNTs, and chiral SWNTs. The quantitative relationships between CVD parameters are always urgent to understand the growth process. (2) A detailed and universal growth mechanism. Comparing VLS and VS modes, carbon dissolution into the catalyst or nanoparticle template is essential for initial cap formation. The critical factors still remain unknown, which severely affect growth kinetics, such as the growth rate, lifetime, and the activity of catalyst. (3) Complete and applicable characterization methods for the chiral structures. Although mathematical models exist for the measurement of the handedness and chiral angle of aligned SWNTs, graphite substrate with zigzag trenches is the distinct shortage. Despite these challenges, we hope that our progressive growth methodology can promote the CVD controlled growth of SWNTs for nanodevice applications.

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Notes

The authors declare no competing financial interest.

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Dr. Yabin Chen received his B.S. from Lanzhou University in 2008. Since then, he joined Prof. Jin Zhang's group for a 5-year Ph.D. program in the College of Chemistry and Molecular Engineering, Peking University. His current research interest mainly focuses on low-dimensional nanomaterials, including the structure controlled growth of SWNTs and layered nanomaterials, and their related applications. Presently, he is a postdoctoral research scholar at the University of California, Berkeley.

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ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China (Grants 21233001, 21129001, 51272006, and 51121091) and the Ministry of Science and Technology of

China (Grant 2011CB932601). The authors thank all researchers who dedicate their spirits and intelligence to carbon nanotube science.

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