Controlled growth of carbon nanotubes on patterned substrates

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

CONTROLLED GROWTH OF CARBON
NANOTUBES ON PATTERNED SUBSTRATES

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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ABSTRACT

Single-walled carbon nanotubes (SWCNTs), the 1D carbon nanomaterials, have attracted tremendous interest since its discovery. The unique structures and properties of SWCNTs made them the attractive building blocks for various promising applications, such as field emitters, field effect transistors, sensors, diodes and inter-connection, etc. The realization of such fundamental studies and advanced applications will be largely dependent on whether the tubes can be organized into ordered arrays with defined locations, orientations and densities, etc. Controlled growth of CNTs from patterned catalyst sites has become a choice for producing such CNT arrays. Since the directly grown tubes are free from the harsh post-growth experimental treatments, they preserve the original structures and intrinsic properties.

In order to study the growth mechanism for further controlling the CNT growth, and to meet the needs of particular requirements of CNT arrays in the wide range of basic studies and advanced applications, in this thesis, three strategies for efficiently generating catalyst patterns on substrates for controlled growth of CNTs have been developed. Also the direct fabrication of all-carbon devices, based on the controlled growth of long-aligned SWCNTs to cross and connect the pre-patterned reduced graphene oxide (RGO) electrodes, was demonstrated.

The first strategy takes the advantages of high resolution and high registration capabilities of dip-pen nanolithography (DPN) to generate molecular templates on Au surface. The templates were obtained by passivation of the exposed Au area with 11-amino-1-undecanethiol (AUT) after the 16-mercaptohexadecanoic acid (MHA)

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patterns were generated by dip-pen nanolithography (DPN) on Au. The electrostatic force drives the 20 nm Au nanoparticles (NPs) specifically and exclusively adsorbed on the amino group-terminated templates. This strategy shows high accuracy and free of non-specific adsorption for assembly of Au NP arrays with controlled particle numbers.

The second strategy is to use DPN to directly pattern Co NPs onto substrates with feature size down to sub-70 nm. Dots, lines and even sophisticated catalyst patterns are generated on Si/SiO_x and quartz substrates. By using chemical vapor deposition (CVD), SWCNTs were specifically grown from the patterned catalyst sites and their alignment is controlled on quartz. In addition, the formation of “L” shaped CNTs is studied. A direct evidence of base-growth mechanism of SWCNTs is provided.

The third strategy is to employ a common syringe needle to fast generate large-scale catalyst patterns on substrates, referred to as “needle scratching method” (NSM). The subsequent CVD process generated high-density SWCNT networks on Si/SiO_x and densely aligned SWCNT arrays on quartz substrates, respectively. The composition of the catalyst is also investigated.

Finally, a simple route towards the integration of all-carbon devices is developed, where the long-aligned SWCNTs, with controlled growth, directly connect the pre-patterned reduced graphene oxide (RGO) electrodes.

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LIST OF SYMBOLS AND ABBREVIATIONS

CNT	Carbon nanotube
MWCNT	Multi-walled carbon nanotube
SWCNT	Single-walled carbon nanotube
LA-CNT	Long aligned CNT
MHA	16-Mercaptohexadecanoic acid
ODT	18-Octadecanethiol
AUT	11-amino-1-undecanethiol
TOPO	Trioctylphosphine oxide
APTES	Aminopropyltriethoxysilane
PAMAM	Polyamidoamine
PMMA	Polymethylmethacrylate
Au NP	Gold nanoparticle
GO	Graphene oxide
RGO	Reduced graphene oxide
CoMo CAT	Co-Mo catalyst
SAM	Self-assembled monolayer
TMV	Tobacco Mosaic Virus
ROP	Ring-opening polymerization
RBM	Radial breath mode
FET	Field-effect transistor
PDMS	Poly(dimethylsiloxane)
DPN	Dip pen nanolithography
NFP	Nano-fountain probe
μ CP	Micro-contact printing
NSM	Needle scratching” method

Symbols and abbreviations

CVD	Chemical vapor deposition
AFM	Atomic force microscopy
FE-SEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
EDS	Energy-dispersive spectroscopy
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background and Current Challenges

Micro- and nano-arrays have attracted tremendous interest due to their fundamental importance in nanoscience and applications in nanotechnology. Single-walled carbon nanotube (SWCNT) is one of the most attractive building blocks for constructing such arrays due to their unique structural, mechanical, electrical, thermal and optical properties. It has been demonstrated that materials consisting of SWCNTs could exhibit extraordinary specialty which allows for a wide range of applications in transistors, sensors, membranes, etc. However, most of these studies and applications are limited by the achievement of addressable CNT-based devices where the CNTs are required to be organized into well-defined CNT arrays with desired parameters including location, orientation, geometry, density, etc.

There are two major strategies have been widely employed to generate CNT arrays. One is called post growth, in which CNTs are assembled onto a pre-patterned template, or manipulated with assistance of the external force, such as alternating current (ac) dielectrophoresis. However, this approach usually requires pre-treatment of CNTs including strong acid and long time sonication that may shorten the nanotubes, generate unnecessary surface defects and worsen the performance of CNT-based devices. Furthermore, the complicated manipulation procedures in device fabrication might also break the CNTs. Alternatively, the direct growth approach, in

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which the CNTs grew on the pre-patterned catalytic sites, provides a better choice for fabricating CNT-based nanodevices. Without the post treatments, CNTs preserve their original structures and intrinsic properties, which make them ideal building blocks for high performance device applications.

To date, a number of techniques have been developed to pattern catalysts for growth of CNTs. For example, micro-contact printing (μ CP) is an inexpensive and high-throughput technique, which can be used to generate micrometer-scale features over large area. However, the mask used to make the poly(dimethylsiloxane) (PDMS) stamps is expensive, and each pattern modification (i.e., shape, size, spacing, etc.) requires re-design of the mask. Moreover, it is not easy for the conventional PDMS stamp to generate sub-500 nm features. Other techniques, such as photolithography, e-beam lithography and ion-implanting, have been successfully used to generate catalyst patterns as well, but all of them showed various limitations, such as complicated experimental procedures, high cost, and strict operation conditions, such as high vacuum, high voltage, etc.

Due to the limitations of the traditional patterning techniques mentioned above, to develop new methods or new strategies for efficiently generating catalyst patterns is expected and required in the controlled growth of CNTs. Currently, it is still a great challenging to grow CNTs with fully controlled location, diameter, orientation, length, density, etc. In addition, some of the growth mechanisms of CNTs are still under debating and not clearly understood, although the different hypothesis and growth mode of CNTs has been proposed base on the experimental observations and theoretical calculations.

1.2 Objective and Scope of This Research

In order to better understand the growth mechanism of CNTs for further controlling the CNT growth, and to meet the needs of particular requirements of CNT arrays in the fundamental studies and practical applications, the objective of this research is to develop new strategies for efficiently patterning catalyst on solid substrates, and then to use these created catalyst patterns as templates for controlled growth of CNTs with desired parameters including location, alignment, density, etc. Also, much effort will be taken on the fundamental investigations of the CNT growth mechanism.

In order to achieve the objectives mentioned above, the detailed works of this research are described in below: First, how to control the assembly of Au nanoparticles (Au NPs) on dip pen nanolithography (DPN)-generated molecular templates will be described. The individual NP arrays and sophisticated NP patterns will be demonstrated. Second, directly depositing catalyst NPs by DPN for generating desired patterns on substrates will be described. Selective growth of SWCNTs from such catalyst patterns with controlled alignment will be addressed. The mechanism of the formed 'L' shaped CNTs on quartz will be investigated. Third, a facile "needle-scratching" method (NSM) for fast patterning catalyst on a substrate, used for growth of high-density SWCNT networks and densely aligned SWCNT arrays, will be investigated. Finally, the direct fabrication of all-carbon devices based on the controlled growth of long-aligned SWCNTs to connect pre-prepared reduced graphene oxide (RGO) electrodes will be described.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Carbon Nanotubes (CNTs)

Since the discovery by Iijima in 1991 [1], carbon nanotubes (CNTs) have received considerable attention due to their unusual structure and properties. CNTs are tubular structures typically of nanometers in diameter and microns in length. It can be considered as a rolled-up graphene sheet (graphene is an individual graphite layer) [2]. Depending on the present of graphene layers, CNTs can be generally divided into multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). The tube consists of a single cylindrical graphene layer is SWCNT, while MWCNT consists of multiple graphene layers.

The rolling-up way of graphene sheet is represented by a pair of indices (n, m) called the chiral vector C (Figure 1) [2]. The n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m = 0$, the nanotube is "zigzag". If $n = m$, the nanotube is "armchair". Otherwise, it is called "chiral". SWCNTs can be either a metallic conductor or semiconductor, depending on the chirality of the structure [2].

Figure 1. Modes of nanotubes with different helicities, showing the rolling of a graphene sheet along different chiral vectors [2].

2.2 Growth Methods of CNTs

In the past years, several methods, including arc-discharge, laser ablation, chemical vapor deposition (CVD), etc., have been developed for the growth of CNTs.

2.2.1 Arc-Discharge and Laser Ablation

The arc-discharge [1] and laser ablation process for growth of CNTs generally takes place in a chamber under high vacuum and high temperature condition. Both methods involve the condensation of carbon atoms evaporated from solid carbon source by discharge plasma or laser. The evaporation temperatures in the above mentioned processes are closed to the melting temperate of graphite, 3000 – 4000 °C [3].

Literature Review

Arc-discharge was the first reported method for the growth of CNTs. In this method (Figure 2), the plasma is generated by high currents (50 to 120 A) at a voltage (~12 to 25 V) passing through the opposing graphite electrodes at inert atmosphere (such as He or Ar) with a pressure of 100 to 1000 Torr. Carbon atoms are evaporated under these conditions and condensed on the cathode to form nanotubes with byproducts like fullerenes and so on. Because CNTs were initially discovered using this method, arc-discharge has been developed to synthesize gram quantities of both high quality MWCNTs and SWCNTs. In the growth of SWCNTs by arc-discharge, metal catalysts are required to put on the anode [4].

Figure 2. Schematic illustration of the setup of arc-discharge.

Laser-ablation used for CNT growth was first reported by Smalley and his coworkers at Rice University in 1995 [5]. A year later, gram scale of high quality SWCNTs synthesized by this method was also achieved in the same group [6]. The use of laser-ablation process for synthesizing SWCNTs was taken place in a tube furnace at high temperature (1200 °C) as depicted in Figure 3. The intense laser pulses were utilized to ablate a graphite composite target containing small amount of metal atoms (such as Ni and Co). The nano-size metal particles were formed on the graphite target during the laser ablation and catalyzed CNT growth from the vaporized carbon. Thus-grown nanotubes were carried by the inert gas (Ar or He) flow and can be collected on a cold finger.

Figure 3. Schematic illustration of the setup of a laser-ablation furnace.

As mentioned above, both arc-discharge and laser-ablation processes include high vacuum and high temperature. The produced CNTs are in tangled forms that are difficult to separate, purify, manipulate, and assemble for construction of desired architectures on substrates. These characteristics of the methods limit the scale-up of synthesis of CNTs, and restrict the CNT applications in electronics.

2.2.2 Chemical Vapor Deposition (CVD)

The CVD growth of CNTs was first reported in 1993 [7]. In the process, MWCNTs were obtained by using iron particles as catalyst to decompose acetylene at 700 °C. The first report of SWCNTs grown by CVD was published by Dai et al. in 1996 [8]. They used nano-sized molybdenum particles as catalyst and carbon monoxide as carbon source, with a reaction temperature of 1200 °C. Compared to the arc-discharge and laser-ablation techniques, CVD has the advantage of ease of scale up and produces high-purity MWCNTs and SWCNTs under a relative low temperature. Unlike the arc-discharge and laser-ablation, CVD is driven by the pure thermal energy rather than by plasma or laser energy, and without the need of high vacuum. Therefore, the CVD system is easier to be handled and is of relatively low-cost. More importantly, the CVD process is compatible with the modern Si-based semi-conductor industry, as CNTs can be directly grown on a substrate with their location, orientation and diameter controlled by simply changing the CVD parameters. The advantages of CVD make it a suitable and ideal method to grow nanotubes for advanced applications, particularly in the fields of electronics and optoelectronics.

(A) Typical Setup of CVD

Figure 4 shows the schematic illustration of a typical tube furnace, comprising three main parts: (1) temperature controlling component: a furnace that is used for

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heating the samples and maintaining high reaction temperature; (2) reactor chamber: a quartz or ceramic tube, in which samples can be placed, serves as the reaction place for CNT growth; and (3) the gas flow controller: it is used for providing different gas mixtures at different growth stages with a controlled flow rate and carbon sources.

In the growth of CNTs by CVD, three steps are mainly involved: (1) heating the catalyst materials to the desired temperature to grow the CNT in a tube furnace; (2) flowing carbon source gas, such as carbon monoxide, methane and alcohol, etc., into the furnace tube to provide the carbon content to grow the CNT; (3) cutting off the supply of carbon sources and slowly cooling down the system to room temperature.

Figure 4. Schematic illustration of the setup of a CVD furnace.

(B) General Growth Mechanism of CNTs in CVD

Since the first report of CNT growth by CVD, extensive research by many groups has produced a better understanding of the growth mechanism [3,9]. Numerous mechanisms have been proposed based on both theoretical and experimental observations, but evidently there is no single mechanism which can explain every CVD processes for CNT growth. Commonly, it is accepted that in a CVD process, at the growth temperature, the catalyst NPs on the surface catalytically dissociate the input hydrocarbon molecules into carbon and hydrogen. The carbon atoms then dissolve into the catalyst NPs. The continuous supply of hydrocarbon gas eventually saturate the metal NPs and carbon atoms precipitate and diffuse on the catalyst, leading to the formation of tubular carbon structures. CNT has a closed structure, which contains no dangling bonds and is in a low energy state. Therefore, it is more favorable to form the tube structures than other carbon forms such as graphitic sheets with open edges. The synthesis of MWCNTs using a CVD method generally happens at relative low temperatures (300-800 °C) in an inert gas environment, while the synthesis of SWCNTs normally requires higher temperatures (600-1150 °C) and a mixture of reduction gas (H_2) and an inert gas (e.g. Ar) [3,10,11].

In the CVD process, aside from the temperature, the type of catalyst and carbon source also directly affects the way of CNT growth. Metallic NPs, typically transition metals such as Fe, Co, Cu, Ni, etc. [12], have been found to be the most efficient catalysts and widely used for growth of CNTs. Recently studies also showed that NPs made from noble metals (Au, Pd, Pt, etc.) [13] and Si-based nonmetallic NPs (such as Si, SiC and SiO_2) [14,15] were also very efficient catalysts for growing the CNTs. The efficiencies vary among the listed materials and thus the eventual morphology of

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nanotubes produced. For example, Lee et al. reported that using transition metal catalysts (Fe, Co and Ni) to grow MWCNT on Si/SiO_x by CVD, the growth rate was found to be highest for Ni, a least for Fe [16]. In contrast, the CNTs grown from Fe catalyst showed the best crystallinity [16]. Another report compared a large number of metal catalysts, including Fe, Co, Ni, Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, and Al, was used to grow aligned tubes on single crystalline quartz substrate under a fixed CVD condition [13]. The results showed the density and the alignment of CNTs varied according to the different catalyst used. The CNT growth from the catalysts of Fe, Co, Cu, Mo, Mn and Au showed high-density and good alignment. Pd catalyst produced high-density but poorly aligned SWCNT arrays, while the rest produced CNT which were both low in density and poorly aligned [13]. Clearly, the choice of catalyst used for growth of CNTs is important. Generally, it is believed that the suitable sized NPs with uniform size distribution are good for producing the homogeneous and high quality nanotubes.

CO was the first carbon source reported to be used to grow SWCNT by CVD [8]. Since then, other hydrocarbon gases including CH₄ [17], C₂H₂ [18], C₂H₄ [19], EtOH [20], and benzene [21], have been successfully used for the CNT growth. Since the growth mechanisms of CNTs are still not fully understood, it is difficult to say which kind of carbon source is optimal. Generally, to grow MWCNT, C₂H₂ and C₂H₄ are the most widely used, while CH₄ and EtOH are the most widely used for growing

Figure 5. (A) Photo image of a 2.5 mm high SWCNT forest grown by water-ethylene CVD on Si. The matchstick at left in the picture used as size reference. (B) High-resolution TEM image of the SWCNT [23].

SWCNT [9,22]. By mixing a small and controlled amount of H_2O with C_4H_4 , Iijima et al. [23] showed they could achieve impurity-free SWCNT forest up to 2.5 mm in height (Figure 5). They suggested that a small amount of H_2O would selectively clean the amorphous carbon without etching the nanotubes during the CVD process, resulting in enhancement and preservation of the catalyst activity. Therefore, the water-ethylene CVD process is highly efficient for growth of the high purity SWCNTs.

Recently, Liu et al. at Duke University demonstrated that well-aligned semiconducting SWCNTs can be readily produced on quartz substrate by introducing appropriate amount of MeOH into EtOH as the carbon source [24]. While it has been extensively shown that several factors, such as temperature, carbon source and catalyst, greatly affect the CNT growth, there is a need to have more in depth study to produce convincing data on the growth mechanism in the process. More details on CVD parameters affecting the CNT growth will be discussed in section 2.3.

2.2.3 Base-Growth Mode and Tip-Growth Mode in CVD Synthesis

According to the position of catalyst NPs on the CNTs, two main growth modes [3] are proposed, which have been experimentally proven, namely, the base-growth mode and the tip-growth mode, as shown in Figure 6.

Figure 6. Two general growth modes of CNTs in CVD. Left diagram shows a base growth mode. Right diagram shows a tip growth mode [3].

In the base-growth mode, catalyst NPs remains on the substrate or support surface during the CNT growth. Carbon sources are fed to the base of a growing CNT, where the nanotube interfaces with the anchored catalyst NPs. This growth mechanism has been well demonstrated by in situ or indirect TEM observation [25,26]. The high resolution TEM images of SWCNTs produced by a methane-CVD method frequently show that the closed tube ends are free of encapsulated catalyst NPs, while the opposite ends were always embedded in the catalyst NPs, Figure 7.

Figure 7. TEM image of a base growth mode [25].

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The base-growth mode happens if the catalyst-substrate interaction is very strong, leading to the catalyst NPs remaining on the substrate. In contrast, in the tip-growth mode, catalyst NPs are lifted off from the substrate or support surface, and carried along at the tip end of a growing tube, as shown in the TEM image in Figure 8A. This mode is popularly used to explain the long aligned CNT growth mechanism [27], Figure 8B.

Figure 8. (A) TEM image of tip-growth mode with a catalyst particle at the tip end of the tube [28]. (B) Schematic illustration of the growth of long aligned CNT with a tip growth mode [20,27].

2.3 Controlled Growth of Single-Walled Carbon Nanotubes (SWCNTs)

2.3.1 Diameter Control of SWCNTs

It is known that the electronic and optical properties of SWCNTs are strongly dependent on their diameter and chirality. However, the controlled growth of SWCNTs is still the big challenge in the CVD synthesis [29]. The choice of the catalyst is one of the key elements for synthesizing CNTs in the CVD methods. It is believed that the diameter of SWCNTs is related to the catalytic particle size. Therefore, the controlled growth of SWCNTs with narrow diameter distribution could be realized by using narrowly distributed or even identical catalyst NPs.

Choi et al. [30] developed a method that applying the polyamidoamine (PAMAM) dendrimers, a branched micro-molecule with functional groups which can coordinate with metallic ions, as templates for synthesis of homogeneous catalytic NPs used for CNT growth. Nanotubes with a narrow diameter distribution between 1 and 2 nm are obtained.

To precisely control the CNT diameter, a family of metal-containing nanocluster complex was found to be good catalyst for CVD growth of SWCNTs [31]. As the clusters have a well-defined chemical composition, they are identical to each other. For example, the cluster, $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\text{H}_4\text{Mo}_{72}\text{Fe}_{30}(\text{CH}_3\text{COO})_{15}\text{-O}_{254}(\text{H}_2\text{O})_{98}]\cdot 6\text{H}_2\text{O}$, contains 84 Mo atoms and 30 Fe atoms in one molecule. Using this cluster complex as catalyst for CVD growth of SWCNTs, a very narrow distribution SWCNTs, with diameter of 1.0 ± 0.18 nm, were obtained.

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More interestingly, several reports showed that the type of the catalyst may affect the diameter / chirality of the produced CNTs. Li and co-workers reported that Cu is not only a good catalyst for growth of SWCNTs, but also a catalyst for producing high percentage of metallic SWCNTs [32]. Meanwhile, Rogers and co-workers used commercialized Ferritin or evaporated sub-monolayer films of iron as catalyst to synthesize high percentage semiconducting nanotubes, which can be used for fabrication of thin film transistors [33]. Bachilo et al. [34] have reported a very promising CVD approach that uses a silica-supported Co-Mo catalyst (CoMo CAT) for high selective growth of SWCNTs. They found that the product composition in this method depends on the Co:Mo ratio and on catalyst treatments. The adjustment of these parameters allows finely control the formation of the active catalyst NPs and eventually the nanotube diameter.

Besides the catalyst NPs, other parameters of the CVD process including the growth temperature and the carbon source may also affect the diameter/chirality of the produced SWCNTs. Liu et al. [35] at Peking University discovered that the diameter of SWCNTs can be effectively tuned by varying the temperature during CVD. In their experiment, they found that changing the growth temperature from 900 to 950 °C resulted in a shift in the radial breathing mode (RBM) band from the Raman mapping along an individual ultralong SWCNT, indicating the diameter changed along the same tube. By periodically changing the temperature between two stages several times, the diameter of the individual ultralong SWCNT grown from this process was found to oscillate in correspondence to the temperature change. These findings provide not only an alternative method for controlling the CNT diameter, but also a potential way for growth of intra-molecular junctions of an individual SWCNT.

In the CVD growth of SWCNTs, the carbon-feeding rate also plays a role in determining the diameter distribution of CNTs. At low carbon feeding rate, uniform small-diameter SWCNTs are synthesized. Increasing the carbon feeding rates increased the tube average diameter [36]. The proposed mechanism, as depicted in Figure 9, shows that only the suitable sized catalyst NPs can be effectively activated to nucleate the SWCNT growth under a given carbon-feeding rate in CVD. The other smaller or bigger catalyst particles always have low efficiency for growth of CNTs. The relative rapid supply of carbon source to the smaller particles will poison catalyst particles by the excessive carbon and stop the growth of CNTs, while the relative slow carbon feeding to the larger particles are not sufficient for the nucleation of SWCNTs [36].

Figure 9. Schematic illustration of the activity of different sized NPs under a given carbon feeding rate. Larger particles are underfed. Smaller particles are poisoned by excess carbon supply. Only particles with a moderate and appropriate size can efficiently catalyze the SWCNT growth [36].

2.3.2 Orientation Control of SWCNTs

Over the last years, great progress has been made in growing horizontally orientated CNTs. For example, the Dai group first reported the direct growth of suspended SWCNTs on microfabricated Si pillars [37]. The Si pillars were first patterned with a lithography method. The catalyst precursor was then selectively deposited onto the top of those pre-patterned Si pillars by contact printing. Finally the methane CVD process leads to the suspended SWCNTs, forming the ordered networks with the tube orientations directed by the patterned pillars, Figure 10.

Figure 10. Side-view SEM image of suspended SWCNTs directed by patterned Si pillars [37].

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This self-directed growth can be simply understood. Since the catalysts are only deposited on the patterned Si pillars, the CNTs only grow from the top pillars. As the tubes grow longer, the gas flow keeps the tubes floating and waving in the “wind”, since the flow velocity near the bottom surface is substantially lower than that of the pillar top, which prevents the CNTs from being caught by the bottom surface. Meanwhile, the nearby pillars provide the fixation points for growing tubes. Once the floating tubes contact the adjacent pillar, the van der Waals interaction between tubes and the pillar will catch and hold the tube, resulting in the suspended SWCNT networks on top of pre-patterned Si pillars. After that, the same group reported an electric field-induced growth of orientated SWCNTs, as shown in Figure 11 [38]. In their experiment, a lateral electric field was applied during the CVD growth. The SWCNTs exhibited alignment guided by the field. The electric field alignment effect is believed to originate from the high polarizability of SWCNTs.

Figure 11. SEM image of SWCNTs aligned along an electric field [38].

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Surface-lattice guided (or called crystal-lattice or atomic step-guided) growth is another promising way for efficiently controlling the alignment of CNTs [33,39,40], which was well demonstrated by Rogers et al. By using a single crystal quartz wafer as substrate, with pre-annealed at 900 °C for 8 hours, the perfectly aligned and high-density (10 SWCNTs / μm) arrays of SWCNTs were obtained. More recently, Liu's group in Duke University illustrated that using copper as catalyst and ethanol as carbon source, high-density parallel arrays of long SWCNT were obtained on the stable temperature (ST)-cut quartz substrates without pre-annealing. The density and length of SWCNTs can reach > 50 nanotubes / μm and a few mm, respectively [41].

Although the surface-lattice guided method is quite successful to grow the high-density and almost perfect aligned SWCNT arrays, growing the ultralong aligned CNTs (centimeters long) is still difficult. Recently, Liu's group developed a "fast-heating" technique [42,43] to produce long and well aligned SWCNTs in large areas on a flat substrate. This technique relies on a quick transfer of sample into high temperature reaction region in the CVD furnace. It was proposed that such "fast-heating" process generates gas phase convection that may help to lift up the catalyst particles during the growth of nanotubes. This results in the grown nanotubes orienting along the gas flow direction. Such a "fast-heating" CVD process can produce millimeter to centimeter long aligned CNTs, and can also be used to prepare multi-dimensional nanotube structures by repeating the growth process on the substrate in different directions.

A laminar flow guided growth strategy has been developed to grow long and aligned SWCNTs using relative low gas flow rates without requirement of external force or specific growth procedures [27,44,45]. Laminar flow is an ordered and

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smooth flow. It is proposed that at the early growth stage, SWCNTs can grow upwards or vertically with no or less effect by van der Waals interactions from the substrate. Therefore, the SWCNTs can be caught by the feeding gas, and follow the gas direction. It is accepted that the stability of gas flow inside CVD reactor plays a very important role, which may greatly affect the growth of CNTs. The gas flow stability and laminar feature in a tube may be characterized by Reynolds number $Re = \rho v d / \mu$, where ρ is fluid density, v is gas velocity, d is tube inner diameter and μ is gas viscosity.

Generally, when the flow is turbulent ($Re > 2000$), the CNT growth direction becomes unpredictable and easily arrested by interactions with the substrate. In contrast, when laminar flow dominates ($Re < 500$), the nanotubes are favorable grown freely in the smooth and ordered flow with their direction parallel to the gas flow direction. More recently, Li and coworkers described that an ultralow feeding gas flow rate in CVD process is very promising and facile for guiding the growth of ultralong horizontal aligned SWCNT arrays [45]. In their study, at ultralow flow rate condition, SWCNTs can be lifted up from the substrate and navigated by the gas flow without applying any other external driving force or “fast-heating process”. High quality long aligned SWCNT arrays can be obtained with several sccm of feeding gas. By mounting small tubes containing Si/SiO_x substrates side-by-side into the quartz tube of CVD system, the batch-scale growth can be achieved under the low feeding gas flow rate.

By combining the surface-lattice and gas-flow guidance techniques, Liu et al. [46] showed that they can conveniently produce a cross-bar CNTs in one CVD process. They selectively deposited two perpendicular catalyst strips on adjacent two edges of a

substrate, and then put the as prepared substrate in the CVD furnace with lattice direction perpendicular to the gas flow direction. After CVD, perfect-aligned SWCNT arrays are grown along the crystal-lattice of quartz, while ultra-long well-aligned SWCNTs are directed by the gas flow, resulting in a high grid density of cross-bar SWCNTs, Figure 12.

Figure 12. (A) Schematic illustration of the formation of crossbar CNTs in CVD. (B) SEM image of high-density cross-bar SWCNTs [46].

In some cases, the growth of ultra-long SWCNTs on quartz substrates is guided not only by the gas flow, but also by the strong interactions between the tubes and quartz substrate. As a result, zigzag or so called “serpentine” shaped long-SWCNTs can be produced [47]. Jeon et al. carefully controlled the CVD conditions to obtain the large-area growth of zigzag shaped long-SWCNT arrays on quartz substrates by using such interplay of gas flow guidance and surface-lattice induced direction [48].

2.3.3 Patterned Catalyst Used for Growth of CNTs

Besides controlling the diameter and orientation of CNTs, controlling the location of the CNTs on a substrate is also a key requirement for the successful fabrication of CNT-based devices. In the CVD method, the CNTs grow from catalysts. Thus, it is a natural strategy to use a patterned substrate with selectively depositing the catalyst for controlling the location of the CNTs.

Controlled growth of SWCNTs on a patterned substrate was first demonstrated by Dai et al. [17]. In their method, the electron-beam lithography was first used to create square holes in a polymethylmethacrylate (PMMA) film on Si/SiO_x substrates. The catalyst precursor was then filled in the holes. After the heat treatment and lift off process to remove the solvent of catalyst precursors and the resist of PMMA film, respectively, the catalyst islands were obtained on the substrate. The SWCNTs were successfully synthesized from the catalyst islands on the patterned substrate by CVD. Interestingly, some of the SWCNTs were found to bridge two catalytic islands. The success of growth of SWCNTs at specified locations greatly benefit the CNT study since the synthesized CNTs are easily located and characterized, and also facilitate the fabrication of CNT-based devices. Later, the Dai group combined the synthesis method with micro-fabrication techniques to further demonstrate the SWCNT-based

devices can be integrated by depositing metallic electrodes over the catalyst islands after the CNT growth [49,50], or by the direct growth of SWCNTs to connect the pre-defined electrodes [51].

To date, a number of techniques have been developed to pattern catalysts for growth of CNTs as mentioned in Chapter 1. However, the conventional methods show various limitations, such as low resolution and complicated procedures in photolithography, high cost and restricted operating conditions in e-beam and ion-beam lithography, etc. This disadvantage greatly hinders the fabrication and applications of CNT-based devices. Therefore, the new strategies, that enable precisely deposit catalysts at specific location to form any desired pattern without contaminating other area, are expected. Also, the strategies, that allow to fast and easily generate large-scale catalyst patterns with low-cost and environmental friendly, are also desired.

2.4 Dip-Pen Nanolithography (DPN)

2.4.1 Introduction to DPN

Dip-pen nanolithography (DPN) is a scanning probe-based lithography method, in which an “ink”-coated atomic force microscopy (AFM) tip is used as a functional pen to directly “write” patterns on a substrate.

DPN was invented by Mirkin et al. in 1999 [52]. In their report, when an alkanethiol molecule, such as 16-mercaptohexadecanoic acid (MHA) or 1-octadecanethiol (ODT), coated AFM tip was brought into contact with a Au surface, the thiol molecules will be transported from the coated AFM tip to the surface through

the water meniscus formed in the narrow gap between the AFM tip and the substrate in the ambient environment. As shown in Figure 13, by varying the holding time of the tip on the substrate in different time, the different size dots can be easily generated. By changing the moving speed of the tip on the substrate, the different wide line can also be obtained.

Figure 13. Schematic illustration shows how DPN works. A water meniscus forms between the AFM tip, which is coated with “ink” molecules, and the substrate of interest (Au thin film used in this case) [52].

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Compared to the conventional lithographic techniques, for example, the electron-beam lithography or photolithography, DPN is a direct-write technique that provides both high resolution and high registration. Since DPN has the direct-write capability, “inks” can be deposited precisely and exactly in any location. In addition, since DPN can be conducted in ambient environments, there is no extremely strict experimental condition required, such as exposure to ultraviolet, electron- or ion-beam radiation, or in high vacuum condition. All these advantages make DPN a unique tool for patterning, especially in patterning biological and soft materials.

To date, more than 200 labs in the world have used DPN as a research tool to fabricate micro- and nanopatterns. To address fundamental scientific questions, a variety of ink-substrate systems were reported. The inks include small organic molecules, polymers, biological materials (such as DNA, proteins, peptides), colloidal NPs, metal ions, sols, etc. The substrates include semiconductors, conductors and insulators [53,54].

2.4.2 DPN-Based Fabrication of Nanostructures

Fabrication of desired nano-architectures onto surfaces with functional materials is a major hurdle for a broad range of fundamental researches and technological applications (e.g., electronic devices and sensors). DPN offers a unique method for directly depositing materials to form nano-architectures and templates on a substrate.

(A) DPN-Patterned Etching Resist Used for Fabrication of Au and Si Structures

Mirkin et al. [53,55] used DPN-generated MHA or ODT as etching resists to creating 3D solid structures with the standard wet-etching technique. Lines and dots of metal structures and even nano-gap as small as 12 nm were fabricated, Figure 14A-C.

Figure 14. (A) SEM image of 45-nm Au nanodots. (B) Topographic AFM image of 60-nm Au nanolines. (C) 12-nm Au nanogap on a Si/SiO_x substrate. (D) 3D Si(100) nanostructures [53,55].

Importantly, DPN can be used to deliberately make patterns with much flexibility, regardless of shapes and sizes. There is no requirement for fabrication of new masks or masters. Even very sophisticated structures can also be routinely created. A miniaturized replica of the US five cent coin generated on a Au/Si substrate has been demonstrated [56].

Moreover, the ability of generating Au (or Ag, Pd) features on semi-conducting surface also provides a simple route to fabricate semiconductor structures. By using the

etched Au features as resists, the Si nanostructures can be obtained by the wet chemical etching, Figure 14D.

(B) Template-Directed Assembly of Building Blocks

DPN-generated chemical templates with tailored chemical compositions and structures have been used to direct the assembly of various materials, such as quantum dots, nanowires, nanotubes and even single virus cell [54,57,58]. Hong et al. demonstrated that SWCNTs could be assembled along line features on the chemical templates through electrostatic forces between SWCNTs and the template [59]. In a different strategy, Wang et al. found that SWCNTs can be assembled onto the DPN-generated MHA templates [60]. In their study, SWCNT nanostructures were formed at the boundaries between MHA patterns and the passivating ODT self-assembled monolayers (SAMs).

In order to understand how the viruses and cells move and grow, Vega et al. [57] developed a novel strategy that utilizes a combination of DPN and coordination chemistry to immobilize and assemble the individual virus particles in large arrays (Figure 15). In their studies, Tobacco Mosaic Virus (TMV), which is anisotropic tubular structure (~300 nm in length and 18 nm in diameter) with well-characterized carboxylate-rich surface, was chosen as a model system. The approach started from DPN-generated MHA patterns passivated with 11-mercaptoundecyl-penta (ethyleneglycol) (PEG-SH) to reduce the nonspecific binding. The COOH groups of MHA were then coordinated to Zn^{2+} ions. The substrate was then immersed into a TMV solution. Virus nanoarrays were subsequently coordinated to metal ions (Zn^{2+}) on the DPN-generated MHA templates.

Figure 15. Schematic illustration of the selective immobilization of virus particles on DPN-generated MHA nanotemplates treated with Zn^{2+} [57].

(C) Template-Directed Growth of Peptides

Recently, our group developed a novel route, based on the combination of DPN and ring-opening polymerization (ROP) of Tryptophan-N-carboxyanhydrides (Trp-NCA), to prepare peptide arrays with varied chain lengths in the nanometer scale [61]. In this study, the DPN-generated amine-terminated polyamidoamine (PAMAM) dendrimer nanoarrays on Si/SiO_x substrates serve as the anchoring scaffolds for further growth of peptide arrays by ROP. The chain length of peptides can be readily

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controlled by the reaction time and the concentration of Trp-NCA solutions. This method provides a facile, inexpensive and convenient way to produce patterned peptide arrays with variable chain lengths. It opens up a new avenue for direct and in situ controlled growth of biomaterials on solid substrates, and will find potential applications in biosensors, optical devices, and cell behavior studies.

In this Chapter, some examples have been chosen to show that the capabilities of the DPN as a nanofabrication tool. It is likely that with more fundamental studies, the method could be developed for other applications in near future.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemical and Materials

16-mercaptohexadecanoic acid (MHA), 11-amino-1-undecanethiol (AUT), 98% H_2SO_4 , 30% H_2O_2 , Iron chloride (FeCl_3), Dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$), trioctylphosphine oxide (TOPO) oleic acid and 20 nm Au colloidal solution were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All the chemicals were used as received without further purification. Milli-Q water produced from Milli-Q system (Millipore, Billerica, MA, USA) was used in all experiments. Graphene Oxide (GO) was prepared by our method [62].

Synthesis of Co Nanoparticles (Co NPs)

The Co NPs were synthesized based on the reported method [63,64]. A stock solution (0.54 g $\text{Co}_2(\text{CO})_8$ dissolved in 3 ml 1,2-dichlorobenzene) was injected into the refluxing 1,2-dichlorobenzene (8 ml) at 182 °C in the presence of 0.2 ml oleic acid and 0.1 g trioctylphosphine oxide (TOPO) for 1 h. during the reaction, Ar was continuously supply through the reaction mixture to remove traces of CO produced and to avoid interferences. The average diameter of synthesized Co NPs was ~ 5 nm, characterized by TEM, Figure 16.

Figure 16. TEM images of synthesized Co NPs used as “ink” materials for DPN.

3.2 Substrate Preparation

A silicon oxide wafers and stable temperature (ST) cut single crystal quartz wafers were purchased from the Bonda Technology (Singapore) and the Roditi International Corporation Ltd. (UK), respectively.

3.2.1 Substrate Cleaning

Silicon oxide wafer or single crystal quartz wafer was cut into $1 \times 1 \text{ cm}^2$ squares. After ultrasonication in acetone for 10 min and rinsed with Milli-Q water, the Si/SiO_x or ST-cut quartz substrate was immersed in a piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 7 : 3$

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v/v) at 100 °C for 30 min (**CAUTION:** Piranha solution is a vigorous oxidant and should be used with extreme caution). The cleaned substrates were rinsed with Milli-Q water and dried with N₂ flow.

3.2.2 Preparation of Au Substrates

The cleaned Si/SiO_x substrates were coated with 2-3 nm adhesion layer of Ti, and subsequently coated with 25 nm Au using a magnetron sputtering system (base pressure $<1 \times 10^{-5}$ Torr) [65]. Thus freshly prepared Au substrates were used for the experiments immediately.

3.2.3 Preparation of Graphene Oxide (GO) and Reduced Graphene Oxide (RGO) Films

GO aqueous dispersion of 0.2 mg / ml were spin coated onto a substrate at 4000 rpm, the same procedure was performed multiple times to obtain the desired thickness. The obtained GO films were reduced by hydrazine vapor [62,66], then rinsed with excess water and blow dry with nitrogen. The resulting RGO film was further dried by heating at 120 °C for 30 min. Typically, 0.28 ml of 0.2 mg / ml GO dispersion drop-casted on the substrate at 10 μ l / drop under spin-coating at 4000 rpm, 10 nm RGO film was produced after reduction.

3.2.4 Creation of RGO Electrodes on Substrates

The RGO electrodes were simply created by using a sharp tip, made of nonmetal objects such as hard plastic or bamboo stick, to scratch the obtained RGO films.

3.3 Catalyst Patterning

3.3.1 Assembly of Au NPs on DPN-Generated Molecular Templates

Freshly prepared Au substrates were used for generating MHA patterns by DPN using an MHA-coated AFM tip prepared by the previously reported method [55,65]. All the DPN experiments were carried out under ambient conditions (22 - 24 °C, 54 - 60 % relative humidity) with an NSCRIPOR DPN system (Nanoink Inc., IL, USA) [67]. The MHA-patterned Au substrate was passivated with AUT by immersing it into an ethanol solution containing 1 mM AUT for 10 min. The as-synthesized AUT template was subsequently immersed into Au NP solution (pH 5-6) for 30 min. the electrostatic forces drive the Au NPs to spontaneously adsorb on AUT templates. The prepared samples were characterized by AFM and SEM.

3.3.2 Direct Generation of Co NP Patterns by DPN

DPN experiments for patterning Co NPs on substrates were carried out under ambient conditions (set point = 0.1 nN, 22 - 24 °C, 54 - 60 % relative humidity) with NSCRIPTOR DPN system (Nanoink Inc., IL, USA) [67].

To efficiently coat the tip with Co NP precursors, one drop of Co NP solution was dropped on a cleaned Si/SiO_x substrate. The condensed small droplets were obtained after the evaporation of solvent. An AFM tip was carefully moved to touch in the condensed small droplet of Co NPs and scan with a typical scan rate of 3 Hz over 10 × 10 μm² areas for ca. 1-2 min. Then it was retracted from the droplet. The obtained Co NP-coated tip was used to generate dot, line, and sophisticated patterns on substrates.

3.3.3 Fast Generation of Large-Scale Catalyst Patterns by Needle-Scratching Method (NMS)

To realize the large-scale patterning of catalyst in a short time, we developed the NSM in which a common syringe needle (Terumo Medical Corporation, Japan) was used to produce catalyst stripes on the substrates. To better control the patterning process, the needle was mounted on a micromanipulator (FX117 3-Axis Micromanipulator, Minitool Inc., USA) which can control the needle movement in X, Y and Z directions freely and accurately (Figure 17A). To improve the throughput, a multiple-needle array can be used for the patterning (Figure 17B).

Figure 17. (A) Photograph of a micromanipulator used for controlling the needle movement on substrate in the NMS. All three vernier reading graduated in 0.1 mm, and the additional fine X-axis vernier movement with 0.01 mm graduations. (B) Optical image of multiple-needle array used for large-scale scratching on a solid substrate.

3.4 Growth of SWCNTs

To grow SWCNTs on patterned substrates, a homemade tube furnace were used for all CVD processes with ethanol as the carbon source.

3.4.1 Growth of Random-Network SWCNTs on Si/SiO_x

To grow the random-network SWCNTs on Si/SiO_x, the CVD process is shown as follow. The substrates patterned with catalysts were placed in the middle of a 1 inch-diameter quartz tube furnace. The temperature was gradually increased to 900 °C in the mixed Ar/H₂ (200 sccm / 100 sccm) gas flow. After purging for 30 min to get rid of the trace amount of O₂/CO₂ and stabilize the Co NP catalyst, the Ar/H₂ flow rate was reduced to 100 sccm / 50 sccm. Then the ethanol vapor (carbon source) was introduced by bubbling the Ar/H₂ (100 sccm / 50 sccm) gas mixture into a glass vacuum trap ethanol bottle. After CVD for 20-40 min, CNTs grew on the catalyst patterns. The furnace was then cooled down to room temperature under Ar flow.

3.4.1 Growth of Densely Aligned SWCNTs on Quartz

In order to grow the densely aligned SWCNT arrays, stable thermal (ST)-cut single crystal quartz is used as substrate. The CVD process is same as that used for growth of random-network SWCNTs on Si/SiO_x which is described above.

3.4.3 Growth of Long Aligned SWCNTs

To grow the long aligned (LA) single-walled carbon nanotubes (SWCNTs), normally, catalysts were selectively deposited on one edge of the substrate and the substrate was placed into quartz tube furnace with gradually increased temperature to

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900 °C in the mixed Ar/H₂ (200 sccm / 100 sccm) gas flow. The CVD process was similar with that used for growth of random-network SWCNTs on Si/SiO_x or densely aligned SWCNT arrays on quartz described above. But, typically, lower gas flow rate (40 sccm / 20 sccm for Ar and H₂, respectively) was used to carry the ethanol vapor during the CNT growth.

3.5 Characterizations

3.5.1 Atomic Force Microscopy (AFM)

The NSCRIPTOR DPN system (NanoInk Inc., IL, USA) [67] and Dimension 3100 AFM (Veeco, CA, USA) were used for AFM imaging. All samples were imaged under ambient conditions in tapping mode using with a Si tip (Veeco, resonant frequency: 320 kHz; spring constant: 42 N/m).

3.5.2 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM was performed with a JEOL JSM-6700 field-emission scanning electron microanalyzer. Except SWCNT samples were imaged with an accelerating voltage of 0.5-1 keV, the rest samples were imaged with an accelerating voltage of 5 keV.

3.5.3 Transmission Electron Microscopy (TEM)

TEM was conducted at 200 keV with a JEOL JEM-2010 instrument. TEM samples of the Co NPs (Figure 16) were prepared by placing several drops of the colloidal suspension on holey carbon films supported by copper grids. The TEM sample of CNTs were prepared by transfer the as-grown SWCNT from the source substrate to target TEM grids with a poly(methyl methacrylate) (PMMA) film as a mediator [68].

3.5.4 Raman Spectra

The Raman spectra were obtained by a WITEC CRM200 Raman System with 532 nm or 633 nm laser and an air cooling charge coupled device (CCD) as the detector (WITec Instruments Co, Germany). The characteristic Raman peak at 520 cm^{-1} in a silicon wafer was used as a reference to calibrate the spectrometer.

3.5.5 Energy-Dispersive X-ray (EDX) Analysis

The EDX analysis was performed with an EDX spectroscopy attached to the SEM (JEOL 6360A) with accelerating voltage of 15 keV.

3.5.6 X-ray Photoelectron Spectroscopy (XPS)

XPS data were collected by Axis Ultra XPS system with AlK α source (1486.6 eV). The analysis area is $300 \times 700\text{ }\mu\text{m}^2$. High resolution spectra for Fe 2p, Co 2p, Ni 2p, Mn 2p and Cr 2p were collected in their respective energy ranges. The C 1s peak (284.5eV) was used as the reference for calibration.

3.5.7 I-V Measurements

The I-V measurements were conducted with a Keithley 4200 analyzer at room temperature under ambient environment.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Controlled Assembly of Gold Nanoparticles on DPN-Generated Templates

4.1.1 Introduction

Gold nanoparticles (Au NPs) have attracted increasing attention recently due to their unique optical and electronic properties, and their potential applications in various fields, such as optics, nanoelectronics, biodiagnostics, etc. [69-72]. In addition, Au NPs are well known catalyst for growth of semi-conducting nanowires, such as Si, ZnO, etc. Recent studies found that Au NPs are also excellent catalyst for producing high quality of multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) [13,73]. Organizing Au NPs into ordered arrays on a substrate with well defined location and geometry is crucially important in addressing their properties, and extremely desirable for catalyzing the growth of nanomaterials including CNTs.

Typically, the patterned substrates [74,75], either generated by chemical modifications [76], topographical structures [77] or the combination of both [70,78], are often used as templates for controlled assembly of Au NPs. Depending on the different interaction between the NPs and patterned substrates, e.g. electrostatic interaction, capillary force, chemical binding and different wetting ability

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[74,76,79,80], the NPs will be selectively adsorbed on the predefined locations to form the desired patterns.

Despite much progress has been made during the past years, further efforts are still in need to precisely control the assembly of individual NP arrays [77,81], which is critically important for generation of the single NP-based devices, especially when the NP size becomes smaller (for example, ≤ 20 nm). It appears more challenging since the smaller templates are required. However, fabrication of such small templates by the conventional photolithography [82] and soft lithography [83-85] methods are quite difficult. In addition, since masks are needed in the lithographic methods, to change and/or re-design of masks are required for fabricating the new patterns. This is tedious and not compatible for generating sophisticated patterns of interest. The other traditional lithography methods, such as e-beam lithography [70,86], ion-beam lithography [87], etc., show various limitations including expensive equipments, strict operation conditions, and so on. Therefore, a simple and efficient method, which allows patterning functional molecules onto a substrate with high registration, resolution and flexibility, is expected. The recently developed dip-pen nanolithography (DPN) [52,74,88-94], a direct-write AFM-based nanolithography, is such a technique which delivers materials, namely “inks”, precisely to a specifically designated location to form any desired pattern with feature size from micrometers to sub-100 nm. Previous reports have demonstrated that metal NPs [81,91,95,96] including Au NPs [96-98] can be directly deposited by DPN. However, unlike other small molecule-based inks, especially the well established thiol molecules [99], metal NPs are relatively difficult to be uniformly coated on AFM tips [98] due to their large size. The mechanism for NPs to transfer onto substrates is still lack of theoretical

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understanding [91]. Therefore, it is relatively difficult to get uniform NP array with the controlled NP number by DPN.

Alternatively, the assembly of NPs on DPN-generated patterns from solutions provides a better control to generate the uniform NP array [91]. Small molecules used as inks are better for the tip coating and subsequent DPN writing, especially the well studied thiol molecules, such as 16-mercaptohexadecanoic acid (MHA) and 18-octadecanethiol (ODT), which allow one to generate any arbitrary pattern on Au surface to form molecular templates [53,56]. In addition, the functionality of the molecular templates generated by DPN can be varied with the used “inks”. These characteristics make the DPN attractive for generating molecular templates used for controlled assembly of particles, such as polystyrene beads [100], magnetic NPs [101,102], and Au NPs [103]. Although the other scanning-probe based lithographic methods have also been used to generate molecular templates for Au NPs assembly [80,104,105], it has not been demonstrated how to control the number of Au NPs assembled on the patterned areas.

In this section, we present a simple but different strategy by using DPN-generated molecule-based patterns, without any complicated procedure, to generate 20 nm Au NP arrays with the controlled particle number (from 1 to 5), highly accurate location and free of nonspecific adsorption. Moreover, our method has been extended to assembly other materials such as graphene oxide (GO) sheets.

The Figure 18 illustrates the designed procedures. Our strategy begins with patterning MHA self-assembled monolayers (SAMs) on Au substrate by DPN, followed by passivating the exposed Au surface with 11-amino-1-undecanethiol (AUT)

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molecules. The resulting AUT patterns serve as the templates for controlled assembly of Au NPs by immersing the patterned Au substrate into Au NP solution. Since Au NPs used here are capped with negatively charged citrate ions [84], they would spontaneously adsorb onto the positively charged AUT patterns via the electrostatic interactions. By varying the experimental parameters of DPN used for generation of MHA patterns, the features of AUT templates can be tailored accordingly, resulting in the controlled adsorption of Au NPs with different spacing, geometry and even the NP number.

(1) MHA patterns generated by DPN

(2) Passivation with AUT

(3) Adsorption of Au NPs

Figure 18. Schematic illustration of the experimental procedures for controlled assembly of Au NPs on AUT templates.

4.1.2 Assembly of Au NPs Specifically on Designated Molecular Templates

Figure 19A-C show the AFM images of 20 nm Au NPs assembled on the AUT templates obtained by passivation of DPN-generated MHA dot arrays with AUT. The AUT templates can be easily controlled through simply varying the size and spacing of MHA dots. Figure 19A demonstrates the large area assembly of Au NPs on the AUT template. Due to the repulsive interaction, there are no Au NPs adsorbed on the MHA dots generated by DPN with diameter ranging from 300 to 1100 nm. By changing the experimental condition, DPN was used to generate 500 nm MHA dots on Au with 500 nm distance between the centers of dots. After passivation with AUT, Au NPs were selectively adsorbed on the AUT templates (Figure 19B). By simply increasing the patterned size of MHA dots, leading to the slight overlap between them, the rhombic geometries of Au NP array are obtained accordingly (Figure 19C). Figure 19A-C clearly show that Au NPs are selectively and exclusively adsorbed on the AUT templates, while the MHA dots are obviously intact and easily distinguished. The MHA dots are free of nonspecific adsorption of Au NPs due to the electrostatic repulsion between the negatively charged Au NPs and MHA patterns. The MHA pattern plays two critical roles in our experiment. It acts as not only a confinement layer, which guarantees that AUT only assembles on the exposed area on Au surface to form the ordered SAMs used for controlled assembly of Au NPs, but also a strong blocking layer to avoid the nonspecific adsorption of Au NPs, which ensures that the Au NPs accurately and selectively assemble on the predesigned AUT templates.

Figure 19. AFM topography images of controlled assembly of Au NPs on AUT templates

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It is worthy to point out that there are three major considerations for generating AUT templates through passivation of DPN-generated MHA patterns, instead of directly patterning AUT molecules by DPN and followed with passivation of MHA. First, in the previously reported DPN experiments, patterning MHA on Au surface is one of the most well established experiments [52,53,67]. In addition, based on our experience, it is easier to pattern MHA by DPN compared with other alkanethiols including AUT. This approach allows the easy control of the MHA patterning process, resulting in the good control of the size, shape and spacing of the resulting AUT templates. Second, it is well known that the resolution of DPN greatly depends on the radius of AFM probe used [67]. Since the typical tip radius of a contact mode AFM probe is 20-40 nm [106], it is practically difficult to generate sub-20 nm features on Au. To date, directly with DPN, the smallest line generated is 14 nm, when a sharp AFM tip (radius = 13 nm) was used to write MHA on a ultra-flat mica-peeled Au film ($\text{RMS} < 1 \text{ \AA}$) [67]. However, the exposed or unpatterned region, for example, the gap between two DPN-generated features, is not related to the tip radius; it is mainly dependent on the patterned feature size and spacing. Therefore, the feature size of such exposed regions could be extremely small and is desirable for the templated-assembly of nanomaterials, e.g., NPs. Accurately, the reported nano-gap obtained this way can reach to 12 nm [55], which is smaller than the tip radius of normal AFM probes [106] used for DPN. The nanogap size could be, in principle, smaller if the size and spacing of DPN patterns can be accurately controlled. Third, it was found that the long chain n-alkanethiols ($n > 14$) normally can form more robust and closed-packed SAMs on Au than do the short chain n-alkanethiols ($n < 12$) [107,108]. This characteristic makes it possible that the long chain n-alkanethiols exchange the short chain n-alkanethiols when the SAMs of short chain n-alkanethiols expose to the solution of long chain

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n-alkanethiols. The chain length of the alkanethiols used in our experiment is $n = 16$ and 11 for MHA and AUT, respectively. Therefore, the MHA SAMs on Au should be more robust than the AUT SAMs. Furthermore, our recent study revealed that DPN-generated MHA patterns typically are close-packed SAMs, which are robust and used for etching resists to protect the underlying Au for in long time [65]. Thus, using the MHA pattern as the resist layer and then passivating AUT on Au will prevent MHA to be exchanged with AUT during the passivation process. This will greatly reduce the nonspecific adsorption of Au NPs on MHA patterns in the Au NP assembly process. All these advantages make our strategy simple and efficient, which allows us to create the desired AUT templates for controlled assembly of Au NPs successfully.

4.1.3 Assembly of Au NPs with Controlled NP Numbers

Since the number of Au NPs adsorbed on the AUT pattern is mainly determined by the AUT feature size, our method allows one to quantitatively controlling the Au NP assembly on AUT templates. Impressively, Au NP dot arrays with a controlled NP number from 1 to 5 were obtained (Figure 20A). Furthermore, an individual Au NP array was successfully fabricated (Figure 20B). Similarly, Au NP line arrays with various NP numbers can also be controlled on the predesigned AUT line patterns (Figure 20C), where the individual Au NP line was also obtained. Note that the Au NPs used here are very small, only 20 nm in size.

Figure 20. SEM images of (A) Au NP arrays with controlled particle number, (B) an individual Au NP array, and (C) controlled assembly of Au NPs on AUT line patterns. Scale bar = 200 nm.

4.1.4 Assembly of Au NPs on Complex Templates

Besides the regular NP dot and line arrays, the flexible patterning ability of DPN allows us to design AUT templates with any geometry of interested used for the assembly of Au NPs. As proof of concept, the complex pattern of the 2008 Beijing Olympic logo, composed of high-density 20 nm Au NPs, was created using our method (Figure 21).

Figure 21. AFM topography images of (A) Au NP array forming the 2008 Beijing Olympic Game logo, and (B) magnified area indicated by the white square in (A).

4.1.5 Assembly of Other Kinds of Nano Building Blocks

As described above, our method of employing DPN to indirectly create AUT templates for the controlled assembly of Au NPs is simple, efficient and highly flexible. This method, in principle, can be used to assemble or organize other kinds of nano-building blocks, which is interesting and expected. Currently, graphene, a two-dimensional sheet of hexagonally-arranged carbon atoms through sp^2 -bond, is attracting much attention due to its remarkable properties and potential applications in chemistry, physics, biology, electronics, and materials science [109-113]. Mass production of single-layer graphene sheet was recently realized based on the reduction of chemically exfoliated graphene oxide (GO) [62,114-117]. Construction of graphene-based devices used for both of scientific studies and future potential applications will require the assembly of such materials into a desired area. However, the controlled assembly of GO sheets onto a patterned substrate still needs to be developed, although the assembly of GO sheets on AUT micropatterns, generated by the microcontact printing, has been investigated recently [114].

It is commonly believed that GO is rich in oxygen functional group, such as $-OH$, $-CHO$ and $-COOH$ groups and negatively charged, which allows GO well dispersed in water [62,115-117]. Therefore, it is reasonable to assemble GO sheets on the positively-charged AUT templates created by our strategy. Motivated from this point of view, we have successfully assembled GO sheet array by immersing the designed AUT templates into the GO aqueous dispersion, which was prepared in our lab [62]. Significantly, a series of GO sheet arrays were obtained as illustrated in AFM images (Figure 22), where the GO sheets only adsorbed on the AUT areas, as expected.

Figure 22. AFM topography images of the controlled assembly of GO sheets on AUT templates. The dashed circles indicate the DPN-patterned MHA dot array. Scale bar = 1 μm .

4.1.6 Short Summary

In summary, a simple and efficient method was developed for controlled assembly of 20 nm Au NPs with accurate location, essentially free of nonspecific adsorption, and controlled particle number on predefined AUT templates, which were obtained from passivation of the exposed area on Au after MHA patterns were generated by DPN. Importantly, the single-particle array was generated by this method. Attractively, the AUT templates are not limited to assembly of Au NPs, they can also be used for controlled assembly of other materials, including GO sheets, as demonstrated herein.

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In addition, our strategy could be combined with the parallel DPN system [56,118] and recently developed polymer-pen lithography [119], which would provide the possibility for rapid production of large-area nano- and bio-material arrays. This could greatly benefit the further applications in optics, nanoelectronics, sensing, and so forth.

4.2 Controlled Growth of Single-Walled Carbon Nanotubes (SWCNTs) on DPN-Patterned Substrates

4.2.1 Introduction

Controlled growth of SWCNTs on specifically designated catalyst patterns is important for fabrication of CNT-based devices. The characteristic advantages of high resolution and high registration of DPN made it an extremely attractive tool to generate catalyst patterns for growth of CNTs. Compared to the traditional lithographic methods, DPN is a maskless and single-step direct-writing method and can be carried out under moderate operating conditions (no need of high vacuum, high-energy ions or beams), which eliminate the possibilities of contamination and sample damage. In principle, DPN is capable of delivering any kind of materials precisely to a specifically designated location, where “inks” transferred from the AFM tip can form any desired pattern with feature size down to sub-100 nm. This is crucial for fabrication of nanodevices in a complex integration system.

In the former section (4.1), we have successfully demonstrated how to control the assembly of individual Au NPs accurately and specifically on DPN-generated molecular templates with controlled pattern geometry and NP numbers. In this section, the effort will be taken to directly generate Co NP patterns by DPN, which can be severed as catalytic templates for growth of SWCNTs by CVD. The experimental procedures are described in Figure 23. It shows how to efficiently coat the AFM tip with the interested catalyst, which is then transferred onto a substrate, such as Si/SiO_x and quartz, by DPN, and then followed by CVD to synthesize CNTs on patterned catalyst sites. The alignment of SWCNTs is controlled on quartz. Various techniques, such as atomic force microscopy (AFM), scanning electron microscopy (SEM),

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Raman spectrum, etc., are used to characterize and investigate the growth mechanism of the obtained SWCNTs.

Figure 23. Schematic illustration of the processes for the tip coating, Co NP patterns generated by DPN, and SWCNTs grown on Co NP patterns.

4.2.2 Patterning Co NPs by DPN

Patterning NPs at the nanoscale resolution is a challenging task, but it is of critical importance for the development of nano-devices [77,120]. Ali et al. have demonstrated a DPN-based method to deposit small islands of Au NPs at a pre-defined position on silica. However, patterning large-area periodical NP arrays have not been achieved due to the lack of full control of the DPN experiment [120]. Kulkarni et al. reported that a pattern of hydrosols, such as Pd, Au, magnetic γ -Fe₂O₃ and Eu³⁺ doped LaPO₄, could be generated by scanning a NP-coated AFM tip on the substrate [96,121-123]. However, the patterning process is so slow. It took 45 min to generate a pattern of five $66 \times 100 \text{ nm}^2$ rectangles. No dot patterns were accessible with this method. Espinosa and co-workers developed a nano-fountain probe (NFP). In this design, the microfluidic channel connects a reservoir to AFM cantilever. NFP enables the deposition of NPs continuously [123], but the preparation of these special probes is sophisticated and relatively high cost.

In comparison, the DPN process reported here is effective, simple and low cost. It allows for routinely generating patterns over large area in a short time. We believe that two factors are key to the success of our DPN experiments. Firstly, as studied previously [120,123], it is crucial to keep the NP inks, coated on an AFM tip, at the liquid-like state in order to efficiently transfer NPs from the tip to a substrate. The NP inks we used here are Co NPs capped by trioctylphosphine oxide (TOPO) and oleic acid, which are long chain ligands and capable of trapping solvent molecules to keep the NP inks, even coated on a tip, remaining the liquid-like state. Moreover, due to the high boiling point of oleic acid (b.p. 360 °C), it ensures the NP inks maintaining the liquid-like state even when the solvent is evaporated. Secondly, unlike the

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conventional dip-coating method, we developed a “scanning-coating” strategy to ink the tip. Briefly, as shown in Figure 23, a small amount of Co NP solution was dropped on a Si/SiO_x surface. After partial evaporation of the solvent under ambient conditions, the condensed mini-droplets of Co NPs were formed. The AFM tip was carefully moved down to touch a mini-droplet and scan for 1-2 min before it was retracted. This process is very efficient to uniformly coat the tip with sufficient inks, which enables us to pattern NP arrays over a large area without re-coating the tip. Furthermore, since the topside of the cantilever does not contact the ink materials and remains clean, this avoids attenuation of the AFM feedback signal, and thus guarantees the following patterning process under a full and accurate control.

Thus-coated AFM tip was then used to generate Co NP patterns. Figure 24 shows AFM images of dot- and line-patterns of Co NPs generated by DPN on the cleaned Si/SiO_x substrates. A typical dot array is shown in Figure 24A. Each dot was generated by holding the Co NP-coated tip in contact with Si/SiO_x surface for 0.8 s. The total time needed for generating this pattern is very short. The average diameter and height of the dots are 381 and 11 nm, respectively. Notably, the dot height is larger than the mean diameter of Co NPs (ca. 5 nm) used here (see Figure 16 in section 3.1), indicating that these dots are composed of 2-3 layered Co NPs. By changing the tip holding time, dots of various diameters can be readily created. The smallest dot generated here is 68 nm (Figure 24B). Similarly, by varying the writing rate of the Co NP-coated tip on the surface, line patterns with different width can be obtained. As an example, a zigzag line with line width of 880 nm was created (Figure 24C).

Figure 24. AFM topographic images of dot- and line-patterns of Co NPs generated by DPN on Si/SiO_x. (A) AFM topographic image of a dot array of Co NPs generated by DPN. (B) AFM topographic image of DPN-generated Co NP dots with diameter of 68 nm. The inserted scale bar in the amplified image is 200 nm. (C) AFM topographic image of a zigzag line of Co NPs generated by DPN.

Furthermore, this method allows for facile generation of more sophisticated Co NP patterns. Figure 25A and B show DPN-generated patterns, where the word of “CNT” composes of the uniform NP dot array, on Si/SiO_x. The mean diameter and height of the dots are 500 and 12 nm, respectively. All the results mentioned above show that DPN can be used for patterning Co NPs with a controlled feature size, shape and spacing, proving that our “scanning-coating” strategy is an effective and simple method for the successful tip coating, which is one of the key factors to make the DPN experiment successful. We believe that this method can also be used to routinely pattern other NPs on solid substrates.

Figure 25. AFM images of DPN-patterned “CNT” word composed of Co NPs on Si/SiO₂ before and after growth of CNTs with CVD. (A) AFM topographic image of patterned “CNT” word. (B) Magnified image of the letter “N” in (A). (C) Phase image of the patterned Co NP dots after growth of CNTs on Co NP patterns in (A). (D) Magnified 3D AFM topographic image of a patterned Co NP dot after growth of CNTs. (E) Height profile of CNTs grown on the Co NP dot indicated by the line in (D).

4.2.3 Growth of SWCNTs on Patterned Si/SiO_x Substrates

Since metal NPs have been extensively used as catalyst for growth of SWCNTs, it is of great interest if the DPN-generated Co NP patterns can serve as templates for controlled growth of SWCNTs. This will be highly desirable for the fabrication and application of CNT-based nanodevices. Although the synthesis of SWCNTs through CVD has been reported, it still remains a considerable challenge for the uniform growth of SWCNTs on the sub-micron features [124], since typically SWCNTs only grow from NP catalyst with diameter < 10 nm [125] and the growth yield is highly dependent on the activity of the catalyst. Normally, most of the catalyst died during the CVD process and only a few of catalyst remains active for growth of CNTs.

In our experiment, a manual setup of the tube furnace was employed to grow SWCNTs on DPN-generated Co NP patterns (see section 3.4 for the details). The AFM images of the patterned area after CVD process clearly show that CNTs grew specifically on the patterned catalyst sites, Figure 25C. The highly magnified 3D AFM image shows that nine individual CNTs grew on the patterned catalyst dot, Figure 25D. The height profile reveals that the diameter of these CNTs is 1.2 ± 0.3 nm (Figure 25E), indicating that the SWCNTs were formed. This is also confirmed by the Raman spectrum of the as-grown CNT sample, in which a characteristic feature, the radial breathing mode (RBM) peak at 210.6 cm^{-1} is shown up (Figure 26).

Figure 26. Raman spectra of SWCNTs grown on Co NPs on SiO_x/Si surface in the same CVD condition used for the DPN samples (He-Ne laser, wavelength 633 nm).

Despite the sub-70 nm dots can be generated by DPN (Figure 24B), we found that the growth of CNTs on such small features is non-uniform, low-yield and more difficult to control. This might be attributed to the reduced active NP catalyst as the patterned feature size decreases. Recently, a similar result was observed by Papadopoulos et al. who reported that only very low-density individual CNTs grew on the nanosphere lithography-generated sub-100 nm catalyst patterns (50 nm Au/10 nm Al/~1 nm Co) on silica [126]. Further experiments will aim at maximizing the activity of Co NPs in such small nanopatterns so as to optimize the growth of CNTs.

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To demonstrate the reliability of our approach, Co NP dot arrays on Si/SiO_x with diameter of ~ 900 nm and inter-distance of $3\ \mu\text{m}$ were generated by DPN. After CVD process, uniform and high-density SWCNTs grew on the patterned area, Figure 27. Interestingly, the flower-like CNT patterns were obtained since the long CNTs grew around the catalysts dots (Figure 27B and C). Similar phenomenon was also observed on the patterned catalyst dots with diameter of $\sim 1.5\ \mu\text{m}$ (Figure 28).³

Figure 27. SEM images of SWCNTs grown on the DPN-generated Co NP dot arrays on Si/SiO_x.

Figure 28. SEM images of SWCNTs grown on the DPN-generated Co NP dot arrays on Si/SiOx.

As described above, taken the advantage of the unique patterning ability of DPN, CNT patterns of any shape and geometry can be easily produced through this approach. Figure 29 presents a special geometry of the CNT pattern grown on a pre-defined Co NP pattern generated by DPN on Si/SiOx. Note that sometimes the special applications need the special structures. The approach presented here provides a convenient way for fabricating CNT patterns with the controlled location and geometry in terms of given requirements. Importantly, the charm of directly patterning catalyst for guiding nanomaterial growth is not limited to the Co NP- SWCNT system as shown in here. Our method could be extended to other systems, such as patterning Au NPs for growth of ZnO nanowires, etc.

Figure 29. SEM images of SWCNTs grown on the special designed Co NP patterns generated by DPN.

4.2.4 Orientation Control of SWCNTs Grown on Quartz

How to grow CNTs with controlled location and orientation is a critical step for fabricating individual CNT-based nanodevices. In recent years, several strategies have been reported to guide the direction of CNT growth, such as external electric field technique [38], “fast heating” method [42], gas-flow assistant growth [44,45] and surface-lattice-induced alignment [39,40]. Among these reports, surface-lattice-induced alignment has shown to be a very efficient way to produce aligned CNT arrays. Because of the high surface energy of the dense atomic steps and edges of a specific crystal lattice, for instance, X direction of the stable temperature

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(ST)-cut single crystal quartz which is equivalent to the [100] crystallographic direction, the NP catalyst and reactive carbon species would preferentially accumulated and absorbed on these locations [27]. By using ST-cut quartz as substrate, Rogers et al. fabricated the large-scale well-aligned CNT arrays by CVD [39,40]. Recently, Liu et al. modified the CVD conditions and obtained well-aligned and high-density long CNTs [41].

As a further work, in order to control the growth direction of SWCNTs on the DPN-generated catalyst patterns, a similar DPN process was performed to generate the Co NP dot arrays on ST-cut quartz substrate, and then CVD process was conducted. In Figure 30, SEM and AFM images clearly show that the SWCNTs grew along the [100] crystallographic direction of quartz and the well-aligned SWCNT arrays were obtained on the DPN-generated Co dot arrays. The growth direction of CNT is independent on the flow direction of gas source and the location of Co NP dot arrays. Interestingly, close to the catalyst dots, some SWCNTs formed the “L” shapes or so-called “sickle” shapes.

Figure 30. (A–C, E) SEM and (D) AFM images of well-aligned arrays of SWNTs grown on DPN-patterned Co NP dots on ST-cut quartz substrates. The DPN-generated Co NP dot array is designated by the circles in (A–C, E). The [100] crystallographic direction is marked with arrows in (A–C).

4.2.5 Investigation of Formation of “L” Shaped CNTs

We believe that the formation of ‘L’ shaped CNTs is related to the CNT growth mechanism on quartz. Recently, based on the observation with AFM, Liu et al. proposed a “tip-growth” mechanism to explain how the “sickle” SWCNTs formed on quartz which was uniformly coated with the NP catalyst [41]. Based on his explanation, the CNT firstly grew along the [100] direction. After it grew longer, the catalyst NP on the tip side collided with another NP on surface to form a bigger particle. As the particle becomes too big to have strong anisotropic interaction with the

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surface lattice, the alignment of CNT on the surface becomes not energetically preferred, resulting in the bending of CNT and the “sickle” SWCNT formed. On the other hand, Rogers et al. observed that in the region with catalyst, the growth direction of SWCNTs is nearly random and the low degree of alignment in this case is likely due to adverse effects of unreacted catalyst particles (~ 90% of the catalyst does not react to form SWCNTs) that coat on quartz [40].

To avoid the effect of the unreacted catalysts on substrates and better understand the formation mechanism of the “sickle” SWCNTs, an individual dot of Co NPs was patterned by DPN on ST-cut quartz. Similar to Figure 30, the “sickle” SWCNTs were observed after CVD. Figure 31A, B and D show that CNTs grew from the catalyst dot in random direction at the initial growth stage. After growth in a certain length, the CNTs started to bend and align along the [100] direction, probably due to the strong interaction between CNTs and the surface, resulting in the “sickle” CNTs. This observation is different from that reported by Liu et al. who demonstrated that the “sickle” CNTs was formed from bending of the originally aligned CNTs, as mentioned above. In other words, the aligned CNTs lost their alignment after bending. However, based on our observation in Figure 31A-B, the CNTs were aligned after bending. Note that, in our case, the effect of unreacted catalyst particles in the formation of “sickle” CNTs can be excluded since the catalyst was only deposited in the patterned dot area.

Figure 31. (A) SEM image of aligned SWCNTs grown on a DPN-generated dot of Co NPs on ST-cut quartz. (B) Magnified AFM image of the square area indicated in (A). (C) AFM topographic images of the tip ends of SWCNTs marked as 1-9 in (A). The size of each image is $500 \times 500 \text{ nm}^2$. (D) High-resolution AFM topographic image of the square area indicated in (B). The catalyst NPs at the root ends of SWCNTs were indicated by the dashed circles.

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In addition, we did not observe any CNT grown in other area without Co NPs, indicating that CNTs only grew on the patterned Co NP dot. More important and direct evidence obtained by AFM as shown in Figure 31C shows that no Co NP catalyst was observed at the tip end of CNT. However, the Co NP catalyst was observed at the root end of CNT in the DPN-patterned area (Figure 31B and D). This observation gives a direct proof on the “base-growth” mechanism for the growth of CNTs in our experiment, and reveals that the bending and alignment of CNTs were caused by the strong interaction between CNT and quartz, other than the effect of unreacted NPs or gas flow.

4.2.6 Growth of SWCNT Arrays on Multi-Pen DPN Generated Catalyst Patterns

To obtain large-area SWCNT arrays, a multi-pen (e.g. 26-pen) probe was used to generate catalyst patterns. By using the same “scanning coating” method described previously (please refer to section 3.3 and 4.2.2 for the details), the multi-pen probe was successfully coated with Co NPs, and then used for routinely generating catalyst patterns on Si/SiO_x and quartz substrates, respectively. The patterned substrates were used to grow CNTs under the similar CVD conditions. Figure 32A and B show one of the typical catalyst dot arrays generated by the multi-pen DPN on a Si/SiO_x substrate. After CVD process, the random CNT network arrays were successfully obtained which are similar to the CNTs grown on the patterns generated by single-pen DPN (Figure 32C and D). It further confirms that DPN is a repeatable and reliable method for generation of catalyst patterns, which are then used for producing CNT arrays.

Figure 32. (A-B) AFM topographic images of multi-pen DPN-generated Co NP dot arrays on Si/SiO_x substrate. (C-D) SEM images of SWCNTs grown on large-area Co NP dot arrays on Si/SiO_x.

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By using quartz as a substrate, the nearly perfect aligned SWCNT arrays grown on the catalyst strips generated by multi-pen DPN are shown in Figure 33.

Figure 33. SEM images of lattice-aligned SWCNT arrays grown from the large-area catalyst lines generated by multi-pen DPN on quartz.

4.2.7 Short Summary

In summary, by using dip-pen nanolithography (DPN) with Co NPs as “inks”, a variety of nanopatterns were successfully generated on Si/SiO_x and quartz substrates. As proof of concept, the DPN-patterned Co NPs were used as catalyst to grow SWCNTs with controlled alignment on ST-cut quartz. Importantly, our experiment gave direct evidence for the “base-growth” mechanism for CNTs. This novel approach provides a convenient way for fabricating SWCNT arrays in a controllable manner. This approach will greatly benefit the fabrication of nano-devices. Especially, the multi-pen DPN provided the rapid production of large-area catalyst patterns, which were successfully used for growth of CNTs. This opens up the opportunity for simultaneously fabricating large amount of SWCNT-integrated nano-devices.

4.3 Controlled Growth of Densely Aligned Single-Walled Carbon Nanotube (SWCNT) Arrays on Patterned Substrates by “Needle-Scratching” Method

4.3.1 Introduction

Benefiting from the multiple transport pathways and without the tube-tube overlapping junction problems, densely aligned single-walled carbon nanotube (SWCNT)-based nanoelectronic devices show a superior performance to that of their random-network counterparts [33,39,47,127,128]. The construction of such kind of transparent thin film transistors (TFTs) has received increasing attention due to the promising potential applications in e-paper, flexible displays and security devices [33,129-132]. Controlled growth of high-density and well-aligned CNTs is an important step for such applications. In section 2.3.2, we have reviewed that the atomic step-induced and surface lattice-guided growth approach is one of the most efficient ways for producing aligned SWCNTs [39,128,133-135]. For example, by using single-crystal quartz as substrate, Rogers et al. were able to fabricate large-scale well-aligned CNT arrays by chemical vapor deposition (CVD) [39]. In a recent report [40], they suggested that the unreacted catalyst particles were likely to cause an adverse effect that would disturb the alignment of CNTs grown on quartz. They demonstrated that in the patterned catalyst region, SWCNTs presented random-network geometry with low degree of alignment; while out of the catalyst region, the SWCNTs adopted a nearly perfect aligned fashion with high density (~ 1 tube / μm). Therefore, pre-defining catalyst into an ordered structure is very important for growth of densely and well-aligned SWCNT arrays.

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In the former section 4.2, by using dip-pen nanolithography (DPN), we developed a method to generate various patterns of Co nanoparticle (NP) catalyst, which were successfully used for controlled growth of SWCNTs. Normally, the single-pen DPN is widely used and its throughput is still one of the main challenging issues [53,54,91]. Although the multi-pen DPN [56,118] can be applied to generate catalyst patterns in relative large area, it is difficult to create wafer-scale patterns in a short time. Other traditional patterning methods, including photolithography, micro-contact printing (μ CP), etc., can be used to successfully generate catalyst patterns used for growth of SWCNT arrays [22,39,41,125,136,137]. However, as mentioned previously, all these techniques exhibit various limitations. For example, photolithography is popular used for fabricating micro-patterns, but the whole process is time consuming. In addition, the specific equipment, such as evaporator, required for depositing the catalyst film, is expensive and complicated. Furthermore, the photoresist and developer solutions are hazardous to the environment. μ CP is considered as a fast and low-cost method for large-scale catalyst patterning. However, the mask used for preparing stamps is quite expensive, and each modification of stamp features requires the re-designing of the mask.

Hence, a facile, fast, low cost, scaleable and environment-friendly method for generating catalyst patterns on substrates is highly desirable for growth of densely aligned SWCNTs, which may create great impact on fabrication of CNT-based nanodevices and studying their applications. In this section, a very simple, fast, machine-controlled, environmental friendly and nearly no cost approach was developed, called needle-scratching method, referred to as NSM. Using NSM, large-area catalyst patterns can be easily generated on substrates, after the subsequent

Results & Discussions

CVD process, high-density SWCNT networks and densely aligned SWCNT arrays were successfully grown on Si/SiO_x and single-crystal quartz, respectively.

4.3.2 Growth of High-Density SWCNT Networks on NSM-Patterned Si/SiO_x

A common syringe needle was used to randomly scratch lines on a Si/SiO_x substrate. After CVD, high-density CNTs networks are found, which specifically grew from the scratched lines area (Figure 34).

Figure 34. (A) SEM image of random CNT networks. (B) Highly magnified SEM image of high-density CNTs grown on the needle scratched lines on a Si/SiO_x substrate.

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Atomic force microscopy (AFM) image shows that there are lots of nanoparticles (NPs) in the scratched areas (Figure 35), which are used as catalyst for growth of CNTs [13-15]. The measured height of CNTs is 1.5 ± 0.4 nm (Figure 35B and C), indicating that SWCNTs are obtained, which is also confirmed by Raman spectrum (Figure 35D), where a radial breath mode (RBM) peak at 157.7 cm^{-1} suggests the CNT diameter is about 1.57 nm, estimated by using $\omega_{\text{RBM}} (\text{cm}^{-1}) = 248/d \text{ [(nm)]}$.

Figure 35. (A) AFM image of the edge of a needle scratched line on Si/SiOx in Figure 34A. (B) Highly magnified 3D AFM image of the white square in (A). (C) Height profile of CNTs indicated by the white line in (B). (D) Raman spectrum of SWCNTs grown on Si/SiOx in Figure 34B. The 532 nm laser was used here.

4.3.3 Growth of Densely Aligned SWCNT Arrays on NSM-Patterned Quartz

To grow large-area aligned SWCNTs, single-crystal quartz is chosen as substrate. The experimental process is depicted in Figure 36. Briefly, a common syringe needle, installed in a micromanipulator (Figure 17A in section 3.3) is brought into contact with a quartz substrate and then used to scratch the surface to generate the line patterns. Since the micromanipulator enables fine control of the movement of the mounted needle in all directions (X, Y and Z) on the substrate, patterns with different location, shape and spacing, can be easily generated in a controlled manner.

Figure 36. Schematic illustration of the procedures for patterning catalyst stripes on quartz by our NSM, which are used for growth of densely aligned SWCNTs by CVD.

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The patterned quartz substrate was subsequently subjected to CVD for growth of SWCNTs. Figure 37A-C show the successful growth of highly aligned SWCNTs on the “needle-scratched” quartz surface. The bright stripes, clearly observed in Figure 37A, B and D, correspond to the scratched patterns, which were successfully used as catalyst for growth of SWCNTs [13-15]. In the highly magnified SEM image, Figure 37C, the densely and well-aligned CNT arrays are observed in the areas between the catalyst stripes. The orientation of aligned SWCNTs is found to be along the [100] crystallographic direction of quartz, which is well consistent with the previous reports and our previous observation (section 4.2.4 and 4.2.6). Some short random CNTs are only found in the catalyst stripe patterned areas (Figure 37D). According to the recent studies [40,41,138], this short random CNTs could be attributed to the adverse effects of large amount of unreacted NPs exists in the catalyst stripes.

Figure 37. SEM images of densely aligned SWCNT arrays grown from the needle scratched catalyst stripes on quartz. The bright stripes in (A, B, D) correspond to the catalyst patterns generated by NSM. (C) Highly magnified SEM image of densely aligned SWCNTs. (D) Magnified SEM image of short random CNTs grown in the scratched stripe.

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Figure 38 shows large areas of patterned catalyst stripes with a uniform spacing of 100 μm on quartz generated by NSM. Similarly, well aligned SWCNTs were successfully grown from catalyst stripes and formed high-density parallel arrays between the catalyst stripes after CVD. The growth direction is along the [100] crystallographic direction of single-crystal quartz, which is independent of the direction of gas flow and the patterned catalyst stripes, and is in agreement with the previous observation in section 4.2.4.

Figure 38. SEM images of densely aligned SWCNT arrays grown on the needle scratched catalyst stripes on quartz.

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Unreacted catalyst particles are believed to be one of the reasons to disturb the alignment [39] and terminate the growth of CNTs [41]. In order to grow long aligned CNTs arrays without the adverse effect of catalyst particles, a single stripe was scratched on a quartz substrate. As expected, well aligned long SWCNT array is obtained on quartz after CVD. Figure 39A shows that the length of most SWCNTs is more than 100 μm , and some of them even exceed 500 μm . The density of obtained SWCNTs can be reached as high as 10 tubes / μm as illustrated by AFM image in Figure 39B. This is very suitable for high performance nano-electronic devices applications [33,131]. It is worthy to note that the density of SWCNTs could be potentially increased by optimizing the needle-scratching conditions to improve the uniformity of the catalyst stripes in order to increase the number of active catalyst NPs, as well as by long-time annealing of the quartz substrates to enhance the order of crystal lattice structure of quartz surface [39,131]. Figure 39C gives the diameter distribution of 163 tubes measured by AFM. The mean diameter obtained is 1.8 ± 0.3 nm, which is well consistent with the TEM result shown in Figure 39D, where an individual SWCNT with diameter of 1.9 nm was observed.

Figure 39. (A) SEM image of densely aligned ultra-long SWCNT array grown on single catalyst stripe on quartz. (B) AFM image of high-density aligned SWCNTs. (C) Histogram of diameter distribution of 163 aligned SWCNTs measured by AFM. Gaussian fitting curve gives the CNT diameter of 1.8 ± 0.3 nm. (D) TEM image of an individual SWCNT.

4.3.4 Study of Composition of NSM-Generated Catalysts

The mechanism for growth of the high-density SWCNTs on the scratched strips is studied. Although Liu et al. [13] claimed that metal particles were generated on quartz due to the hardness of quartz after a steel blade or tungsten carbide blade was used to scratch lines on quartz, no direct evidence was given. Very recently, Huang et al. [14] and Chen et al. [15] found that SiO_2 nanoparticles (NPs) with a suitable size can be efficiently used as catalyst for growth of SWCNTs. Furthermore, they also reported the low-density SWCNTs grew on the scratched Si/SiO_x surface by using nonmetal objects, such as diamond blade and sharp Si/SiO_x substrate. In order to identify the chemical composition of the catalyst induced by NSM in our experiment used for growth of SWCNTs, the energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were performed on the needle scratched Si/SiO_x substrate after CVD process. From the EDS (Figure 40) and XPS (Figure 41) results, no obvious metal element signal from the scratched area is observed. The strong signals of Si and O suggest that the catalyst NPs generated by the needle-scratching are dominated by nonmetal NPs, SiO_2 , which come from the substrate itself during the scratching process, rather than the metal-based NPs left off from the syringe needle. This result is very similar with the recent reports [14,15], in which a diamond blade and sharp Si/SiO_x substrate were used for scratching the substrate. In other words, the high-density SWCNTs are mainly catalyzed by the scratched production, i.e. SiO_2 NPs.

Figure 40. EDS spectrum of the needle scratched region on quartz substrate after growth of SWCNTs. No metal elements were detected. Insert: the corresponding SEM image.

Figure 41. (A) XPS survey of the “needle scratched” region on Si/SiO_x substrate after growth of SWCNTs. (B-F) The detailed XPS spectra for Fe, Ni, Co, Mn and Cr, respectively. No obvious metal element peak was observed.

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Based on this speculation, nonmetal-containing sharp objects, especially made of SiO_2 , may also be suitably used for scratching the substrate to generate catalyst patterns for growth of SWCNTs. To eliminate the influence of metal species and further confirm whether SiO_2 NPs are responsible for the SWCNT growth in our experiments, we employed nonmetal objects, including the sharp quartz substrate, sharp Si/SiOx substrate, and diamond scribe, to scratch Si/SiOx and quartz substrates used for the growth of SWCNTs under the same experimental conditions as those used for the needle-scratched substrates. The results clearly show that SWCNTs can grow on the nonmetal object scratched patterns (Figure 42). However, the density of SWCNTs is quite low. More importantly, the reproducibility for the growth of SWCNTs on the nonmetal object-scratched substrates is low. The possibility of successful growth of SWCNTs is less than 10%. After carefully comparing the patterns generated with the “nonmetal object-scratching” method and NSM, we found that there are many large particles around the nonmetal object scratched areas (Figure 42) which are similar with the recent reports that utilized diamond blade [14] and Si/SiOx substrate [15] to scratch solid substrates. However, no obvious large particles are observed in our experiment (Figure 35). In addition, very uniform and high-density NPs are found in the needle scratched region, as shown in the AFM image (Figure 35A). It is known that only nanosized NPs (normally the size less than 10 nm) can catalyze the growth of SWCNTs efficiently [14,125].

Figure 42. SEM images of CNT growth on the scratched regions on Si/SiOx and Quartz substrates by using nonmetal objects. Si/SiOx substrates were scratched by diamond scribe (A), Si/SiOx substrate (C) and quartz substrate (E), respectively. Quartz substrates were scratched by diamond scribe (B), Si/SiOx substrate (D) and quartz substrate (F), respectively. Scale bar: 20 μm in all SEM images.

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Above observations suggest that the high quality of the catalyst NPs generated by NSM could be the reason for the growth of high-density SWCNTs, which indicates that the syringe needle plays an important role in producing such high-quality catalyst NPs. Note that, although the EDS and XPS data do not show any metal elements in the needle scratched substrates (Figure 40 and 41), a metal catalyst can not be ruled out since the strong background signals of the substrates may lead to a trace-amount of metal NPs being undetectable. Therefore, the metal NPs may also act as catalyst for SWCNT growth, but only played a subordinate role in our experiments.

All the results shown above demonstrate that the NSM is a simple but reliable technique for patterning catalyst used for growth of densely aligned SWCNT arrays. Compared with the traditional lithographic methods, the advantages of our NSM are obvious. Firstly, the process is very simple and cheap, no photo-resist or sacrifice layers is required, no extra lift-off or burn-out processes are needed, and no high-cost equipment is required. A common syringe needle is able to generate catalyst patterns. Secondly, the method is highly flexible, easily scalable and extremely fast. With a syringe needle, one can draw various catalyst patterns of interest to any location on the substrate over large areas. Since the catalyst was directly generated by needle-scratching without any extra procedure, the processing time is significantly shortened. Currently, a multiple needle array (Figure 17B) is designed, which can be easily used for generation of large-area patterns in very short time. Thirdly, the catalyst was only generated along the pathway of needle movement. Therefore, the other regions are kept intact and remain clean. This is good for growth of ultra-long and high-density SWCNTs (Figure 39A). Lastly and importantly, it is chemical-free and therefore the approach is environmentally friendly. All the characteristics of this

method are highly desirable for patterning catalyst for the growth of high-density aligned SWCNTs over a large-area.

4.3.5 Short Summary

In summary, an extremely simple, nearly no cost and green method to generate catalyst patterns on quartz and Si/SiO_x substrates, obtained by scratching the substrates with a common syringe needle, was developed. Large-scale, dense and well aligned SWCNT array was successfully grown on the patterned quartz substrates. In principle, this general method can be used for any solid substrate. Also, the catalyst stripes could be easily generated and controlled by the micromanipulator. We believe that this simple approach will open up an avenue for the fundamental studies, and applications of high-performance CNT-devices made from the densely aligned SWCNT array.

4.4 Direct Growth of Single-Walled Carbon Nanotubes (SWCNTs) for Electronic Devices with Reduced Graphene Oxide (RGO) as Electrodes

4.4.1 Introduction

Directly grown single-walled carbon nanotubes (SWCNTs) are free from the harsh post-growth experimental treatments, such as in strong acids, with long time sonication, etc. This preserves the original structures and intrinsic properties of CNTs and make them the ideal building blocks for high performance devices used in electronics, chemical and biological sensors, etc. [10,22,49,51,131,139-141]. Integration of the directly grown SWCNTs into addressable electronic devices is a crucial step and pre-requirement not only for fundamental studies but also for further applications.

Two strategies, i.e. direct fabrication of metal electrodes on CNTs [33,139,140] and direct growth of CNTs between the pre-fabricated electrodes [51,142], are normally used to fabricate CNT-based electronic devices. Although the first strategy is popular and commonly used, the shadow mask and/or the use of photoresist may contaminate or destroy CNTs, leading to a lower device performance or even the failure of devices [51]. The second strategy, i.e. direct growth of CNTs between the electrodes, possesses some advantages, including no purification of CNTs and no photolithography steps required. This could be a better choice to produce clean and high-performance CNT-devices since the pristine structures and intrinsic properties of CNTs are preserved.

Results & Discussions

In the previous sections in Chapter 4.1, 4.2 and 4.3, three efficient methods for patterning catalyst on substrates have been developed. The growth of CNTs from patterned catalyst sites with controlled alignment has also been achieved. In this section, a simple route towards integration of all-carbon device will be presented, in which the long-aligned (LA) SWCNTs were successfully grown and crossed the pre-patterned reduced graphene oxide (RGO) electrodes.

To choose RGO rather than other traditional metals as the electrodes materials is mainly because the RGO are compatible with the high temperature in CVD process. The RGO electrodes also possess the following merits, including low resistivity, high mechanical strength, chemical stability, low cost, scaleable, etc.

Figure 43 depicts the device fabrication procedures which include: (1) preparation of RGO films by chemical reduction of GO films which are spin-coated on a substrate; (2) creation of electrode patterns from the RGO film; (3) selective deposition of catalyst on pre-designed positions; and (4) controlled growth of CNTs by CVD to cross and connect the RGO electrodes to form electronic devices.

Figure 43. Schematic illustration of experimental procedures for generation of CNT-based electronic device with patterned RGO as electrodes. (1) Preparation of RGO film on Si/SiO_x; (2) Creation of electrodes pattern from the RGO film; (3) Selective deposition of catalysts in selected positions on the substrate; (4) Controlled growth of CNTs to cross and connect RGO electrodes by CVD.

4.4.2 The Realization of RGO Electrodes

Although many attempts to directly grow CNTs for device applications have been reported [51,141,142], compared to the advances in the synthesis of CNTs achieved recently [14,22,34,45,131], the fabrication of electronic devices with directly grown CNTs is far below its potential [51,143]. This is mainly because that the traditional metal electrodes are not stable at high temperature during the CNT growth in the chemical vapor deposition (CVD) process. For instance, gold (Au) becomes discontinuous and the resistivity of titanium (Ti) and tantalum (Ta) increases to an unacceptable level after CVD process [51]. Other metal electrodes such as molybdenum (Mo) and palladium (Pd) suffer from the increased resistivity due to the

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slight oxidation in ambient condition, although they can survive at high temperature [144]. Therefore, in order to successfully integrate CNT-based devices with the direct CVD growth of CNTs, the exploration of new electrode materials with high thermal stability is needed.

Graphene, a single layer of sp^2 -bonded carbon material, is an excellent candidate for electrodes because of its low resistivity, high mechanical strength, and high thermal and chemical stability [66,112,115,116,139,145]. In addition, the mass production of graphene from chemical reduction of graphene oxide (GO) provides an inexpensive source for large-scale applications. More interestingly, recent studies have demonstrated that the high temperature annealing could not damage the graphene films, but help to reduce GO [66,146], resulting in the increase of conductivity in the obtained RGO film. It indicates that graphene films used as electrodes are possibly compatible with the high temperature CVD process. Recently, several groups have reported the good performance of RGO electrodes used in solar cells [145,147] and organic field-effect transistors (FETs) [146].

The preparation of GO was described in our recent report [62]. AFM measurement reveals that the synthesized GO sheets are single layer with size from tens of nanometers to several micrometers (Figure 44). The conductive RGO film was obtained by chemical reduction of GO film which was spin-coated on substrate. Note that the thickness of the resulting RGO film can be tuned by changing the spin-coating parameters. Typically, when 28 droplets of GO dispersion (concentration: 0.2 mg / ml) are drop-casted (with 10 μ l / drop) on a substrate at 4000 rpm, 10 nm RGO film can be produced after the reduction. Such films have been proved highly conductive and robust enough for electrical measurements [146].

Figure 44. AFM topography image and height profile of obtained GO sheets.

Graphene electrode is one of the most important components in devices. To get regular and well-defined graphene electrodes is necessary for the device fabrication. Several stamping techniques have been recently developed to transfer graphene sheets [148,149], which could potentially be used for preparing the graphene electrodes. However, the obtained patterns are often irregular and vary in thickness that restricts its application as electrodes. These methods require the further development for the practical usage. Recently, Müllen et al. demonstrated that the regular graphene patterns can be generated from solution-prepared GO films by using plasma etching [146]. But the chemicals involved and multi-steps required make the processes relatively complicated and time consuming. Different from these reported complex

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methods, we demonstrate a “scratching” method to create the electrode patterns. By using a sharp tip, made of nonmetal objects such as hard plastic or bamboo stick, to simply scratch the RGO film, the desired patterns for RGO electrodes can be easily generated on the substrate. SEM image in Figure 45A shows the resulted electrode patterns are uniform and have well defined geometry. AFM characterization reveals that the edge of the electrodes are continuous and sharp, while the underlying substrate are clean and smooth after the scratching (Figure 45B), indicating that our “scratching” method yields high-quality electrodes without damaging the beneath substrate. The thickness of the as prepared electrodes is about 10.7 nm.

Figure 45. (A) SEM image of RGO electrodes generated by “scratching” method. (B) 3D AFM image of the edge of a RGO electrode. The measured thickness of RGO film is 10.7 nm.

4.4.3 Growth of Long-Aligned CNTs (LA-CNTs) on Substrates

Besides the successfully creating RGO electrodes with “scratching” method, the other key factor for successful fabrication of CNT-RGO devices is the controlled growth of CNTs. The CNTs need to grow at the desired locations along certain directions. Also they have to grow long enough to bridge two RGO electrodes to form a device. The recent advances in CNT synthesis [24,27,34,39,45] make it possible. With the gas-assisted CVD process, well-separated LA-CNTs are routinely synthesized on the cleaned Si/SiO_x substrates (Figure 46A and B). Normally the length of the grown CNTs can reach several millimeters or even a centimeter after 30 min growth (Figure 46A). The Raman spectrum proved the as-grown CNTs are SWCNTs (Figure 46C).

Figure 46. (A-B) SEM image of well dispersed LA-CNTs on Si/SiO_x. (C) Raman spectrum of an as-grown LA-SWCNT. A 633 nm laser was used.

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However, the substrates pre-patterned with RGO electrodes are different from the original bare Si/SiO_x substrates. As contaminations and unreacted catalyst particles might play adverse effects for growth of LA-CNTs, CNTs may change their growth directions or even terminate the growth once they encounter the RGO electrodes. Whether the LA-CNTs can be achieved on pre-patterned RGO substrates and cross the 10 nm thick RGO electrodes is still unknown. To examine the feasibility of our strategy and understand the LA-CNT growth mechanism, control experiments were carried out on self-assembled GO line patterns and relative thicker RGO films, Figure 47. From the SEM images in Figure 47A and B, one can easily distinguish the LA-CNTs and the GO line patterns, indicating that LA-CNTs are able to grow across the GO films by gas-assisted CVD process. The GO line patterns were fabricated by self-assembly of GO sheets from GO suspensions on the aminopropyltriethoxysilane (APTES) patterns generated by micro-contact printing (μ CP). The electrostatic attraction between the oxygen functional group-riched GO sheets and amino group-terminated APTES films leads to the spontaneous adsorption of GO sheets on the APTES templates, and eventually to form patterned GO lines. Figure 47A and B illustrate the successfully fabricated GO lines with 10 μ m linewidth and 10 μ m inter-distance.

In another experiment, the substrate was partially covered with a relative thicker RGO film, after the CVD process, CNTs were found to cross the gap of the cracked RGO films (Figure 47C and D). The AFM characterization clarified that the CNTs are on top of the RGO films (Figure 47E). This indicates that the LA-CNTs mediated by

Figure 47. (A-B) SEM images of LA-CNTs crossing GO line patterns. (C-D) SEM and (E) topography AFM images of LA-CNTs growth cross thick RGO films. (D-E) The magnified images of the squared area in (C). Black arrows in (E) indicate the as-grown CNT on top of the RGO film.

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the gas flow during gas-assisted growth do “fly” above the substrate without significant influence by GO or RGO films. The above observations strongly suggest that our strategy for integrating CNT-based devices by the direct growth is feasible.

4.4.4 Integration of CNT-RGO Devices and Its *I-V* Properties

Following the control experiments mentioned above, the same CVD process for growth of LA-CNTs was performed on pre-patterned RGO electrodes. As expected, SWCNTs are found to cross the gap between the electrodes. The SEM image in Figure 48A shows a typical example where an individual CNT clearly bridges two RGO electrodes with 25 μm gap. Note that the RGO electrodes patterned here was simply created by “scratching” with sharp tip of objects. The gap distance between the electrodes is determined by the sharpness of the scratching tools used. Therefore, by choose different scratching tools, the different gap width can be obtained. The SEM images show devices with the gap from several micrometers to tens of micrometers are obtained (Figure 48B and C).

Figure 48. SEM images of typical CNT-RGO devices with different gap width.

Electrical properties of the obtained device were investigated. Figure 49 shows the measured I - V results of a prototype device (1 μm thick SiO_x) at room temperature. Several individual as-grown LA- CNTs are found to bridge the 100 μm-gap RGO electrodes (similar to Figure 48C). The source-drain current (I_D) decreases with

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increasing gate voltage (V_{gs}), revealing the p-type behavior of CNTs in the channel. However, the weak gate dependence characteristic suggests that metallic tubes also contribute to the conductance of the device [150]. The device performance could be improved by the precisely controlled CNT growth for producing the large portion of semi-conducting nanotubes [24,34], or using electrical burning process to eliminate the metallic nanotubes [131]. Further experiments are currently ongoing in our lab.

Figure 49. Output Current-voltage (I-V) curves of several CNTs connecting the RGO electrodes under different gate voltage in room temperature.

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In the former section 4.3 of this Chapter, by using a common syringe needle, we have developed a simple but efficient way to generate catalyst patterns on quartz and Si/SiO_x substrates. The densely aligned SWCNT arrays and random-network SWCNTs were successfully grown on the patterned quartz and Si/SiO_x substrates, respectively. Hence, using needle to scratch the RGO film allows one to create the gap and simultaneously deposit the catalysts in the gap. After CVD, densely aligned CNT arrays and random CNT networks are expected to grow in the gap, which connect the separated RGO films on quartz (Figure 50A) and Si/SiO_x substrates (Figure 50B), respectively. Since the catalyst patterned by this way does not need any sophisticated equipments and extra processes, this method could facilitate the CNT-RGO device fabrication and promote the study on basis of such devices.

Figure 50. SEM images of the CNT-RGO devices on quartz (A) and Si/SiO_x (B), obtained by growth of CNTs on the needle scratched gaps between RGO electrodes.

4.4.5 Short Summary

In this section, we have demonstrated a convenient and reliable “scratching” method to pattern well defined RGO electrodes without using any sophisticated and expensive equipments. We have also successfully developed a method to integrate CNT-based devices with the pattern RGO electrodes, where CNTs grown by CVD directly connect the pre-patterned RGO electrodes. Our preliminary study shows the promising electrical properties of the obtained prototype all-carbon electronic devices. It opens up a new avenue for fabrication and study of CNT-RGO devices, and will benefit the future practical applications.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results presented in this thesis, three strategies for efficient patterning of catalysts on substrates, from individual nanoparticle (NP) arrays to sophisticated catalyst patterns, and to large-scale catalyst patterns, have been developed. Also a simple route towards fabrication of all-carbon devices based on the long-aligned single-walled carbon nanotubes (SWCNTs) and pre-patterned reduced graphene oxide (RGO) electrodes have been achieved. The conclusions obtained from each approach are summarized as follows.

A simple and efficient method for controlled assembly of 20 nm Au NPs on 11-amino-1-undecanethiol (AUT) templates with high accuracy and free of non-specific adsorption has been developed. In this method, dip-pen nanolithography (DPN) is employed to generate 16-mercaptohexadecanoic acid (MHA) patterns on Au. After passivation of the exposed Au area with AUT, the AUT molecular templates can be easily obtained. The electrostatic force drives the 20 nm Au NPs specifically and exclusively to adsorb on the AUT templates. The individual NP arrays with controlled particle number from 1 to 5 are achieved on the designated AUT templates.

By using DPN with Co NPs as the “ink” materials, various catalyst patterns including dots, lines and even sophisticated arrays have been successfully generated

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on Si/SiO_x and quartz substrates with the smallest feature size down to sub-70 nm. SWCNTs specifically grew from the patterned catalyst sites after subsequent chemical vapor deposition (CVD). Their alignment can be controlled on quartz. Evidences from AFM concluded that the “L” shaped CNTs formed on quartz are resulted from the base-growth mechanism other than the reported tip-growth mechanism.

A facile “needle-scratching” method (NSM) for fast patterning large-scale catalyst on a substrate has been developed. The catalyst patterns generated by NSM were successfully used for growth of high-density SWCNT networks and densely aligned SWCNT arrays on Si/SiO_x and quartz, respectively. Base on the EDS, XPS and AFM studies, it concluded that the catalyst generated by NSM is dominated by nonmetal NPs (i.e. SiO₂), which are believed to be responsible for the growth of high-density CNTs.

A simple route towards the integration of all-carbon devices has been developed, where SWCNTs are controlled grown by CVD to connect the pre-patterned RGO electrodes. The electrical properties of the prototype all-carbon electronic devices were measured.

5.2 Recommendations for Future Work

The presented methods are able to accomplish the goal for growing CNTs on patterned substrates with controlled location, orientation and geometry. But to meet the specific requirements in the future applications, further works on more precisely controlling the CNT growth and deeper understanding the growth mechanism are recommended.

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- (A) Ease in synthesis and commercial availability of Au NPs with various sizes made Au NPs the expected catalyst for the CNT growth. The author believes that the accomplishment on assembly of individual Au NPs with controlled particle number will allow the synthesis of CNT in a single tube level. It is worthwhile to optimize the CVD conditions for controlled growth of CNTs on Au NPs. It is well known that the diameter of the obtained CNTs is strongly related to the catalytic particle size. Hence, the author also recommends that the controlled assembly of Au NPs with different size, used for the more precise diameter control of the grown CNTs.
- (B) Since the catalyst plays an important role in CVD process, investigating different size and type of metal catalyst for SWCNT growth will help us to further understand the relation between catalyst and the produced nanotubes, and further study the growth mechanism of CNTs. Based on the results of successfully grown SWCNTs on DPN-generated catalyst (Co NP) patterns, the author recommends to deposit different metal catalyst by DPN to a defined region of a substrate, that provides the same CNT growth condition on the different catalyst. The grown CNTs on different catalyst will be characterized by a series of characterization techniques, including AFM, SEM, Raman, etc. It will provide us the useful information about how the catalyst affects the CNT growth, which is useful for us to further understand the CNT growth mechanism.

In order to obtain the well controlled particle size of different catalyst, the author recommends using Polyamidoamine (PAMAM) dendrimers, hyperbranched macromolecules with functional groups, which are able to

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coordinate with metal ions, as templates to prepare catalyst precursors. The size of metal particles can be easily controlled by choosing the appropriate generation of PAMAM dendrimers or by varying the metal ion–dendrimer ratio.

- (C) Based on the results presented in this thesis, the nonmetal NP, SiO₂, was found to be an excellent catalyst for CNT growth. The author believes that the SiO₂ catalyst can also be created by using a bare Si AFM tip to scratch the Si/SiO_x substrate. This simple method can be an alternative way for patterning SiO₂ catalyst used for controlled growth of SWCNTs at a precisely predefined location.
- (D) Most reported CNT-based devices are based on the metal electrodes. The controlled growth of CNTs to connect the pre-patterned RGO electrodes deserves more attentions as it can potentially open up a new avenue for fabrications of all-carbon devices. The CNTs grown in our devices are the mixture of semiconducting and metallic tubes. This could be the main reason for the low performance of the prototype devices. But the author believes that the performance can be improved by controlling the CNT growth, especially the chirality of CNTs, based on the proper selection of the catalyst together with optimization of CNT growth conditions, such as temperature, carbon source, and so on.

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APPENDIX A

LIST OF PUBLICATIONS

A.1 Peer-Reviewed Journal Papers

- [1] **Li, B.**; Cao, X. H.; Ong, H. G.; Cheah, J. W.; Zhou, X. Z.; Yin, Z. Y.; Li, H.; Wang, J. L.; Boey, F.; Zhang, H.,* Direct Growth of Single-Walled Carbon Nanotubes for Electronic Devices with Reduced Graphene Oxide as Electrodes: A Simple Route Towards Integration of Carbon Nanotube-Reduced Graphene Oxide Devices. **2009**, *in preparation*.
- [2] **Li, B.**; Cao, X. H.; Huang, X.; Lu, G.; Huang, Y. Z.; Goh, C. F.; Boey, F. Y. C.; Zhang, H.,* Facile "Needle-Scratching" Method for Fast Catalyst Patterns Used for Large-Scale Growth of Densely Aligned Single-Walled Carbon-Nanotube Arrays. ***Small* 2009**, 5, 2061-2065.
- [3] **Li, B.**; Lu, G.; Zhou, X. Z.; Cao, X. H.; Boey, F.; Zhang, H.,* Controlled Assembly of Gold Nanoparticles and Graphene Oxide Sheets on Dip Pen Nanolithography-Generated Templates. ***Langmuir* 2009**, 25, 10455-10458.
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[8] Zhou, X. Z.;† Chen, Y. H.;† **Li, B.**;† Lu, G.; Boey, F. Y. C.; Ma, J.; Zhang, H.,* Controlled Growth of Peptide Nanoarrays on Si/SiO_x Substrates. ***Small*** **2008**, 4, 1324-1328. (†These authors contributed equally to this paper).

A.2 Conference Papers

[1] **Li, B.**; Zhou, X.; Chen, Y.; Lu, G.; Ma, J.; C. F.; Boey, F. Y. C.; Zhang, H.,* Fabrication of Peptide and Metallic Nano-Arrays on Basis of Dip-Pen Nanolithography. *AsiaNano Conference*, Singapore, 3-6 Nov. **2008**. *Poster Presentation*.

[2] Zhou, X.; Chen, Y.; **Li, B.**; Lu, G.; Boey, F. Y. C.; Ma, J.; Zhang, H.,* Controlled Growth of Peptide Nanoarrays on Si/SiO_x substrates. *AsiaNano Conference*, Singapore, 3-6 Nov. **2008**. *Oral Presentation*.

[3] **Li, B.**; Zhou, X.; Lu, G.; Cao, X. H.; C. F.; Boey, F. Y. C.; Zhang, H.,* Fabrication of Bio- and Nano-Arrays on Basis of Dip-pen Nanolithography. *The International Conference on Materials for Advanced Technologies 2009 (ICMAT 2009)*, Singapore, 28 June-3 July **2009**. *Poster Presentation*.

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