Engineering of the structures of carbon nanotubes and graphene-based materials for electronic applications

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**ENGINEERING OF THE STRUCTURES OF CARBON
NANOTUBES AND GRAPHENE-BASED MATERIALS FOR
ELECTRONIC APPLICATIONS**

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Abstract

Carbon nanotubes and graphene have been studied extensively for transparent conductors as replacement of ITO, high performance transistors as replacement of silicon and other electronic applications. The current graphene-based transparent conductors face three main problems: 1) high cost and limited size for the epitaxial grown graphene films; 2) low conductivity for chemically exfoliated graphene films due to the defects on graphene sheets and sheet-sheet junction resistance; 3) instability of doping. The junction resistance and instability of doping causes troubles for the SWNT based transparent conductors as well. To address the above problems, several types of solution-based flexible transparent conductors have been developed in this thesis, including reduced graphene oxide films, hybrid films of self-assembled silver network with unsorted SWNTs, sorted metallic SWNTs, and CVD-grown graphene. While all the hybrid films show similarly excellent performance in terms of sheet resistance, transmittance, stability in ambient conditions and bendability, unsorted SWNT-Ag hybrid films ($R_s \sim 5.8 \Omega \text{ sq}^{-1}$ at $T \sim 83.7\%$) are more suitable for industrial applications due to the all solution-based scalable process and low cost. The application of the hybrid films as photovoltaic electrodes is also demonstrated.

In addition, reduced graphene oxide (RGO) thin films were applied as platforms for gold nanostructure synthesis. By different reduction methods, *viz.* hydrazine vapor reduction, H_2 annealing, and ethanol/ H_2 reduction, the RGO reduction degree was controlled from low, to moderate, and to high, respectively. By simply immersing the RGO thin films into Au^{3+} solution, Au nanoparticles, long Au nanowires and semicircular-shaped Au nanoplates were produced on slightly-, moderately-, and highly-reduced

graphene oxide surfaces, respectively, without the need of any templating agent. The growth of various gold nanostructures is related to size and distribution of the $-sp^2$ / $-sp^3$ domains of reduced graphene oxide with different reduction degree.

Semiconducting SWNTs are considered to be the most promising material to replace single crystalline silicon in high performance transistors. However, all current methods for semiconducting/metallic SWNT sorting suffer from either high cost or low efficiency. In this thesis, we studied the sorting of large diameter arc-discharge SWNTs into semiconducting and metallic fractions with high purity *via* a simple repulsion chromatography method using non-ionic surfactants. Semiconducting SWNTs with >99.9% purity or metallic SWNTs with >90% purity can be obtained after a single-pass separation through functionalized agarose beads. Network field-effect transistor (FET) devices were fabricated with the sorted semi-SWNTs, and the performance of a typical network FET device reaches on/off ratio 10^4 - 10^5 and mobility $15\text{-}30\text{ cm}^2\text{ V}^{-1}\text{s}^{-1}$. The method which is simple, fast, cost-effective and easy to scale up for industrial applications is envisaged to reduce the price of sorted carbon nanotubes to a fraction of today's price.

1 Introduction

Carbon nanotubes (CNTs) and graphene have attracted enormous interest due to their superior electrical, optical, and mechanical properties.[1-7] And they are believed to be the most promising materials for the next generation flexible/printable electronic devices for two applications: flexible transparent conductors,[8-12] transistors,[13, 14] sensors,[15, 16] *etc.*

1.1 Graphene and CNTs Based Flexible Transparent Conductors

1.1.1 Background

Transparent conductors are key components of electronic devices such as touch screens, liquid crystal displays (LCD), organic light-emitting diodes (OLED) and thin-film photovoltaics. The current dominant material for transparent conductors is ITO, coated on either rigid (*e.g.*, glass) or flexible (*e.g.* polyethylene terephthalate, *abbr.* PET) substrates, with typical sheet resistance (R_s) $\sim 30\text{-}80\ \Omega\ \text{sq}^{-1}$ while transmittance (T) $\sim 90\%$. Although ITO shows superior high transparency and low resistance, it also has some intrinsic drawbacks, including resource shortage and rising price of indium, low efficiency,[17] high cost of sputtering deposition process, and its brittleness. Researchers are looking for novel materials as ITO replacements for cheaper, lighter, and more flexible electronic devices.[12]

Various materials have been studied for ITO replacement, including thin films of indium free metal oxides,[18] polymers,[19-21] metallic nanostructures,[22-26] graphene,[8, 27-29] and CNTs.[11, 30-32] Each material has its advantages and

disadvantages. However, among all, graphene and CNTs, especially single walled carbon nanotubes (SWNTs), are considered to be the most promising materials for flexible transparent conductors because they are great combination of superior electrical conductivity, high optical transparency and high flexibility.

Graphene is a two dimensional (2D) single atomic graphite layer with $-sp^2$ hybridized carbon atoms arranged in a honeycomb lattice.[1-3] The intrinsic electron mobility of graphene is measured up to $230000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$,[33] while the corresponding resistivity is as low as $10^{-6} \Omega\cdot\text{cm}$ which is even lower than that of silver. Since it is a single atomic layer, graphene shows unexpectedly high optical transparency, absorbing only $\sim 2.3\%$ white light in vacuum.[34] This unique optical property makes graphene really attractive for the application of ITO replacement. The Young's modulus of graphene is reported to be $\sim 1.0 \text{ TPa}$,[7] and it is called the strongest material in the world. Many studies have been reported to apply graphene as transparent conductors. Currently, the typical sheet resistance of synthesized graphene ranges from 2 to $5 \Omega \text{ sq}^{-1}$, and decreases to $\sim 350 \Omega \text{ sq}^{-1}$ by stacking 4 layers of graphene together with $T \sim 90\%$. And the above value could be further reduced to $\sim 30 \Omega \text{ sq}^{-1}$ by nitric acid treatment.[8]

Carbon nanotubes can be considered as seamless cylinders of rolled-up monolayer or few-layer graphene sheets with ultrahigh length-to-diameter ratio (up to 132000000:1).[35] The ultra high aspect ratio causes unique electrical properties of CNTs, for example, the electrons propagate only along the axial direction and thus CNTs are considered as one-dimensional materials. CNTs show superior electrical conductivity due to the one-dimensional structure. It has been reported that DC conductivity (σ_{DC}) of a single CNT can be up to 200000 S cm^{-1} [36] with a mobility in excess of $100000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

¹. [37] The ultrahigh aspect ratio and nanoscaled diameter make CNTs easy to be fabricated to thin films with high optical transparency, while the strong mechanical properties assure the tenacity and flexibility. The best result to date for CNT transparent electrode is $R_s=60 \Omega \text{ sq}^{-1}$ with $T=91\%$, doped by superacid. [32] More studies on graphene and CNTs based flexible transparent conductors are reviewed in Chapter 2.

1.1.2 Challenges

- 1) The ultra high mobility of graphene, as mentioned in Section 1.1, has only been observed on suspended graphene mechanically produced from highly ordered pyrolytic graphite (HOPG). Larger area graphene synthesized by the scalable methods, such as epitaxial growth on silicon carbide, [38] chemical vapor deposition (CVD) [27, 39] have only achieved $5100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [8] at room temperature. Therefore, the typical experimental sheet resistance of un-doped synthesized graphene is only $2\text{-}5 \text{ k } \Omega \text{ sq}^{-1}$, roughly 100 times higher than the theoretical minimum. Although the resistance can be reduced by various doping processes, [8, 28, 29] the doping effect is not stable in ambient condition. There is great challenge on how to produce stable graphene-based transparent conductors with high performance.
- 2) CVD method seems to be the most effective method to synthesize graphene with no or few defects. However, the cost of CVD method is too high for industrial applications due to the high energy consumption and un-recoverable usage of substrates. Various solution-based processes for graphene preparation have been reported. But the size and quality of the graphene sheets remains a concern.

- 3) The major impediment towards applying CNTs network thin films for transparent electrodes is the junction resistance between CNTs. Doping by strong acid could reduce the sheet resistance of CNTs network film to an acceptable value,[32] however, once again, it is unstable and the process is too corrosive with the superacid involved.
- 4) From all the above, it is still a huge challenge to produce SWNTs or graphene based transparent flexible conductors with high performance *via* a simple, low-cost, and stable process.

In this thesis, a solution-based method to prepare SWNTs based transparent flexible conductors is reported to address the above problems. The method is simple, fast, low-cost and easy to scale up.

1.2 Carbon Nanotube Field-Effect Transistors

1.2.1 Background

Conventional field-effect transistors (FETs) use silicon as the semiconducting materials. As the transistors develop towards faster speed, lower energy consumption and lower cost, the improvement of conventional FETs becomes more and more difficult because the size of the FETs has approached the physical limit.[13] Single walled carbon nanotubes are considered as the most promising material to replace single crystalline silicon in high performance FETs due to their one-dimensional structure and quasi-ballistic conductivity. However, as-produced SWNTs are always mixtures of different electronic types. Usually, 67% of the as-produced SWNTs are semiconducting while 33% show metallic behavior;[40] the actual relative abundance of semiconducting and metallic

species in as-produced SWNT samples depends on the details of the synthesis process. Although for some applications, *e.g.*, SWNTs-based composites,[41, 42] the electronic type (semiconducting or metallic) of SWNTs has little effect on material performance, however, for transistors, the presence of metallic SWNTs (met-SWNTs) may short the channel gap, making the transistors un-switchable and not usable.[43, 44] Therefore, semiconducting SWNTs (semi-SWNTs) with homogeneous electronic properties are desired for best device performance.[45-48]

In the past decade, a great deal of research effort has been invested into the problem of sorting SWNTs by electronic structure type. Successful sorting has been achieved by various methods such as selective reaction/removal,[49-53] selective dispersion,[54-56] electrophoresis,[45, 57, 58] density gradient ultracentrifuge (DGU),[59-61] chromatography[47, 62-64] and the combination of the above mentioned technologies.[46, 65] All the methods are effective but each has one or more intrinsic drawbacks which hinder the technologies from implementation in large-scale industrial processes. To the best of our knowledge, until now the only commercialized technique for electronic structure type sorting is DGU. Although high purity (~99%) semiconducting and metallic SWNTs can be achieved, the DGU method suffers from the high cost of the density gradient reagent and the intrinsic slowness of the DGU process, which combine to make the price of SWNTs sorted by this method much too high for industrial applications.

Therefore, to unlock the market of SWNT-based electronics, it is urgent and essential to develop a highly effective and low-cost technology for SWNTs sorting by electronic types.

1.2.2 Challenges

- 1) Ultrahigh purity of semi-SWNTs ($\geq 99.9\%$) is required for electronic applications.

Although various methods for SWNT sorting have been reported, till now, few can reach this high purity stably due to the very small physical and chemical difference between semiconducting and metallic SWNTs.

- 2) The cost for SWNT sorting by electronic types is a huge challenge. The price of commercial 99% semi-SWNTs product (NanoIntegris, sorted by DGU method) is US\$799 per milligram, which is too high for industrial applications. The high cost comes from the expensive equipment, the costly density gradient medium, the time-consuming DGU process, and low yield. Therefore, a cost-effective while efficient sorting method is needed to unlock the market for sorted SWNTs.
- 3) Chromatography is an effective technology for SWNT sorting with low-cost, and it is easy to scale up. However, most of the previous studies only reported the sorting of SWNTs with small diameter, *e.g.*, HiPco or CoMoCat SWNTs, which are not suitable for high performance electronics. To sort large diameter SWNTs, *e.g.*, arc-discharge, *via* chromatography remains a huge challenge.

1.3 Objectives

As mentioned above, although the potential applications of graphene and SWNTs have been talked about for decades, their electrical applications such as transparent flexible conductors and electronic devices remain as huge challenges. The objective of this thesis is to develop low-cost and effective technologies for 1) graphene or SWNTs based

transparent flexible conductors with high performance, and 2) sorted semi-SWNTs with ultrahigh purity for electronics, especially SWNT network field-effect transistors.

1.4 Organization of Thesis

The thesis is organized into 6 chapters. The content of each chapter is briefly summarized as follows:

In Chapter 2, a brief review of the currently available literatures is presented on the structure and properties of graphene and SWNTs, various characterization techniques of graphene and SWNTs, preparation and performance of transparent flexible conductors, and previously reported sorting methods for SWNTs by electronic types.

In Chapter 3, we developed various graphene / SWNTs based transparent and flexible conducting films on PET films, which have been patterned with solution self-assembled Ag nanoparticles in simple, cost-effective and solution-based processes. While the performance of all the hybrid films (Ag with unsorted SWNTs, met-SWNTs and CVD-grown graphene) are similar in terms of sheet resistance and optical transmittance, those with unsorted SWNTs are the most cost-effective. Such flexible and transparent electrode exhibits sheet resistance down to $\sim 5.8 \Omega \text{ sq}^{-1}$ at $\sim 83.7\%$ optical transmittance. The hybrid films are stable in ambient condition and offer excellent bendability.

In Chapter 4, the properties of reduced graphene oxide (RGO) films and their application as synthesis platform of gold nanostructures were studied. Uniform graphene oxide (GO) films were spray-coated and reduced to different extents by various methods. We found that the morphologies / dimensions of Au nanostructures can be tailored by

merely controlling the reduction degree of graphene oxide surface. Au nanoparticles, long Au nanowires, and semicircular-shaped Au nanoplates are *in situ* synthesized on slightly-, moderately-, and highly-reduced graphene oxide films respectively, without the need of any templating agent.

In Chapter 5, we reported the sorting of large diameter SWNTs (arc-discharge) into semiconducting and metallic fractions with high purity *via* a simple repulsion chromatography method using non-ionic surfactants and the application of semi-SWNTs as network field-effect transistors (FETs). Semiconducting SWNTs with purity >99.9% and metallic SWNTs with purity >90% can be obtained after one-pass sorting through functionalized agarose beads. The performance of a typical semi-SWNTs network FET device reaches on/off ratio $10^4 - 10^5$ and mobility $15\text{-}30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The method is simple, fast, cost-effective and easy to scale up for industrial applications and is envisaged to reduce the price of sorted carbon nanotubes to a fraction of today's price.

In Chapter 6, conclusions drawn from the experimental studies in this thesis are reviewed and future research is proposed as a continuing study of this work.

2 Literature Review

2.1 Graphene

Graphene is a two dimensional (2D) single atomic graphite layer with $-sp^2$ hybridized carbon atoms arranged in a honeycomb lattice with thickness ~ 0.34 nm.[1-3] Ever since first time exfoliated in 2004,[66] graphene has been considered as one of the most promising materials to develop new generation flexible conductors transparent conductors[8-10] due to its superior electrical (mobility up to $200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$),[67, 68] optical (transmittance 97.7%),[34] and mechanical properties (Young's Modulus ~ 1.0 TPs).[7]

Figure 2.1 (A) The 2D graphitic structure of graphene. It can be rolled up into 0D fullerene, 1D carbon nanotubes, or stacked into 3D graphite.[69] (B) Photograph of a few-layer graphene flake with thickness ~ 3 nm on top of an SiO_2 wafer.[66] (C) Photograph of a $50 \mu\text{m}$ aperture partially covered by monolayer and bilayer graphene. The optical absorbance of each layer was measured to be 2.3%. Inset shows the sample design with apertures of 20, 30, and $50 \mu\text{m}$ in diameter.[34]

2.1.1 Synthesis of Graphene

During the past few years, many methods have been developed to produce graphene. Generally, these methods can be divided into four categories: mechanical exfoliation,[2, 66] epitaxial growth,[27, 70-74] liquid phase exfoliation[75, 76] and reduction of graphene oxide (GO). [77]

Mechanical exfoliation was first introduced by Novoselov and Geim,[66] who won the Nobel Prize for Physics in 2010. Single layer and few layer graphene sheets were exfoliated from highly oriented pyrolytic graphite (HOPG) by repeated peeling with Scotch tape. The graphene sheets exhibited excellent electrical properties with a strong ambipolar electric field effect of electrons and holes in concentrations up to 10^{13} cm^{-2} and with room-temperature mobility of $\sim 10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by applying gate voltage. Graphene produced by the mechanical exfoliation method has the most perfect structure, compared to the products from the other preparation methods. However, this method is time consuming and the product is not applicable for conducting films due to its low yield and discontinuity.

The other approach to obtain monolayer graphene is to grow on the silicon carbide (SiC) wafer or transition metal surface. The former is to convert SiC (0001) to graphene via sublimation of silicon atoms at high temperature. High quality wafer scale (2 inch) graphene with switching speed of 100 GHz has been reported using this method.[78] With the superior performance of the electronic devices, this technique is promising for the application of radio and high frequency electronics. However, the high price of SiC wafer and the requirement of high temperature make this method not applicable to scale up for

large-scale conducting films. To grow graphene on the surface of transition metals is another widely used method. Several metals have been reported as substrates in this technique, including Ni,[72] Pd,[79] Ru,[80] Ir[81] and Cu.[27, 82] Unlike the decomposition process on SiC wafer, this is a chemical vapour deposition (CVD) process with the surface catalysis of the metal substrates. Graphene with large area (up to 30 inches) has been demonstrated to grow on the polycrystalline Cu foil and the product has been demonstrated as transparent electrode for touch screens.[8] The cost of the CVD method is relatively lower than that of the epitaxial growth on SiC. However, the process still needs high temperature (usually 1000 °C) and vacuum condition (graphene grown at atmosphere condition on Cu foil is always with defects). In addition, the size of graphene is always limited to the size of the metal substrates.

The most inexpensive and readily accessible approach towards processable application is to produce graphene as dispersion, either in aqueous phase or organic solvents. In the past a few years, a lot of research has been done towards mono-dispersed reduced graphene oxide (RGO) suspension and liquid-phase-exfoliated graphene dispersion.

The history of graphite oxide preparation can be traced back to 1859, when Brodie achieved this “graphitic acid” by repeated treatment of Ceylon graphite with an oxidation mixture consisting of potassium chlorate and fuming nitric acid.[83] Later, Brodie’s method was modified by Staudenmaier, Hofmann, and Hamdi, who added potassium chlorate to a mixture of concentrated sulfuric acid, concentrated nitric acid and graphite. In 1958, Hummers and Offeman reported a less hazardous and more efficient method to prepare graphite oxide in a mixture of sodium nitrate, potassium permanganate, and

concentrated sulfuric acid.[84] This method is the most commonly used approach for graphite oxidation nowadays, and is referred to as the “Hummers’ method”. In the recent years, Hummers’ method has been further modified by researchers to decrease the processing time or towards larger/smaller lateral dimensions[85-87] (Figure 2.2 A & B).

After oxidation, GO sheets are mixed with the non-exfoliated graphite, oxidizing reagents, and the by-products (salts). To extract pure GO, dialysis, centrifuge or filtration is used to remove the unwanted components.[88, 89] After purification, the monolayer GO dispersion shows a yellow-brown color. The size of GO sheets can be selected by multi-step centrifuge, or by density gradient centrifuge (DGU).[85]

Figure 2.2 (A) AFM image of nanometer-sized GO sheets obtained by extensive sonication.[85] (B) Optical microscope image of large GO sheet deposited on a Si/SiO₂ substrate.[86]

GO sheets are insulating due to the existence of the functional groups including hydroxyl, carboxyl and epoxy, *etc.*[90] The graphitic structure and conductivity can be restored by reducing GO into RGO (Figure 2.3). Many approaches have been reported for GO reduction, including chemical reduction,[77] thermal annealing,[91, 92] and other

methods (microwave-assisted approach,[93] flash conversion,[94] electrochemical route,[95] *etc.*). The most commonly used reducing reagents are hydrazine (N_2H_2),[77, 96] sodium borohydride (NaBH_4),[97] while several other reagents were also reported to be effective, such as dimethylhydrazine (DMH),[98] hydroquinone,[99] hydrohalic acid,[100] ethanediamine (EDA),[101] and sodium citrate.[102] Aggregation happens when GO sheets are reduced in solution form because the solubility of RGO in water decreases greatly as the hydrophilic functional groups are removed. Therefore, various additives were involved to enhance the stability while and after reduction.[103-105]

Figure 2.3 Schematic structure of GO and RGO.[90]

GO can be reduced in solid state (for instant, as GO film) by thermal annealing as well, either in ultra high vacuum (UHV) or under Ar/H_2 protection.[106] High temperature (usually $900\text{-}1000^\circ\text{C}$) is proved to be effective for good reduction. Su *et al.* introduced an approach that GO sheets was reduced by high-temperature alcohol

vapors.[92] The RGO restored by their method exhibits highly graphitic structures and excellent electrical conductivity.

2.1.2 Characterization of Individual Graphene Sheets

Atomic force microscopy (AFM) is a widely used technology to characterize graphene. The two-dimensional graphene sheets are quite obvious under AFM. The thickness of ideal monolayer graphene is ~ 0.34 nm, while that of monolayer GO sheet is reported to be 1-1.4 nm due to the presence of functional groups and adsorbed molecules[77] (Figure 2.4). After the functional groups are partially removed by reduction, the thickness of monolayer RGO slightly changes.[107]

Figure 2.4 AFM image of monolayer GO sheets. The height profiles show that the thickness of individual GO sheet is approximately 1 nm.[77]

Another critical characterization method for graphene is Raman spectroscopy. The major features of the Raman spectra of graphite and graphene are the G band at ~ 1582 cm^{-1} and the 2D (G') band at ~ 2700 cm^{-1} . [108] G band is due to the E_{2g} vibrational mode,

and 2D band is a second-order two-phonon mode. 2D peak shows a significant change in both shape and intensity as the number of layers decreases. In bulk graphite, 2D band is comprised of two components, the intensities of which are roughly 1/4 and 1/2 that of G peak for the low and high shift, respectively. The relative peak height of G and 2D bands indicates the number of layers of the present sample.[92, 109] For monolayer graphene, 2D band is a single sharp peak at the lower shift, with intensity over 2 times that of G peak (Figure 2.5A).

D band at $\sim 1350\text{ cm}^{-1}$ is not Raman active for pristine graphene but can be observed in the samples with a high density of defects. D band of GO sheets becomes dominate indicating the decrease of -sp^2 domain size in the sample due to the extensive oxidation (Figure 2.5B). After reduction, D band of RGO becomes sharper and the D/G ratio is even higher because of the newly formed smaller-sized -sp^2 domains after reduction.[77]

Figure 2.5 (A) Raman spectra (532 nm laser) of HOPG and graphene with 1, 2 and 3 layers.[110] (B) The Raman spectra (514.5 nm) of graphite (top), GO (middle), and RGO (bottom).[77]

2.1.3 Fabrication and Properties of Graphene Thin Films

With its high carrier mobility, electrical conductivity and optical transmittance in the visible range, graphene is considered a promising material for transparent conductors. It is predicted that the sheet resistance of highly doped graphene conductors will be $\sim 62.4/N \Omega \text{ sq}^{-1}$, [111] where N is the number of graphene layers, and the transmittance of the graphene film will be $100 - 2.3N \%$. [34] However, no experimental result can reach this performance due to the defects on graphene sheets and the junction resistance between graphene sheets for stacked films. Till now, the best performance for graphene films is reported by Bae *et al.* with sheet resistance $\sim 30 \Omega \text{ sq}^{-1}$ at $\sim 90\%$ transparency, which is the performance of graphene films stacked of four graphene layers and doped by HNO_3 . [8]

The CVD grown graphene sheets are usually transferred to transparent substrates by etching away the metal substrates (Figure 2.6C). [8, 27, 39, 72] PDMS stamp [72] or a thin PMMA layer [112] are commonly used to protect graphene during the etching and transfer process. Figure 2.6A shows a roll-to-roll transfer process of large scale CVD grown graphene, including the adhesion of polymer supporting layer, etching of copper foils, and dry transferring graphene onto the target substrate *via* lamination. A 30-inch graphene film transferred on PET substrate and a patterned graphene sheet transferred onto PDMS substrate are shown in Figure 2.6B and 2.6D, respectively.

Figure 2.6 (A) A schematic of a roll-to roll transfer process of graphene grown on copper foils by CVD method.[8] (B) A 30-inch graphene film transferred onto PET substrate.[8] (C) A graphene sheet floating on FeCl₃ solution after the Ni substrate is etched away.[72] (D) A patterned graphene film transferred onto PDMS substrate.[72]

For graphene or graphene oxide (GO) in solution, the films can be deposited by various methods, including spin-coating,[113] filtration and transfer,[10] spray,[114] Langmuir-Blodgett (LB) deposition,[115] *etc.* GO can be either reduced in solution or on substrates as films to restore the conductivity, as shown in Figure 2.7. It is easier to deposit a uniform film with GO sheets than their reduced form, because RGO sheets tend to aggregate in solution. Surfactant or stabilizing agent are needed to stabilize RGO sheets in solution, but the existence of those molecules will affect the uniformity and reduce the conductivity of the RGO films. The GO films can be reduced in hydrazine vapour,[116] HI solution,[117] or by thermal annealing,[89] as mentioned in Section 2.1.1. For the chemically reduced RGO films, the sheet resistance is usually in a range of 10^5 - $10^6 \Omega \text{ sq}^{-1}$ when transmittance $>80\%$, while for those reduced by a high temperature ($>1000^\circ \text{C}$)

thermal annealing, the sheet resistance of a few thousand is achievable (Figure 2.8). Although the RGO-based films are not comparable to the CVD-grown graphene films in terms of conductivity, they are applied as conductive layers for some applications with their advantages of scalable solution-based process and low cost.[111, 118, 119]

Figure 2.7 Process for RGO (referred as rGO in the figure) film preparation.[120]

Figure 2.8 Transmittance vs. sheet resistance of RGO films reduced by various methods.[120]

2.1.4 In-situ Synthesis of Nanostructures on Graphene Oxide

The existence of functional groups makes GO and RGO perfect platforms for nanostructure synthesis. Various metal and metal oxide nanoparticles have been reported to be produced on GO or RGO surface.[121-126] Conventionally, reducing agents are necessary for synthesis of metal nanoparticles in solution. Taking Au nanoparticles as an example, zero-dimensional (0D) small Au nanoparticles are commonly synthesized by reducing Au^{3+} (e.g. HAuCl_4) in solution with reducing agents such as sodium citrate.[127] However, GO and RGO have been used as substrates for directly producing gold nanostructures.[128-131] In these cases, electrons from GO or RGO can be transferred to Au^{3+} spontaneously due to galvanic displacement and redox reaction, so that other reducing agents are not necessary in these systems.[129] Usually, when no templating agents are used, the resulting Au nanostructures are nanoparticles without any shape

control. Using cetyltrimethylammonium bromide (CTAB) as a template, Kim and his co-workers have synthesized one-dimensional (1D) Au nanorods (AuNRs) on RGO thin film.[132] In 2011, Huang *et al.* reported an *in situ* route to synthesize Au square sheets on GO, using 1-amino-9-octadecene to direct the formation of the two-dimensional (2D) structures.[133] They reported that GO enhanced the shape and size distribution homogeneity of the Au square sheets. Metal oxides with 1D or 2D nanostructures synthesized on GO and RGO surfaces have also been reported. In 2010, Chen *et al.* synthesized MnO₂ nanoneedles on GO in a water-isopropyl alcohol system.[134] In the same year, ZnO nanorods were electrochemically grown on transparent RGO electrodes for solar cell applications.[135] The metal/metal oxide nanostructures deposited on GO/RGO surfaces can be used for various applications, including surface enhanced Raman scattering (SERS) substrates,[121] biosensors,[125] photovoltaics,[135] and supercapacitors.[134]

Figure 2.9 (A) 0D Au nanoparticles grown on GO sheets.[131] (B) 1D Au nanorods synthesized on RGO film.[132] (C) 2D Au nanosheets synthesized on GO sheets.[133] (D) MnO₂ nanoneedles on GO sheets.[134]

2.2 Single Walled Carbon Nanotubes (SWNTs)

2.2.1 Structures of SWNTs

Single walled carbon nanotubes are basically seamless hollow cylinders of rolled-up monolayer graphene sheets with aspect ratio usually around 1000. Different directions of rolling up a graphene sheet results in various SWNT helicity. The helicity of a SWNT is defined by its chiral vector C_h :[136, 137]

$$C_h = na_1 + ma_2 \equiv (n, m) \quad (\text{Equation 2.1})$$

where a_1 and a_2 are unit vectors of the honeycomb graphene lattice, while n and m are integers representing the number of unit vectors along the direction of a_1 and a_2 . The helicity also can be defined by the tube diameter d_t and chiral angle θ . d_t and θ are uniquely defined by integer (n, m) as follows:[136, 137]

$$d_t = \frac{C_h}{\pi} = \frac{\sqrt{3}a_{C-C}\sqrt{m^2+mn+n^2}}{\pi} \quad (\text{Equation 2.2})$$

$$\theta = \tan^{-1} \frac{\sqrt{3}m}{2n+m} \quad (\text{Equation 2.3})$$

where a_{C-C} is 1.421Å, the distance of carbon-carbon bond. The range of θ is $0^\circ \leq |\theta| \leq 30^\circ$.

Three types of SWNTs are defined with θ and (n, m) : armchair ($\theta=0^\circ$, $m=n \neq 0$), zigzag ($\theta=30^\circ$, $n \neq 0$, $m=0$) and chiral ($0^\circ < |\theta| < 30^\circ$, $n \neq m \neq 0$), as shown in Figure 2.10.[136, 138]

Figure 2.10 (A) SWNT helicity map. The integer pairs (n, m) specify the chiral vector C_h of SWNTs. The circled dots denote the metallic SWNTs while the small dots without circle denote the semiconducting ones. (B) Examples of armchair, zigzag and chiral nanotube structures.[136]

The electronic properties of SWNTs are determined by the integer pair (n, m) as well. The SWNTs are metallic if $n-m$ is divisible by 3, and the SWNTs are semiconducting if it is not.[139] Therefore, in general, 1/3 of the as-synthesized SWNTs are metallic, and 2/3 of those are semiconducting. Armchair SWNTs (metallic) have a continuous electronic density of state (DOS) near the Fermi level, while other metallic SWNTs have a small pseudo-band gap (~ 50 meV) which can be neglected at room temperature. On the other hand, the DOS of semiconducting SWNTs exhibit a much more significant band gap (1-2 eV), as shown in Figure 2.11.

Figure 2.11 Schematic view of the electronic density of states (DOS) of metallic and semiconducting SWNTs. The dashed blue line shows the Fermi level (E_F), and the black arrows show the electronic transitions between the van Hove singularities (vHs).[138]

2.2.2 Characterization of SWNTs

Several technologies and tools have been used for characterizations of SWNTs. To characterize their electronic structures and morphologies, absorption spectroscopy (UV-vis-NIR), Raman spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) are commonly used.

As shown in Figure 2.11, DOS of SWNTs is not a continuous function of energy, but it forms several sharp peaks at certain energy levels, which are called van Hove singularities (vHs). When adsorbing light, the electrons in vHs of the valence bands are elevated to the corresponding vHs of conduction bands. v_1-c_1 denotes the optical transition from the first valence band to the first conduction band (“first van Hove” optical transition, E_{11}), while v_2-c_2 denotes the “second van Hove” optical transition (E_{22}), and so on. The optical transitions are also labelled as S_{11} , S_{22} ... or M_{11} , M_{22} ..., respectively, for semiconducting and metallic SWNTs. For most semiconducting SWNTs, S_{11} , S_{22} , S_{33} , and S_{44} fall in the UV-vis-NIR range of 350-1600 nm. For metallic SWNTs, only M_{11} (500-700 nm) can be probed in the UV-vis-NIR region due to their larger spacing between van Hove singularities.[139] In general, the absorption peaks of SWNTs with wide diameter distribution can be classified into four groups with the energy order S_{44} , $S_{33} > M_{11} > S_{22} > S_{11}$. [139] S_{33} and S_{44} are usually considered as one group since they are greatly overlapped. Actually, all the other groups also have some overlap with their neighbouring groups, especially for the SWNT samples with wide diameter distribution. For example, for arc-discharge SWNTs, M_{11} usually ranges from 525 nm to 750 nm, while S_{11} and S_{22} range 900 - 1340 nm and 800 - 1075 nm, respectively (Figure 2.12).[59, 140, 141] To identify the actual electronic structure of a SWNT absorption peak, deconvolution of the

absorption spectrum is usually a necessary step. For the more accurate assignment of (n, m) chirality, Kataura plots which shows the relationship between energy and SWNT diameter is a very helpful tool (Figure 2.13A).

Figure 2.12 UV-vis-NIR spectra of arc-discharge SWNTs dispersed in sodium cholate/sodium dodecyl sulfate (SC/SDS) co-surfactants. Dashed curve: unsorted arc-discharge SWNTs; red curve: sorted semi-SWNTs; blue curve: sorted met-SWNTs.[59]

Resonance Raman spectroscopy is another important tool to determine the electronic structure of carbon nanotubes. Resonance occurs when the SWNT's electronic transition energy equals or is close to the laser energy ($E_{ii} = E_{\text{Laser}} \pm 0.1 \text{ eV}$). [139] The resonance Raman scattering is so sensitive that even an individual SWNT's signal is able to be detected.

Figure 2.13 Kataura plots with (A) linear diameter axis and (B) linear Raman shift axis. Black plots are semiconducting SWNTs, and red plots are metallic SWNTs.[142]

The main Raman features of SWNTs are the first-order radial breathing mode (RBM) and tangential mode (G band), while the second-order disorder-induced mode (D band) and the D band overtone (2D or G' band) are also shown (Figure 2.14A).[139] For 2D graphite, G band ($\sim 1582 \text{ cm}^{-1}$) is the only first-order Raman scattering peak. However, for SWNTs, there are two first-order Raman modes: RBM and G band. RBM is a unique phonon mode for SWNTs which appears only in the samples that contain SWNTs. RBM is a bond-stretching out-of-plane phonon mode in which all the carbon atoms move in the radial direction. The relationship between RBM frequency and SWNT diameter can be expressed as $\omega_{\text{RBM}} = 248/d_t$ for isolated SWNTs on SiO_2 substrate.[137, 143] For the identification of SWNT chirality in the Raman spectroscopy, again, Kataura plots are very important and helpful. The frequency of RBM ranges from 100 to 350 cm^{-1} for the SWNTs with diameter 0.7 nm to 2.4 nm , as shown in Figure 2.13B.

G band in SWNTs is split to multi-peaks (up to 6 peaks) from 1500 to 1600 cm^{-1} due to the quantum confinement along the tube circumference.[144] Among those, the most prominent G features are the G^+ feature $\sim 1590 \text{ cm}^{-1}$ due to the in-plane vibration along the tube axis and the G^- feature $\sim 1570 \text{ cm}^{-1}$ due to the in-plane vibration along the circumferential axis.[57] G^- feature shows great difference for metallic and semiconducting SWNTs. For metallic SWNTs, G^- peak is broader, more symmetric and with lower frequency compared to that of semiconducting SWNTs.[142] This difference can be used as a strong evidence to distinguish metallic and semiconducting SWNTs by Raman spectra, and is widely used as an important characterization for SWNT sorting by electronic types (Figure 2.14B).[46, 145, 146]

Figure 2.14 (A) Raman spectrum of a HiPco SWNTs sample using a red laser (633 nm).[147] (B) G-peak of an arc-discharge SWNTs sample becomes narrower after sorting (633 nm). Black: pristine arc-discharge SWNTs. Blue: sorted semiconducting SWNTs.[146]

SEM is commonly used to determine the existence of impurities or surfactants in the SWNTs (Figure 2.15A). AFM is a useful microscopy technique to characterize the length of SWNTs and the size of bundles. The diameter of individual tubes and the size of

bundles can be easily determined by the height profiler of the AFM image (Figure 2.15B).

The length of the SWNTs can be measure by AFM as well.

Figure 2.15 (A) SEM images of SWNTs before (top) and after (bottom) purification.[148] (B) AFM image (top) and height profiler (bottom) of SWNTs on Si wafer.[149]

2.2.3 Sorting of Semiconducting and Metallic SWNTs by Electronic Types

As mentioned in Section 2.2.1., in general, 1/3 of the as-synthesized SWNTs are metallic while the other 2/3 are semiconducting. The ratio can be slightly different for different synthetic methods. The unique electronic structures and electrical properties of met-SWNTs and semi-SWNTs determine their totally different electrical applications. For instance, semi-SWNTs are considered one of the most promising materials for the new generation transistors as the replacement of single crystalline silicon,[13] while met-

SWNTs are attractive candidate of ITO replacement for transparent conductors.[150] To achieve the best performance of semi- and met-SWNTs in their electrical applications, sorting of SWNTs by their electronic types is a necessary step. Researchers have spent more than 10 years on this topic and various methods have been developed, including selective reaction/removal,[49-53] selective dispersion,[54-56] electrophoresis,[45, 57, 58] density gradient ultracentrifuge,[59, 60] chromatography[47, 62, 63] and the combination of the above mentioned technologies.[46, 65] Above all, towards effective sorting, the SWNTs have to be individually dispersed or isolated on substrates.

Met-SWNTs have higher DOS at their Fermi level and lower ionization potential compared to semi-SWNTs, which makes met-SWNTs more reactive than semi-SWNTs. By careful control of the reaction condition, met-SWNTs can be selectively functionalized while semi-SWNTs remain the pristine form.[40] Therefore met-SWNTs and semi-SWNTs can be separated by centrifuge due to the solubility difference between the functionalized and pristine SWNTs. The highest cited work on selective reaction was reported by Strano *et al.* in 2003.[50] In this work, particular metallic SWNTs are selectively functionalized with diazonium salts due to the availability of electrons near their Fermi level which stabilize a charge-transfer state preceding bond formation and then removed by the following centrifuge step (Figure 2.16). Various compounds have been reported in addition to diazonium salts, *e.g.*, hydroxyl radicals,[151, 152] nitronium ions,[153] OsO₄,[154] 1,10-azobis-(cyanocyclohexane),[155] anthraquinones,[156] *etc.*

Figure 2.16 UV-vis-NIR spectrum of sodium dodecyl sulfate-suspended carbon nanotubes after the addition of various amounts of 4-chlorobenzenediazonium tetrafluoroborate. Semiconductor transitions are unaffected under the controlled condition, whereas metals react with high selectivity (see inset).[50]

For the SWNTs on chip, certain types of SWNTs can be removed by converting them to vapour or amorphous carbon. For example, met-SWNTs can be destroyed by a high current (Figure 2.17A), so that the on/off ratio of the aligned SWNT thin film field effective transistors (FETs) can be increased by more than 4 orders (Figure 2.17B).[53, 157, 158] Hydrogen plasma[52] and methane plasma[51] have also been reported for selective removal of medium-diameter met-SWNTs while the semi-SWNTs remain unaffected. However, the plasma etching will lose selectivity when the diameter of the SWNTs is too small or too large. Li *et al.* reported two compounds, 2-ethylanthraquinone[44] and acid yellow[43], which can preferentially convert met-SWNTs within a certain diameter range to semi-SWNTs by covalent or non-covalent functionalization. In those cases, although the met-SWNTs haven't been removed, but

they are so called “silenced” so that the on/off ratio of SWNT based FETs is also increased.

Figure 2.17 (A) A schematic illustration of electrical breakdown of met-SWNTs (blue) while semi-SWNTs (red) remaining unaffected.[157] (B) Transfer curves from a transistor using aligned arrays of SWNTs before (open triangles) and after (open circles) electrical breakdown. The on/off ratio of the device increases more than 10,000 times after the electrical breakdown process.[158]

In contrast to the destructive selective reaction or removal processes, some compounds/polymers can selectively disperse one type SWNTs by non-destructive physisorption. Chattopadhyay *et al.* reported that octadecylamine (ODA) can selectively disperse acid treated semi-SWNTs due to the higher affinity of amine groups to semi-SWNTs (Figure 2.18 A&B).[54] Pan *et al.* found that polymethacrylates with different pendant aromatic functional groups have different selectivity for small diameter CoMoCat SWNTs. Poly(methyl-methacrylate-co-fluoresceino-acrylate) (PMMAFA) and poly(9-anthracenylmethyl-methacrylate) (PAMMA) preferentially disperse semi-SWNTs while poly-(2-naphthylmethacrylate) (PNMA) preferentially disperses met-SWNTs in dimethylformamide (DMF).[159] In 2013, Wang *et al.* reported that semiconducting arc-discharge SWNTs with larger diameter range (1.1 – 1.8 nm) can be enriched by selective

dispersion using dithiafulvalene/thiophene copolymers (Figure 2.18C).[160] The common problem for selectively dispersing methods is the contamination from attached compounds/polymers on the sorted SWNTs.

Figure 2.18 (A) Schematic illustration of possible ODA interactions with acid-functionalized SWNTs through Zwitterion Formation (left) and physisorption-assisted organization (right) of ODA on SWNTs sidewalls.[54] (B) Raman spectra of precipitated met-SWNTs fraction (blue curve) and supernatant semi-SWNTs fraction (pink curve) after ODA treatment.[54] (C) UV-vis-NIR spectra of unsorted and sorted semi-SWNTs using dithiafulvalene/thiophene copolymers in N-methyl-2-pyrrolidone (NMP).[160]

Electrophoresis is a widely used technology in bioseparation. Recently, it has been applied for SWNT sorting according to electronic type. Agarose is found to be a suitable matrix for SWNT sorting because its pore sizes are close to the size of SWNTs. Tanaka *et al.* have shown that the met- and semi-SWNTs can be effectively separated *via* agarose gel

electrophoresis with sodium dodecyl sulfate (SDS) as surfactant.[58, 161-163] Once voltage is applied, the metallic fraction will move down much faster than the semiconducting fraction (Figure 2.19). And it is believed that the separation is due to the better dispersion of met-SWNTs in aqueous SDS solution[164] and the stronger affinity of semi-SWNTs to agarose gel.[58] More recently, Mesgari *et al.* reported that the agarose gel electrophoresis sorting process can be further improved with addition of chondroitin sulfate as dispersing agent for the SWNTs.[45]

Figure 2.19 (A) Sequential photographs showing the progress of SWNT separation agarose gel electrophoresis. (B) UV-vis-NIR spectra of fractions after electrophoresis. Spectra i–iii in (B) corresponding to the samples from fractions i–iii in (A), and the black curve is for the unsorted SWNT dispersion.[58]

Another bioseparation technology that has been successfully applied for SWNT sorting is density gradient ultracentrifuge (DGU) which is commonly used to isolate proteins and poly(nucleic acids) based on the subtle variations in their buoyant density.[59, 60, 150, 165] In a bioseparation process, the sample is loaded into an aqueous solution

with a known density gradient and the species will sediment in their respective density layers during ultra-high centrifugation process. For SWNT sorting, the SWNTs are dispersed in a certain aqueous solution with suitable surfactants. Therefore, the separation effect is not only a result of the geometry of SWNTs but also affected by the thickness and hydration of the surrounding surfactants.[40] Arnold *et al.* have reported that the population of co-surfactants has great effect on the optimization of metallic-semiconducting separation for SWNTs in the diameter range of 1.1 - 1.6 nm.[59] 1:4 SDS/SC co-surfactant is especially optimal for semi-SWNTs isolation, and 3:2 SDS/SC ratio is the optimal for met-SWNTs. Besides SDS/SC co-surfactant, non-ionic block copolymers (Pluronic and Tetronic) have also been reported as effective dispersing agent for DGU separation of SWNTs according to their electronic types.[60] In 2010, Antaris *et al.* reported 99% purity semiconducting SWNTs isolated with the linear block copolymer Pluronic F68 and 74% purity metallic SWNTs isolated using the X-shaped block copolymer Tetronic 1107.[60] Two years later, the same group reported better separation results by modulating the pH during DGU (Figure 2.20).[165]

Figure 2.20 (A) Photographs of centrifuge tubes after DGU process with Pluronic F68 at pH 3 (left) and pH 7.5 (right). (B) Normalized optical absorbance spectra of 99% met-SWNTs and 99% semi-SWNTs obtained with pH-shifted Pluronic F68, compared against an unsorted SWNT spectrum.[165]

DGU is one of the best methods for metallic-semiconducting sorting of SWNTs in terms of purity and reproducibility, and it's the only commercialized technology so far. However, this method suffers from the long-time process and high cost from expensive equipment and density gradient medium. Therefore, the price of the sorted product is too high for industrial application, as mentioned in Chapter 1. Chromatography is a cheap and simple technology where only glassware is needed and it's easy to scale up. Inspired by the experience in chemical and biological separation, researchers tried to apply chromatography for SWNT sorting, and several successful approaches have been reported.

Zheng *et al.* developed a DNA-assisted ion-exchange chromatography (IEX) method in which the small diameter SWNTs (<1.2 nm) are first dispersed with single-stranded DNA (ssDNA) in aqueous solution, then fractions with different electronic type can be isolated during the following IEX process.[63, 166] The mechanism of separation by this method is not clear yet, but it is believed that it is due to the variations in the electrostatics interaction between ssDNA-SWNT hybrid and the positively charged anion exchange resin.[166] Another widely studied system is the SDS dispersed SWNTs through gel chromatography.[47, 62, 163, 164, 167, 168] Tanaka *et al.* reported that the SDS dispersed semi-SWNTs were trapped in the chromatography column with agarose beads while met-SWNTs passed through. The trapped semi-SWNTs were later eluted by deoxycholate (DOC) aqueous solution (Figure 2.21).[168] However, the SDS-agarose chromatography system works only on the SWNTs with smaller diameter (CoMoCat or HiPco). Another gel, Sephacryl which is composed of allyl dextran and *N,N'*-methylene bisacrylamide, was also investigated for the separation of SDS-dispersed SWNTs, and it was shown to be more effective for SWNT sorting compared to agarose because the

adsorption reaction of SWNTs onto Sephacryl was more endothermic.[167] In 2013, Tulevski *et al.* reported isolation of short (estimated to be about 200nm long) arc-discharge SWNTs through Sephacryl column, which is the only method (reported to date) for arc-discharge SWNTs separation *via* chromatography method. By using SDS aqueous solution as dispersing agent and eluting solution, 98.3%, 99.5% and 99.9% semi-SWNTs have been achieved after one, two and three separation iterations.[47]

Figure 2.21 (A) Sequential photographs showing the progress of SWNT separation using an agarose gel column. (B) UV-vis-NIR and (C) Raman spectra (633 nm) of the unsorted (black), sorted metallic (red) and semiconducting (blue) SWNTs.[168]

2.2.4 SWNT-Based Transparent Conductors

One of the advantages of using SWNTs for transparent conductors over metals or metal oxides is that SWNTs can be deposited on transparent substrates *via* various solution-based methods, including filtration and transfer,[31, 169] spin-coating,[170] dip-coating,[171] spray,[171, 172] printing,[173] or simply immersion[174] (Figure 2.22). Vacuum filtration is probably the simplest way to get a SWNT thin film, by simply passing the SWNT dispersion through a porous filter membrane, followed by rinsing the thin film with solvents or water to remove the surfactants that was used to disperse and stabilize the SWNT dispersion. The SWNT thin film on filter membrane can be then transferred onto transparent substrates (rigid or flexible) by PDMS stamp,[169] lamination,[175] or dissolving the membrane in solvents.[31] The size of the transparent conductors is limited by the dimension of the filter membrane, which is available as a roll with the size 10 m $\times$ 30 cm from Millipore.[31] SWNT-based transparent conductors with even larger size can be deposited by roll-to-roll printing, with the width 2 m at the speed of 500 m min⁻¹. [12]

Figure 2.22 Transparent SWNT thin films prepared by (A) filtration and transfer,[31] (B) roll-to-roll printing,[12] and (C) spray coating.[172]

The sheet resistance and transmittance of the SWNT thin films depends on their DC conductivity (σ_{DC}). SWNT films with higher σ_{DC} have low sheet resistance and high transmittance simultaneously. There are two pathways to enhance σ_{DC} : 1) to increase the number of charge carriers (n) by doping, or 2) to increase mobility (μ) of the SWNT films, according to the equation $\sigma_{DC} = ne\mu$. [12]

It is important to notice that although σ_{DC} of a single CNT can be up to 200000 S cm^{-1} [36] with a mobility in excess of 100000 $cm^2V^{-1}s^{-1}$, [37] σ_{DC} can only reach 6600 S cm^{-1} [31] with mobility 1-10 $cm^2V^{-1}s^{-1}$ [176, 177] for the un-doped random SWNT films. This significant difference is caused by the large junction resistance between the overlapping tubes. For the typical range of SWNT length 2-4 μm , the junction resistance in a SWNT film is much larger than the resistance of the tubes and thus becomes the dominant resistance. [178] The shorter the tubes, the larger the junction resistance, with a power law $\sigma_{DC} \sim L^{1.46}$. [179] Therefore, longer tube length will be greatly helpful to reduce the sheet resistance of the SWNT films. Besides, it has been reported that the junction resistance between metallic-metallic and semiconducting-semiconducting SWNTs is much smaller than that between metallic-semiconducting SWNTs. [180] At transmittance of 75%, the sheet resistance of unsorted HiPco SWNT thin films is $\sim 1340 \Omega sq^{-1}$, while that of the sorted metallic HiPco SWNTs decreases to $\sim 231 \Omega sq^{-1}$. [150] Figure 2.23 A&B show the improvements in the performance of metallic SWNTs *versus* unsorted SWNTs with conductivity enhancement factors over 5.6 in the visible and up to 10 in the infrared. [150]

Figure 2.23 Transmittance vs. sheet resistance for a series of transparent conductive films generated from HiPco SWNTs at (A) 550 nm and (B) 1600 nm wavelengths. The materials used were metallic SWNTs with principal diameters of 0.9 nm (red diamonds), 1.0 nm (blue squares), and unsorted material (gray triangles).[150] (C) Conductivity vs. thickness for pristine and nitric acid doped SWNT thin films.[181] (D) Sheet resistance vs. time for SOCl₂ doped SWNT thin film exposed in different solvents.[182]

Since SWNTs are *p*-type doped by oxygen in air, and the hole mobility of SWNTs is higher than their electron mobility, *p*-type dopants are usually applied to increase the mobility of SWNT thin films. The commonly used *p*-type dopants are mostly strong oxidizing agents, including HNO₃,[181, 183] SOCl₂,[184] NO₂,[185] Br₂,[186] Nafion,[187] and tetrafluorotetracyano-*p*-quinodimethane (F₄TCNQ).[188] The conductivity of the SWNT films can be increased by 3-4 times as shown in Figure 2.23C. However, the SWNT films doped by small molecules all face the stability problem once exposed to elevated temperature, high moisture or solvents. The transitory nature of the

doping effect of thionyl chloride over time when exposed to various solvents is shown in Figure 2.23D.[182] It has been reported that the use of larger molecules, such as Au nanoparticles,[189] might be a solution to increase the doping stability. However, more studies are still needed to find an effective and stable dopant to increase the conductivity of SWNT thin film.

2.2.5 SWNT-Based Field-Effect Transistors (FETs)

SWNT is one of the most promising materials to replace single crystalline silicon in the application of high-performance transistors due to their ultra-thin body, quasi-ballistic transport and nearly transparent contacts to metal electrodes. The SWNT-FETs were first reported in 1998 by researchers in Delft University[190] and IBM.[191] In SWNT-FETs, the individual, array or network of semiconducting SWNTs play the role of the semiconductor channel connecting the source and drain electrodes. The current flowing through the SWNT conduction channel is modulated by an external electric field applied through a third gate electrode. An insulating thin layer (dielectric layer), usually SiO_2 , separates the gate electrode from the channel and the source and drain electrodes. The configurations of a top-gate and a bottom-gate SWNT-FET are shown in Figure 2.24.

Figure 2.24 Schematic of a (A) bottom-gate network SWNT-FET[192] and (B) top-gate individual SWNT-FET.[193]

A potential barrier called Schottky Barrier at the SWNT-metal interfaces inhibits the transporting of carriers (electrons or holes) from the metal electrode to SWNTs. The Schottky Barrier is in the conduction band for an electron (n -type semiconductor), or in the valence band for a hole (p -type). The conductance of the semiconducting channel can be modulated by sweeping the gate voltage (V_g) between positive and negative values. For the hole conduction (p -type), the application of a very positive V_g raises the barrier, thus the current flows through the channel is very small, and the device is said to be in a “off-state”. Negative V_g lowers the barrier so that the current increases and the device is “turned on”. Towards a very negative V_g , the current is saturated and the device is said to be in the “on-state”; *vice versa* for the electron conduction.[192, 193] Current *versus* gate voltage (I - V_g) curves obtained with an array SWNT-FET is shown in Figure 2.25. The ratio between the saturated on-state current (I_{on}) and the off-state current (I_{off}) is called on/off ratio which is one of the most important performance characteristics of FETs. For the individual semi-SWNT devices, on/off ratio is always >100 . Those individual tube devices with on/off ratio <100 are considered to be metallic.[53] In a SWNT network, if the density of metallic SWNTs exceeds the percolation threshold, the SWNT network will become metallic conductive and thus lose the on/off switch. Therefore, the isolation of semi-SWNTs from the as-synthesized mixture is critical for the industrial applications of SWNT-FETs. Various methods have been developed in the past decade, as mentioned in Section 2.2.3, and a semi-SWNT purity of 99.9% has been achieved. However, for the high-performance logic applications requiring billions of transistors integrated on a chip, an ultra-high semi-SWNT purity of 99.9999% or above is needed,[194] which is still a huge challenge.

Figure 2.25 Typical I - V_g curve of array SWNT-FETs with as-synthesized SWNTs (black curve) and sorted semi-SWNTs (red curve). The FET with as-synthesized SWNTs shows metallic performance due to the existence of met-SWNTs.[53]

Another important factor to characterize FET devices is the mobility (μ) which indicates the pace at which the charge carriers respond to the external electric field. Mobility can be calculated using the following equation:[195]

$$\mu = \frac{L_C}{W_C} \frac{1}{C_{ox}} \frac{1}{V_d} \frac{\partial I_d}{\partial V_g} \quad (\text{Equation 2.4})$$

where L_C and W_C is the channel length and channel width, respectively, V_d is the source-drain bias, I_d is the drain current, V_g is the gate voltage, and C_{ox} is the gate capacitance per unit square. For SWNT-FETs, it is important to consider the electrostatic coupling between SWNTs and the planar gate electrode on capacitance estimation when the SWNT density is low, especially when the average spacing between SWNTs is large compared to the thickness of the dielectric. In this case, the gate capacitance can be estimated using the following expression:[48]

$$C_{ox} = \left\{ C_Q^{-1} + \frac{1}{2\pi\epsilon_{ox}\epsilon_o} \ln \left[\frac{\Lambda_o}{R} \frac{\sinh(2\pi t_{ox}/\Lambda_o)}{\pi} \right] \right\}^{-1} \Lambda_o^{-1} \quad (\text{Equation 2.5})$$

where C_Q (0.4 nF M^{-1}) is the quantum capacitance of SWNTs, Λ_o is the linear density of the SWNTs, R is the radius of SWNTs, ϵ_o is the vacuum permittivity, ϵ_{ox} and t_{ox} corresponds to the relative permittivity and thickness of the dielectric layer. The nanotube density is a critical factor to improve mobility of the network or array SWNT-FETs. Higher nanotube density will increase the number of transport pathways and thus reduce the parasitic contact resistance ($2R_C$) per unit device width proportionally, and this effect will be more dominant when $2R_C$ is much higher than channel resistance (short channel FETs).[13] The target towards high performance FETs is to achieve 125 nanotubes per μm (Figure 2.26).[194] But again, the density of metallic SWNTs will be a concern when the nanotube density is high. Jin *et al.* reported array SWNT-FETs with mobilities exceeding $1,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and on/off switching ratios of $\sim 10,000$ by selectively removing the metallic SWNTs from the CVD-grown aligned SWNT arrays using nanoscaled thermocapillary flows.[53] The method suggests a promising future for the SWNT-FETs, however, the nanotube density is still limited by the CVD-grown method (up to 55 tubes per μm).[196] Solution-processable approaches with highly purified SWNTs are expected to further improve the performance of SWNT-FETs with higher nanotube density.

Figure 2.26 Target for SWNT-FETs.[194]

3 Solution-Processed Flexible Transparent Conductors Based on Carbon Nanotubes and Silver Grids Hybrid

3.1 Introduction

Thin-films of CNT network have been developed to serve as transparent electrodes due to their good transparency and conductivity.[197, 198] A major issue that hinders the adoption of CNT network to replace ITO is the resistance caused by tube-tube junctions existence in the network of CNT film,[178, 180, 199] as explained in Chapter 2. The best result to date for CNT transparent electrode is $R_s = 60 \Omega \text{ sq}^{-1}$ and $T = 91\%$; the nanotubes in this study were doped by super acid.[32] However, studies on CNT-dopant systems have shown limited stability of the doping effects in air and under thermal loading.[200] Thus, although CNTs offer many advantages, such as low cost and superior adaptability to flexible substrates, it remains difficult to apply CNT networks as a replacement for ITO in transparent electrodes.

Metal thin films ($< 10 \text{ nm}$ thick) have also been explored as transparent conductors. But the conductivity of metallic films drops dramatically when their thickness is smaller than the mean free path length of charge carriers and because of discontinuity commonly resulting from the deposition process.[201] Random networks of long metallic nanowires with small diameter have also been explored for transparent electrodes. As reported by De *et al.*, sheet resistance of $13 \Omega \text{ sq}^{-1}$ at transmittance (T) 85% is achieved by transferring a 107 nm-thick Ag nanowire film onto PET substrate.[24] A recent study shows that the addition of 6 wt% SWNTs decreases the sheet resistance of hybrid network electrodes ($28.9 \Omega \text{ sq}^{-1}$) to one-fourth that of the pure Ag nanowire network electrodes ($132 \Omega \text{ sq}^{-1}$),

since the added SWNTs improve the conductive path percolation in the Ag nanowire network.[202] Another idea for enhancing transparency while keeping conductivity high is to use metal grids on transparent substrates. Metal grids as transparent conductors have been investigated and fabricated by lithography,[22, 203] and roll-to-roll printing[204] and self-assembly of metallic nanoparticles.[205-207] The empty areas of these grids transmit light but compromise the continuous electrical interface with other functional components in the device. In addition, the metallic nanostructure based electrodes (both networks of metallic nanowires and metal grids) exhibit local discontinuities in the sheet resistance which are problematic for many applications. For instance, the excitons generated in the active layer of a solar cell may be quenched before reaching the nearest conduction path (this effect dominates if the size of the void areas in the metal grid or the percolating network of metallic nanowires is larger than the charge diffusion length).[12, 25] In an effort to tackle this issue, Ghosh *et al.* have deposited a 2 nm thick nickel film on top of a copper grid to yield a continuous electrode.[22] A sheet resistance of $6.5 \Omega \text{ sq}^{-1}$ at transmittance $\sim 75\%$ is achieved. More recently, Zhu *et al.* demonstrated a method to prepare hybrid films of graphene and photolithography-produced metal grids.[208] At $T = 79\%$, sheet resistances of $\sim 18 \Omega \text{ sq}^{-1}$ and $\sim 8 \Omega \text{ sq}^{-1}$ were achieved for, respectively, graphene-aluminum grid and graphene-copper grid hybrid films on flexible substrates.[208] Compared to ultra-thin metal films, graphene is more transparent, more flexible, and more chemically inert. However, the high cost and limited area of CVD-grown graphene make it still not an ideal solution for commercial applications.

In this chapter, we demonstrate hybrid transparent conductor films produced by solution coating a thin-film network of single walled carbon nanotubes (SWNTs) onto a

silver (Ag) network self-assembled from Ag nanoparticles on polyethylene-terephthalate (PET) substrate. These hybrid films (measuring up to 16 cm by 12 cm) exhibit low sheet resistance and high transparency ($R_s \sim 5.8 \Omega \text{ sq}^{-1}$, $T = 83.7\%$ at $\lambda = 550 \text{ nm}$), high stability in ambient conditions, and excellent bendability. And the simple solution-based coating method makes it scalable to the large-scale low-cost production necessary for widespread applications. We also demonstrate a proof-of-concept application of this hybrid transparent film for photovoltaics. Specifically, with an additional electrochemically deposited ZnO layer, the resulting ZnO-SWNT-Ag-PET film exhibits remarkable enhancement of photocurrent efficiency compared to the SWNT-free ZnO-Ag-PET film.

3.2 Experimental Methods

3.2.1 Materials

The Ag-PET films ($R_s < 10 \Omega \text{ sq}^{-1}$, $T > 80\%$) were obtained from Cima NanoTech and used as received. The P2-SWNTs (purified, carbonaceous $> 90\%$, diameter 1.2 nm-1.6 nm, bundle length 500 nm-1.5 μm) were purchased from Carbon Solutions and used as received. 99% met-SWNTs (0.01 mg mL^{-1} aqueous dispersion, diameter 1.2 nm-1.7 nm, length 300 nm-5 μm) was purchased from NanoIntegris and used as received. All other chemicals were purchased from Sigma and used as received. Deionized water (D. I. water) was used in all experiments.

3.2.2 Fabrication of SWNT-Ag-PET hybrid electrodes

10 mg P2-SWNTs (bundled) were mixed with 10 mL of 1% sodium cholate (SC) aqueous solution. The mixture was ultrasonicated using a 130-Watt Ultrasonic Processor

(VCX130, Sonics & Materials, Inc., USA) for 1 h (60% amplitude). The suspension was then centrifuged at 50,000 g for 1 h to remove the remaining bundles. The top 80% supernatant with individually dispersed SWNTs (~60% of the initial SWNTs) was carefully extracted and diluted 10-fold with 1% SC solution. The diluted solution was bath-sonicated for 10 min before use. The purpose of the sonication-centrifuge step is to disperse the bundled SWNTs into individual suspension for uniform deposition of the SWNT network. No metallic/semiconducting selection was achieved during the sonication-centrifuge process.

The as-received Cima Ag-PET film was covered with sacrificial thin PET layers, front (the side with Ag grid) and back (the side without Ag grid). The front sacrificial PET layer was removed before any surface treatment of the Ag network side of the film, while the back layer was kept in place during all processing steps to avoid any contamination to the back side. The back sacrificial layer was removed before characterization or use.

The front sacrificial plain PET layer on the Ag-PET was removed, and the Ag-PET films were exposed to Ar plasma for 60 s at 100 W power. Then the films were immersed in 0.5 vol.% of (3-Aminopropyl)triethoxysilane (APTES) solution in ethanol for 45 min. The excess APTES was rinsed away with ethanol. The films were rinsed with D.I. water and blown dry with compressed air. Then the APTES-treated Ag-PET films were immersed in the diluted SWNT dispersion for 1 h. After immersion, the hybrid films were rinsed with D.I. water and blown dry. The films were dried at 70 °C overnight before characterization. The preparation of the control SWNT-PET samples followed the same procedure except that the plain PET film was purchased from Higashiyama Film (Singapore).

3.2.3 Fabrication of graphene-Ag-PET hybrid electrodes

Graphene was synthesized via an optimized atmospheric chemical vapor deposition (CVD) method. Copper foil (99.8%, 25 μm thick) was purchased from Alfa Aesar and cut into pieces of the desired size. The copper foil pieces were carefully rolled and transferred into a quartz tube with inner diameter of 22 mm. The tube was purged with 500 sccm Ar for 20 min, and then heated to 925 $^{\circ}\text{C}$ in a split tube furnace. 60 sccm H_2 was introduced during the heating process. The system was kept at 925 $^{\circ}\text{C}$ for several minutes to reduce the surface oxidation of copper foils. Ar was cut off and 5 sccm CH_4 was introduced for 5 min while H_2 was kept at 60 sccm. After 5 min, during which graphene was grown, the CH_4 was cut off and Ar was introduced again in the cooling stage.

The synthesized graphene was transferred by an improved wet transfer process. The as-grown graphene film on Cu foil was dip-coated with a thin layer of poly(methyl methacrylate) (PMMA) (5 mg mL^{-1} in chloroform) before transfer. The PMMA coated graphene-copper foil was cured for 5 min on hot plate at 120 $^{\circ}\text{C}$. Since graphene grew on both sides of the Cu foil, one side was polished to remove the PMMA and graphene to make Cu exposed to the environment. Then the PMMA-graphene-Cu foil was immersed in $\text{Fe}(\text{NO}_3)_3$ solution (3 M) for overnight. After Cu foil was totally dissolved, the graphene film with PMMA (floating on water) was transferred into 1 M HCl for 30 min to remove the Fe particles that may stay on the graphene film. Then the film was transferred into D.I. to remove all the ions and then transferred onto Ag-PET film. The film (with its PMMA sacrificial layer) was exposed under UV light for 10 min to degrade the PMMA into methyl methacrylate monomers which were then removed by acetone.

3.2.4 Fabrication of met-SWNT-Ag-PET hybrid electrodes

99% met-SWNTs solution was purchased from NanoIntegris and diluted with D.I. water. The diluted solution was bath-sonicated for 10 min and vacuum filtered through 0.2 μm pore size PTFE membrane (diameter 47 mm). The met-SWNTs film on PTFE membrane was then washed with D.I. water and directly transferred onto Ag- PET film with a laminator at 130 $^{\circ}\text{C}$.

3.2.5 Electrochemical deposition of ZnO

ZnO nanosheets were electrodeposited on a PET/Ag/CNT substrate (1 cm $\times$ 2 cm) in a three-electrode cell with the PET/Ag/CNT as working electrode, a Pt plate as counter electrode, and a Ag/AgCl (sat. KCl) electrode as reference electrode. The electrolyte contained 50 mL of 0.05 M ZnCl_2 and 0.5 M KCl. The deposition was performed at -1.0 V for 1 h at room temperature.

3.2.6 Measurement of photocurrent

The photocurrent was measured on an electrochemical workstation (CHI660c, CH Instruments) with a three-electrode configuration. The as-prepared sample, Pt-wire electrode, and Ag/AgCl electrode were employed as the working, counter, and reference electrodes, respectively. The samples were illuminated by a Xenon-lamp light source (100 mW cm^{-2}) at the open circuit potential. 0.5 M Na_2SO_4 solution was used as the electrolyte.

3.2.7 Characterizations

The sheet resistance was measured with a Keithlink four-point probe station (probe spacing 1.6 mm, probe pin diameter 40.6 μm). Scanning electron microscopy (SEM) was performed using LEO 1550 Gemini field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV. The ZnO-SWNT-Ag-PET sample was coated with Pt for 10 seconds under a current of 10 mA. All the other samples were scanned directly, without Pt coating. Raman spectroscopy was conducted using a Renishaw inVia Raman microscope with 514.5 nm (2.41 eV) laser wavelength in a backscattering configuration. UV-vis-NIR absorption spectra were measured using a Varian Cary 5000 UV-vis-NIR spectrophotometer. The substrate absorption for background subtraction was measured using a blank PET substrate. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance, equipped with a Cu K α photon source (40 kV, 20 mA, $\lambda=0.15406$ nm) scanned at the rate of $1.0^\circ \text{ min}^{-1}$ over the range 32° - 80° (2θ).

3.3 Results and Discussion

Figure 3.1 Schematic illustration of SWNTs-Ag-PET hybrid transparent electrodes (not to scale). The light grey network in the figure represents the Ag nanoparticle network self-assembled on the PET substrate.

Figure 3.1 schematically illustrates the SWNT-Ag hybrid electrode. The PET film with patterned Ag nanoparticles is commercially available (Cima NanoTech); it is made by large-scale solution-based self-assembly of Ag nanoparticles. Figure 3.2A and 3.2B show low magnification scanning electron microscopy (SEM) images of the Ag-PET film without and with SWNT network, respectively (no Pt coating before SEM imaging). The size of the empty areas bounded by the Ag lines range from 100 μm to 500 μm . For the sample without SWNT network, the empty area (without Ag) is PET substrate only. As PET is non-conductive, these areas were heated and deformed (bulged) under electron beam. The image of Ag-PET with SWNT network on top is free of this problem and appears clearer because the highly conductive nature of SWNT network. SEM high magnification imagery shows that the Ag network is composed of densely packed Ag nanoparticles (Figure 3.2C). The CNTs were P2-SWNTs purchased from Carbon Solutions, and used as received. Immersion of Ag-PET film into a dispersion of these SWNTs results in deposition of a network of SWNTs on the Ag-PET surface. To enhance SWNT/substrate adhesion, the Ag-PET film was treated with Ar plasma and (3-Aminopropyl)triethoxysilane (APTES) prior to immersion in the SWNT dispersion. Ar plasma introduces abundant surface $-\text{OH}$ groups on the Ag-PET film. The $-\text{OH}$ groups react with the APTES molecules, resulting in the formation of a monolayer of APTES molecules on Ag-PET surface. The $-\text{NH}_2$ groups at the end of the APTES molecules attract carbon nanotubes and thus enhance the adhesion between SWNT and Ag-PET substrate. In order to avoid deposition of SWNTs on the underside of the Ag-PET film, which would reduce transparency without improving the conductivity of the film, the underside was protected with a sacrificial layer of plain PET film during all surface treatment steps. The sacrificial layer can be easily removed after SWNT deposition. The

SWNT network on top of the packed Ag nanoparticles is evident in the high magnification image (Figure 3.2D). The SWNT network thin film at the empty area is shown in Figure 3.3. The SEM image in Figure 3.2E shows that the SWNT network conforms to the vertical relief of the Ag conductor and the PET substrate. Figure 3.2F shows the gross appearance of a 5.5 cm $\times$ 5 cm SWNTs-Ag-PET film. The right side of this film was covered to prevent SWNT deposition; and the boundary between the regions with/without SWNTs, which differ only slightly in transparency, is marked in the image. Large-sized hybrid films can be fabricated (Figure 3.4). The size of hybrid film need not be constrained by the dimensions of a container of SWNTs dispersion; the SWNT film may be deposited by printing or spray-coating for effective large scale manufacture.

Figure 3.2 (A) and (B) show low magnification SEM images of Ag-PET films without and with SWNT network. The SWNT network covered areas are darker and flat in (B). (C) High magnification SEM image of Ag nanoparticles, assembled into part of a network gridline. (D) High magnification SEM image of SWNT-Ag-PET hybrid film, showing the network of SWNTs on top of a portion of an Ag network gridline. (E) SEM image of SWNT-Ag-PET hybrid film. Left part: with Ag nanoparticles below the SWNT network; right part: without Ag nanoparticles, SWNT network adheres on PET substrate directly. The SWNT network adheres and follows the topology of the Ag-PET substrate very well. (F) A photograph of Ag-PET film with (left) and without (right) a SWNT network. The red arrows show the boundary between the regions with/without CNT thin film. The size of the SWNT-Ag-PET sample is 5.5 cm $\times$ 5 cm.

Figure 3.3 (A) SEM image of SWNT network thin film on Ag-PET. (B) High magnification SEM image of the SWNT network thin film in the empty area, marked with red square in (A).

Figure 3.4 Gross visual appearance and transparency of SWNT-Ag-PET film (16cm ×12cm sample). The red arrows show the boundary between the regions with (left) / without (right) SWNT network thin film.

The unpredictable character of circuit continuity and conductive percolation through the Ag network of the Ag-PET film is reflected in large variations in sheet resistance measured by a four-point probe station. As shown in Figure 3.5A, the majority of measurements at different locations show low or no conductance. The three different groups of R_s value are due to the different locations measured. The four-point probe measurement is illustrated in Figure 3.6A. Low sheet resistance is obtained when all the 4 probes are located on the main stem of Ag grids while high sheet resistance results when any of the probes is located in the empty area. The intermediate resistance is resulted when probe 2 or 3 is on a branch of the Ag-grids (highlighted by the circles in Figure 3.6B). In the third situation, the circuit is still closed, but the voltage measured between Probe 2 and Probe 3 will be much smaller because most of the current flows through the main stem rather than the branches. In contrast, SWNT-Ag-PET hybrid films provide homogeneous and low sheet resistance ($5.8 \pm 1.1 \, \Omega \, \text{sq}^{-1}$, $n=50$) at all measured points. The sheet resistance of the SWNT network itself (on PET substrate) is high ($13.7 \pm 1.9 \, \Omega \, \text{sq}^{-1}$, $n=50$) (Figure 3.5A). Therefore, the high conductivity of SWNT-Ag-PET film is mainly due to the Ag network. For comparison of SWNT-Ag-PET with other potential advanced conductive materials as the deposited conductivity enhancing layer, CVD-grown graphene and 99% metallic-enriched SWNTs (met-SWNT), were also applied on top of the Ag-PET substrates. As shown in Figure 3.7-3.10, the graphene and met-SWNT thin-film hybridized electrodes give similar performance in terms of sheet resistivity, transparency, and bendability. However, from the standpoint of cost, the un-sorted SWNTs are much less expensive than the other two materials. Another cheap alternative material would be reduced graphene oxide (GO).[209] Additional processing is required to reduce deposited

GO to conductive reduced GO, so that un-sorted SWNT deposition appears superior even to this alternative from the standpoint of process simplicity.

Figure 3.5 (A) Sheet resistance of Ag-PET film (red), thin film of SWNT network (blue), and SWNT-Ag-PET hybrid film (green). 50 points were measured for each sample. (B) Transmittance of SWNT-PET film (blue curve), Ag-PET film without (red curve) and with (green curve) deposited SWNT network. (C) Flexibility test of the SWNT-Ag-PET film. The plot shows the sheet resistivity of the SWNT-Ag-PET film, as a function of bending cycles, up to 1000 cycles. Inset shows the extent to which the SWNT-Ag-PET film was bent in the flexibility test.

Figure 3.6 (A) Schematic of the four-point probe configuration (not to scale). The probe spacing is 1.6 mm and the probe pin diameter is 40.6 μm . (B) Optical microscope image of the Ag-PET film. Some branches of the Ag-grids are highlighted in red circles.

Figure 3.7 (A) Visual appearance of graphene-Ag-PET hybrid film (9.5 cm $\times$ 5 cm sample). The blue arrows show the boundary between the regions with (bottom) /without (top) graphene. (B) Raman spectrum of graphene used in this work. (C) Optical microscope image of a graphene-Ag-PET film. Graphene covers the top part of the image, indicated by the white dashed line. (D) SEM image of graphene-Ag-PET film in the red square of (C).

In addition to bridging the discontinuities in the Ag network conductive paths, the CNT network improves the homogeneity of the electrode and also modestly increases the electrode conductivity by electrically bridging the voids in the conductive Ag network. The deposited CNT network slightly decreases the optical transmittance, from 85.4% to 83.7% at 550 nm wavelength (Figure 3.5B).

SWNT-Ag-PET film is flexible and is durable under repeated bending stress. After 1000 cycles bending (bending radius = 8 mm), the sheet resistivity of the hybrid film remains below $10 \Omega \text{ sq}^{-1}$ (Figure 3.5C), while that of thin ITO films was reported to increase irreversibly by almost 2 orders of magnitude after <200 bending cycles.[210] SEM images show the excellent adhesion of SWNT thin film to the Ag-PET substrate even after 1000 cycles of bending (Figure 3.11). No mechanical degradation is observed for either the Ag nanoparticles or thin film of SWNT network after the bending test (Figure 3.11C&D).

Figure 3.8 (A) Optical microscopy image of Ag-PET with (top) and without (bottom) thin film of met-SWNTs network. (B) A SEM image of met-SWNTs-Ag-PET hybrid film in the red square of (A). (C) Visual appearance of a met-SWNTs-Ag-PET film. The met-SWNTs film was prepared by vacuum filtration on PTFE membrane (47 mm diameter) and then transferred onto the Ag-PET film.

Figure 3.9 (A) Sheet resistance of Ag-PET film (red), CVD-grown graphene (green), and graphene-Ag-PET film (magenta). 50 points were measured for each sample. (B) Transmittance of Ag-PET film without (red curve) and with (magenta curve) graphene. (C) Flexibility test of the graphene-Ag-PET film. The plot shows the sheet resistivity of the graphene-Ag-PET film, as a function of bending cycles, up to 1000 cycles.

Figure 3.10 (A) Sheet resistance of Ag-PET film (red), met-SWNTs network (green) and met-SWNTs-Ag-PET film (dark cyan). 50 points were measured for each sample. (B) Transmittance of Ag-PET film without (red curve) and with (dark cyan curve) met-SWNT network thin film. The absorbance peak between ~600-800 nm is attributed to the M11 transitions of met-SWNTs. (C) Flexibility test of the met-SWNT-Ag-PET film. The plot shows the sheet resistivity of the met-SWNT-Ag-PET film, as a function of bending cycles, up to 1000 cycles.

Figure 3.11 (A) SEM image of SWNT-Ag-PET hybrid film before bendability test. (B) High magnification SEM image of pre-bending SWNT-Ag-PET hybrid film, marked with red square in (A). (C) SEM image of SWNT-Ag-PET hybrid film after bendability test (1000 cycles), showing no mechanical degradation of Ag nanoparticles or thin film of SWNT network after 1000 cycles of bendability test. (D) High magnification SEM image of pre-bending SWNT-Ag-PET hybrid film, marked with red square in (C).

The conductance of the hybrid films is more stable than that of the sole Ag-PET films or the thin films of SWNT network. The SWNT network or graphene layer plays the role of a protecting layer which isolates the Ag nanoparticles from environmental corrosion (O_2 , moisture, oxidizing agents, *etc.*)[211] and keeps the conductance of Ag network stable. The conductance of SWNT network may decrease significantly due to humidity,[212, 213] however, the conductance of the hybrid film is hardly affected by that of the SWNT/graphene layer, as discussed above, as long as the layer is conductive. Therefore, the electrical performance of the hybrid films is quite stable under ambient conditions, showing no difference in sheet resistance, compared with freshly-prepared samples, after >1 month exposure to ambient conditions.

Table 3.1 Sheet resistance and transmittance of SWNT-Ag hybrid electrode (No. 1) graphene-Ag hybrid electrode (No. 2) and met-SWNT-Ag hybrid (No. 3) compared to commercial transparent electrode materials and previous research results (No. 4-18).

No.	Product	Substrate	Sheet Resistance (Transmittance) ^{a)}	σ_{DC}/σ_{Op}
1	SWNT-Ag hybrid (this work)	PET	$5.8 \pm 1.1 \Omega \text{ sq}^{-1}$ (83.7%)	349
2	graphene-Ag hybrid (this work)	PET	$5.6 \pm 0.6 \Omega \text{ sq}^{-1}$ (82.3%)	329
3	met-SWNT-Ag hybrid (this work)	PET	$6.1 \pm 0.4 \Omega \text{ sq}^{-1}$ (82.0%)	296
4	ITO	glass	$30\text{-}80 \Omega \text{ sq}^{-1}$ (90%)	44-116
5	PEDOT/PSS[19]	glass/PET	$100 \Omega \text{ sq}^{-1}$ (91%)	39
6	SWNTs[32]	PET	$60 \Omega \text{ sq}^{-1}$ (90%)	58
7	graphene[112]	glass	$350 \Omega \text{ sq}^{-1}$ (90%)	10
8	graphene/SWNTs[106]	glass	$280 \Omega \text{ sq}^{-1}$ (86%)	9
9	Cu nanofibers[214] ^{b)}	glass	$12 \Omega \text{ sq}^{-1}$ (80%)	133
10	Ag nanowires[24]	PET	$13 \Omega \text{ sq}^{-1}$ (85%)	171
11	graphene[28] (doped by AuCl_3)	glass	$150 \Omega \text{ sq}^{-1}$ (87%)	17
12	graphene[29] (doped by AuCl_3)	PET	$54 \Omega \text{ sq}^{-1}$ (85%)	41
13	graphene[8] (doped by HNO_3)	PET	$30 \Omega \text{ sq}^{-1}$ (90%)	116
14	Cu grid-Ni thin film hybrid[22]	fused silica	$6.5 \Omega \text{ sq}^{-1}$ (75%)	187
15	Cu-Ti bilayer thin film[23]	fused silica	$16 \Omega \text{ sq}^{-1}$ (86%) ^{c)}	150
16	graphene-Au grid ^{d)} hybrid[208]	glass	$4 \pm 1 \Omega \text{ sq}^{-1}$ (79%)/ $20 \pm 4 \Omega \text{ sq}^{-1}$ (91%)	377/195
17	graphene-Al grid ^{e)} hybrid[208]	PET	$18 \pm 9 \Omega \text{ sq}^{-1}$ (79%)/ $60 \pm 15 \Omega \text{ sq}^{-1}$ (91%)	84/65
18	graphene-Cu grid ^{e)} hybrid[208]	PET	$8 \pm 3 \Omega \text{ sq}^{-1}$ (79%)/ $30 \pm 6 \Omega \text{ sq}^{-1}$ (91%)	188/130

a) Transmittance of all the electrodes (except No. 15) was measured at 550 nm (substrate absorption subtracted). b) Copper nanofibers were prepared by electrospinning. c) Transmittance at 630 nm. d) The metal grids were prepared by sputtering. e) The metal grids were prepared by thermal evaporation.

Figure 3.12 (A) SEM image of ZnO-SWNT-Ag-PET at low magnification, showing the uniformly deposition of ZnO nanostructure on SWNT thin film, with or without Ag grids. (B) Zoom-in SEM image of the area in blue square, showing the rose-like morphology of the ZnO nanostructures. (C) SEM image of ZnO-Ag-PET at low magnification, showing no ZnO nanostructure deposited. (D) Zoom-in SEM image of the area in red square. (E) XRD pattern of ZnO-SWNT-Ag-PET photoanode. The peaks marked with * are from Ag nanoparticles. (F) Amperometric I-t curve of ZnO-SWNT-Ag-PET photoanode (blue curve) and ZnO-Ag-PET photoanode (red curve).

We compare the sheet resistance and transmittance performance metrics of our hybrid film with other transparent conductors in Table 3.1. However, sheet resistances obtained at different transmission levels cannot be directly compared. A useful figure of merit for comparison of material properties in this situation is the ratio $\sigma_{\text{DC}}/\sigma_{\text{Op}}(\lambda)$, where $\sigma_{\text{Op}}(\lambda)$ is the optical conductivity at wavelength λ and σ_{DC} is the DC conductivity of the film. Higher values of this figure of merit imply better performance. This ratio can be derived from the measured transmittance T and sheet resistance R_s through the following relation:[12, 24]

$$T(\lambda) = \left(1 + \frac{188.5}{R_s} \frac{\sigma_{\text{Op}}(\lambda)}{\sigma_{\text{DC}}}\right)^{-2} \quad (\text{Equation 3.1})$$

As shown in Table 3.1, for commonly used commercial ITO with $R_s = 30\text{-}80 \, \Omega \, \text{sq}^{-1}$ at $T = 90\%$, $\sigma_{\text{DC}}/\sigma_{\text{Op}}$ is calculated to be $\sim 50\text{-}120$ (No. 4 in Table 3.1). While the best results for doped graphene and carbon nanotube films are ~ 120 and ~ 60 respectively (No. 13 and 6 in Table 3.1).[8, 32] The $\sigma_{\text{DC}}/\sigma_{\text{Op}}$ of our SWNT-Ag-PET film is ~ 350 which is significantly higher than that of ITO, doped CNTs and graphene. The performance of our hybrid films is comparable to that of graphene-gold grid films demonstrated by Zhu *et al.* (No.16 in Table 3.1, $R_s = 4 \pm 1 \, \Omega \, \text{sq}^{-1}$, $T = 79\%$, $\sigma_{\text{DC}}/\sigma_{\text{Op}} \sim 377$).[208] However, these graphene-gold grid films were made on rigid substrates and their fabrication requires costly photolithography and thermal evaporation processes. Using similar technique, the same authors also fabricated CVD graphene-aluminum grid films and CVD graphene-copper grid films on both glass and PET substrates. But these films showed poorer performance than our SWNT-Ag-PET film, with lower $\sigma_{\text{DC}}/\sigma_{\text{Op}}$ of 65-188 ($R_s = 18 \pm 9 \, \Omega \, \text{sq}^{-1}$ for graphene-Al hybrid; and $R_s = 8 \pm 3 \, \Omega \, \text{sq}^{-1}$ for graphene-Cu hybrid; both at $T = 79\%$

and on PET substrates). Besides, the SWNT-Ag-PET presented in this study was prepared by a totally solution-based method and no expensive material or equipment was needed. It's easy to scale up and much more cost-effective than the sputtering or e-beam evaporation conducting film depositing methods.

To demonstrate a potential application of the SWNT-Ag-PET hybrid film as photovoltaic electrode, we electrochemically deposited ZnO nanoplates on SWNT-Ag-PET electrode, and on as received Ag-PET as a control, and used the semi-transparent ZnO-decorated electrodes as photoanodes of photo-electrochemical cells. ZnO, a *n*-type semiconducting metal oxide, has been intensively studied for application in dye-sensitized solar cells due to its wide band gap and high electron mobility.[215] The SEM image at low magnification (Figure 3.12A) shows that the SWNT-Ag-PET hybrid electrode is fully and uniformly covered with ZnO nanoplates. Higher magnification SEM (Figure 3.12B) shows the rose-like morphology of the ZnO nanoplates. The XRD pattern confirms the crystallinity of ZnO nanoplates (Figure 3.12E). In contrast, ZnO nanostructures are not observed in the SWNT-free Ag-PET films (Figure 3.12C&D). In addition, Ag wires appear to be degraded to some extent due to the electrochemical migration of Ag under electrical field.[216] The problem of Ag migration is relieved for the SWNT-Ag-PET sample because of the protection offered by the well-adhered SWNT thin film.[209, 216] The photocurrent responses of the ZnO-decorated electrodes are shown in Figure 3.12F. Upon excitation with visible light, a weak current ($\sim 1 \mu\text{A cm}^{-2}$) was observed on the SWNT-free ZnO-Ag-PET anode, while a remarkably enhanced current ($13\text{-}16 \mu\text{A cm}^{-2}$) was generated with the ZnO-SWNT-Ag-PET anode. Although the current is low, compared to that produced by complicated heterostructured photoanodes reported

recently,[217] the significant improvement of photocurrent efficiency with the CNT thin film is clearly demonstrated in this experiment, as a concept proof. The CNT network enhances the photocurrent in two ways: 1) during the electrochemical fabrication process, the CNT network bridges the Ag grid to make the hybrid electrode homogeneously conductive, permitting homogeneous deposition of ZnO nanoplates to fully cover the hybrid electrode; 2) in use, the excellent electron-accepting ability of the CNTs facilitates charge collection and transport.[218, 219]

3.4 Conclusion

In summary, we have demonstrated a solution-based method for fabrication of hybrid transparent and flexible electrodes which combines Ag nanoparticle networks and thin films of SWNT network. This type of electrode can be simply and scalably fabricated at low-cost. Its outstanding performance ($R_s \sim 5.8 \Omega \text{ sq}^{-1}$, $T = 83.7\%$ at $\lambda = 550 \text{ nm}$, $\sigma_{\text{DC}}/\sigma_{\text{Op}} \sim 350$) together with its robustness and flexibility suggest a wide range of potential industrial and commercial applications.

Declaration

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4 Template-Free Synthesis of Large Anisotropic Gold Nanostructures on Reduced Graphene Oxide

4.1 Introduction

As mentioned in Chapter 1 and 2, graphene is a single 2D honeycomb lattice layer of $-sp^2$ carbon atoms with extraordinary physical and electrical properties.[2, 3, 220-222] Graphene can be chemically derived by reducing exfoliated graphene oxide (GO) using scalable solution processes.[77, 101] GO is a non-conducting lattice of $-sp^3$ carbon within which are embedded isolated conductive $-sp^2$ nanodomains.[89, 223] With chemical reduction, the $-sp^3$ carbon can be restored to $-sp^2$ carbon, thereby increasing the percolating conduction pathways between $-sp^2$ domains in reduced graphene oxide (RGO). Many routes have been developed to restore the graphitic $-sp^2$ structure from GO, including chemical reduction (*e.g.* by hydrazine[103]), thermal annealing,[91] and alcohol vapor restoration.[92] The properties of RGO are greatly dependent on the degree of reduction.

GO and RGO have been used as substrates for directly producing gold nanostructures.[128-131] Electrons from these substrates can be transferred to Au^{3+} spontaneously due to galvanic displacement and redox reaction, so that other reducing agents are not necessary in these systems.[129] In this chapter, we demonstrate a simple, template-free, *in situ* synthesis of gold nanostructures with different dimensions/morphologies on RGO with different reduction degrees. Three reduction levels of RGO were achieved using three different reducing methods, specifically, hydrazine vapor reduction, H_2 annealing (at 1000 °C, 20% H_2 in Ar), and ethanol/ H_2

reduction (at 1000 °C, ethanol vapor carried by 20% H₂ in Ar), which are hereafter referred to as the HZ, H₂/Ar and EtH₂ methods respectively. HZ, H₂/Ar and EtH₂ methods respectively produce slightly-, moderately-, and highly-reduced graphene oxide surfaces. By simply immersing the RGO thin films with different reduction degrees into AuCl₃ solution, gold nanoparticles (AuNPs), gold nanowires (AuNWs, 1D), and semicircular-shaped gold nanoplates (AuNPLs, 2D) are formed on the slightly-, moderately-, and highly-reduced GO surfaces respectively (as summarized in Figure 4.1).

Figure 4.1 Schematic illustration of distinct gold nanostructures formed on different graphene substrates which differ in the density of oxygen-containing functional groups. A representation of the -sp²/sp³ domain distribution of GO and slightly-, moderately-, highly-reduced GO surface and the corresponding gold nanostructures formed is shown in Figure 4.11.

4.2 Experimental Methods

4.2.1 Materials

Natural graphite flakes (300-mesh in size) were obtained from Qingdao Haida Graphite Co. Ltd (Shandong, China). 98% H_2SO_4 , 30% H_2O_2 , potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), 36%-37% HCl , 98% hydrazine monohydrate (N_2H_4 64-65%) and gold chloride (AuCl_3 , 99.9%) were purchased from Sigma-Aldrich (Milwaukee, WI). Absolute Ethanol was purchased from Fisher. All the reagents were used as received. Fused quartz slides were purchased from Jiangsu Jinghe Optical Instrument Factory (Jiangsu, China). Ultrapure deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$) (D.I. water) from a Milli-Q System (Millipore, Billerica, MA) was used in all experiments.

4.2.2 Synthesis of Graphene Oxide (GO)

The GO sheets were synthesized by a modified Hummers' method.[86] The as-prepared GO sheets were sorted by size via a two-step centrifugation. Firstly, the GO solution was centrifuged at 10,000 g to remove the impurities and small sheets. Then the precipitant was re-dispersed in D.I. water and centrifuged at 1,000 rpm. The supernatant was carefully extracted. The GO sheets produced were 15-20 μm in size.

4.2.3 Deposition and Reduction of GO Thin Films

GO solution was sprayed onto fused quartz slides with an air brush. The quartz substrates were pre-treated with Piranha solution at 120 $^\circ\text{C}$ for 45 min, followed by rinsing with D.I. water and blown to dry with N_2 . The cleaned substrates were heated to 130 $^\circ\text{C}$ on a hot plate, and 6 ml of 0.2 mg mL^{-1} GO solution was sprayed on them. Heating the

substrate above the boiling point of the carrier liquid prevents liquid buildup on the substrate during solution spraying, which improves the uniformity of the GO films.

The as-prepared GO thin films were reduced by three methods. (1) Low-reduction: The GO thin films were placed in a glass container with 100 μL of hydrazine (not in direct contact with the GO films). The container was sealed and heated to 100 $^{\circ}\text{C}$ overnight. (2) Medium-reduction: The GO thin films on quartz plates were transferred into a furnace and annealed at 1000 $^{\circ}\text{C}$ for 2 h, under the protection of forming gas (20% H_2 in Ar at 500 sccm). (3) High-reduction: These samples were loaded into a quartz tube, and forming gas (20% H_2 in Ar at 500 sccm) was introduced to the tube to purge undesired moisture and oxygen. The quartz tube was then heated to 1000 $^{\circ}\text{C}$, followed by introducing absolute ethanol vapor into the tube using the forming gas as carrier, with bubbling of the forming gas through ethanol maintained at 0 $^{\circ}\text{C}$ (total flow rate decreased to 100 sccm while bubbling).

4.2.4 Synthesis of Gold Nanostructures

After reduction, the RGO thin films on quartz substrates were immersed into 10 mM AuCl_3 solution (25 $^{\circ}\text{C}$) for 90 min, rinsed, and blown dry with N_2 . For semicircular AuNPLs, the substrates were immersed in 10 mM AuCl_3 solution at 80 $^{\circ}\text{C}$ for 40 min. Then the samples were put in an oven at 80 $^{\circ}\text{C}$ for 1 h before further characterization.

4.2.5 Characterization

Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) in ac mode. Scanning electron microscopy (SEM)

was performed using JEOL JSM-6700F and LEO 1550 Gemini field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV. Analysis of particle composition was carried out using X-ray energy dispersive spectroscopy (EDS) with an accelerating voltage of 15kV. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 high-resolution transmission electron microscope with an accelerating voltage of 200 kV. The AuNWs were scraped from the fused quartz substrates and dispersed in ethanol, and then dropped onto a 1000-mesh Ni TEM grid. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance, equipped with a Cu K α photon source (40 kV, 20 mA, $\lambda=0.15406$ nm) scanned at the rate of $1.0^\circ \text{ min}^{-1}$ over the range of $35\text{-}100^\circ$ (2 θ). Raman spectra were recorded with a WITec CRM200 confocal Raman microscopy system with 488 nm excitation and an air cooled charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany).

4.3 Results and Discussion

GO was synthesized by a modified Hummers' method.[84, 86] Figure 4.2A shows an atomic force microscopy (AFM) image of a GO sample. The typical width of an individual GO sheet is 15-20 μm . The thickness of the GO sheets is around 1 nm, indicating that the obtained GO sheets are monolayers. RGO thin films (2.5 cm in diameter) on quartz substrates were produced by spray-coating of GO followed by reduction via one of the three processes (HZ, H_2/Ar or EtH_2). Figure 4.2B shows the Raman spectra of GO/RGO thin films before and after the different reduction procedures. The ratio of the integrated Raman peak area of the D band (at $\sim 1360 \text{ cm}^{-1}$) to that of the G band (at $\sim 1585 \text{ cm}^{-1}$), *i.e.* $I(\text{D})/I(\text{G})$, is a commonly used criterion to determine the reduction degree of RGO.[77, 91] The $I(\text{D})/I(\text{G})$ ratios (derived from the spectra shown in

Figure 4.2B) for GO, HZ-RGO, H₂/Ar-RGO, and EtH₂-RGO are 0.855, 1.187, 1.222, and 1.270, respectively, confirming that the GO films were reduced to different extents by the three methods. The increase of $I(D)/I(G)$ after reduction suggests a decrease in the average size of the -sp² domains, which can be explained by the creation of numerous new and small -sp² domains after reduction.[77] In addition, from the Raman spectra (Figure 4.2B), the intensity ratio between the 2D band (at ~2700 cm⁻¹) and the G band, *i.e.* $I(2D)/I(G)$, is an indicator of the degree of recovery of -sp² carbon from -sp³ carbon with the chemical reduction treatment.[92, 109] The $I(2D)/I(G)$ ratios of GO and RGO films after HZ, H₂/Ar and EtH₂ reduction are 0.109, 0.135, 0.147, and 0.529 respectively. These results confirm that HZ, H₂/Ar and EtH₂ methods respectively produce low, medium, and high degrees of reduction. Su and co-workers have also demonstrated that the EtH₂ method is a more effective way to restore the oxidized carbon to graphitic carbon among the three reduction approaches.[92] They attributed the effectiveness of EtH₂ method to the fact that ethanol acting as the carbon source facilitates the repairing of the disrupted carbon lattice.[92] Our Raman results are further supported by resistivity measurements. It is widely recognized that higher reduction levels result in lower resistivity in RGO. Keeping the transmittance of the thin films at about 85% ($\lambda=550$ nm), the average sheet resistivity from 5 samples for HZ, H₂/Ar, and EtH₂ RGO films (mean $\pm$ standard deviation) are $\sim(4.7\pm0.5)\times10^5 \Omega \text{ sq}^{-1}$, $\sim(4.5\pm0.3)\times10^3 \Omega \text{ sq}^{-1}$, and $\sim(2.2\pm0.6)\times10^3 \Omega \text{ sq}^{-1}$, respectively. This trend is also consistent with the measurements by Su *et al.*[92]

Figure 4.2 (A) AFM image of GO sheets. (B) Raman spectra of GO films before and after different reducing processes. Black: GO (before reduction); Blue: slightly-reduced by HZ method, *i.e.*, hydrazine vapor, 100 °C, overnight; Olive: moderately-reduced by H₂/Ar method, *i.e.*, forming gas (20% H₂ in Ar, 500 sccm), 1000 °C, 2h; Red: highly-reduced by EtH₂ method, *i.e.*, ethanol/H₂ reduction (ethanol vapor carried by 20% H₂ in Ar, 100 sccm), 1000 °C, 2h.

Scanning electron microscopy (SEM) and AFM images (Figure 4.3) show that distinct Au nanostructure morphologies are formed on the three types of RGO films after incubation with 10 mM AuCl₃ solution for 90 min at room temperature (25 °C). Gold nanoparticles (AuNPs) (~170 nm in height) were formed on slightly-reduced GO (with HZ treatment, Figure 4.3A). Closer inspection reveals that the AuNPs are composed of several smaller Au nanorods (AuNRs) (Figure 4.4). The sometimes observed ~30 nm step-increase in the AFM height profile of AuNPs (Figure 4.3A, ii) likely corresponds to the height of individual AuNRs.

Figure 4.3 Morphology of gold nanostructures on RGO films with different degrees of reduction. (A) SEM (i) and AFM (ii) images of Au nanoparticles on slightly-reduced GO film. (B) SEM (i) and AFM (ii) images of Au nanowires on moderately-reduced GO film. A layer of small Au nanoparticles formed on the RGO surface, surrounding the nanowires. (C) SEM (i) and AFM (ii) images of semicircular Au nanoplates on highly-reduced GO film. Inset of C (i) shows the high magnification image of the edge indicated by the blue square. There was also a layer of small Au nanoparticles on the RGO film, in addition to the semicircular nanoplates.

Figure 4.4 AFM (A) and SEM (B) images of AuNPs formed on slightly-reduced GO thin films. The appearance of the particles as aggregates of nanorods is manifest.

On moderately-reduced GO surface (with the H_2/Ar method), ultra-long gold nanowires (AuNWs), with a background of densely distributed small AuNPs ($\sim 1-3$ nm in diameter), were observed. The diameter of the AuNWs was measured to be 20-30 nm by both AFM (Figure 4.3B, ii) and transmission electron microscopy (TEM) (Figure 4.10A, inset), while the length of the AuNWs exceeded the scanning range (~ 50 μm) of SEM at low (but still high enough to detect individual nanowires) magnification (Figure 4.5). Some irregular shaped Au nanostructures were also observed in Figure 4.5, which may due to the non-uniformity of the graphene oxide film or the disturbance of the $AuCl_3$ solution during the crystallization. It should be mentioned that ultra-long AuNWs are not easy to synthesize, and the previously reported length of AuNWs usually ranged from <1 μm to 20 μm . [224-227] The AuNWs obtained in our experiments have very high aspect ratio (>2000). The physical and optical properties of 1D nanomaterials directly correlate with their high aspect ratio. [228, 229]

Figure 4.5 SEM images of AuNWs in low magnification.

When the same immersion procedure at room temperature was applied to the highly-reduced (with EtH₂ method) GO substrates, only a few irregularly shaped gold nanoplates (AuNPLs) were observed, together with a low areal density background of small AuNPs (Figure 4.6). Warming the AuCl₃ solution from 25 °C to 80 °C resulted in the production of a considerably higher areal density of larger, regular semicircular-shaped AuNPLs in addition to the small AuNPs background, as shown in Figure 4C. The AuNPLs are 10-20 μm in diameter, and ~60 nm in thickness (Figure 4.3C, ii). Figure 4.7 shows an Au nanoplate in an intermediate growth stage. Evidently, the plate consists of two stacking layers with a single layer thickness of ~30 nm.

Figure 4.6 Irregular-shaped AuNPLs together with low areal density small AuNPs formed on highly-reduced GO film (10 mM AuCl₃, 90 min, 25 °C).

Figure 4.7 AFM image of an Au nanoplate in an intermediate stage of formation with a complete first stacking layer and a partially formed second stacking layer. The inset shows the height along the yellow highlighted section. Each layer is about 30 nm thick.

X-ray diffraction (XRD) patterns of AuNPs, AuNWs and AuNPLs are shown in Figure 4.8. The five characteristic peaks in the XRD pattern of AuNPs correspond to Au (111) (38.3°), (200) (44.6°), (220) (64.7°), (311) (77.5°), and (222) (82.4°) planes (JCPDS #04-0784). Only the Au (111) and Au (222) peaks are observed in the XRD patterns of AuNWs and AuNPLs, which are consistent with their oriented growth on the substrate. Energy dispersive spectroscopy (EDS) of the nanoplates (Figure 4.9) also confirms their gold identity. Figure 4.10A shows a TEM image of AuNWs produced on RGO reduced with H_2/Ar . High Resolution TEM (HRTEM) (Figure 4.10B) analysis reveals the crystalline structure of the AuNWs. The d-spacing determined from the fringes is 0.236 nm (Figure 4.10B, inset) which is close to the d-spacing of Au (111) plane, 0.235 nm.[225] The calculated lattice parameter a is 0.407 nm which agrees well with the theoretical value of Au.

Figure 4.8 XRD patterns of gold nanostructures. Black: Au nanoparticles on slightly-reduced GO film; Red: Au nanowires on moderately-reduced GO film; Blue: Semicircular-shaped Au nanoplates on highly-reduced GO film.

Figure 4.9 EDS spectrum of semicircular AuNPLs on highly-reduced GO surface. The inset is a low-magnification SEM image of semicircular AuNPLs.

Figure 4.10 (A) TEM images of AuNWs. The inset shows the indicated region at higher magnification. (B) HRTEM image of AuNWs indicating that the nanowires are polycrystalline. The inset shows the lattice distance of 0.236 nm, which agrees well with the d-spacing of Au (111), 0.235 nm.

The formation of gold nanostructures on GO/RGO surface involves nucleation and growth stages.[230, 231] It is well known that GO and RGO sheets possess various oxygen-containing functional groups (*e.g.* carboxylic acid, hydroxyl, and peroxide groups).[129, 232] Au^{3+} can be spontaneously reduced on GO/RGO surface by galvanic displacement and redox reaction owing to the existence of the functional groups (associated with $-\text{sp}^3$ domains) which provide active sites for the nucleation of metal nanoparticles and electron donation from the $-\text{sp}^2$ domains.[92, 129] The dipole or electrostatic interaction between the functional group of the $-\text{sp}^3$ carbon and the Au^{3+} ion helps to complex the Au^{3+} ion to increase the concentration of the ions at these defects, so that the threshold Au^{3+} concentration for nucleation is exceeded. On the other hand, the $-\text{sp}^2$ domains surrounding the Au seeds act as pools of electrons, and hence, as reducing agents. The involvement of these functional groups was also confirmed in our control experiments which show that small AuNPs were densely formed on unreduced GO surface but no gold nanostructures were formed on a pristine graphene surface as illustrated in Figure 4.1 a&f. Note that it has been reported that AuNPs can form on CVD graphene when it is electrically grounded.[28, 233] The Au atoms reduced from Au^{3+} can easily migrate along the GO/RGO surface in both the nucleation and growth stages because they only weakly interact with graphene.[234] We hypothesize that the spatial arrangement and density of the $-\text{sp}^3$ and $-\text{sp}^2$ domains of RGO affects the spatial distribution of seeds and the growth dynamics, and that both are crucial to the final nanostructures.

A representation of the $-\text{sp}^2/-\text{sp}^3$ domain distribution of GO and slightly-, moderately-, highly-reduced GO surface and the corresponding gold nanostructures

formed is shown in Figure 4.11. When there are many functional groups on unreduced GO (Figure 4.11A), Au seeds can be formed with high density and grow isotropically to small AuNPs (Figure 4.1a & 4.12). When GO is slightly reduced (Figure 4.1b & 4.11B), fewer functional groups remain as nucleation sites, resulting in the formation of fewer seeds. With increased $-sp^2$ domains with slight reduction (Figure 4.1b & 4.11B) compared to unreduced GO (Figure 4.1a & 4.11A), the growth of Au nanostructures will increase, resulting in bigger particle size, though of fewer count. When GO is further reduced to a moderate extent (Figure 4.1c & 4.11C), more $-sp^2$ domains are formed and the $-sp^3$ domains are cut into smaller and narrower areas. Although Au seeds are formed randomly on the remaining $-sp^3$ sites, we hypothesize that the Au nanostructures prefer to grow along the edges of nearby $-sp^2$ domains where the electrons necessary for Au^{3+} reduction are acquired, directing the anisotropic growth of AuNWs (Figure 4.1c).

To confirm that it is the moderate reduction degree that results in the evolution of gold nanostructures anisotropy on H_2/Ar moderately reduced GO, we did some control experiments using the same H_2/Ar gas composition but at lower reduction temperatures (*i.e.* changing the reduction temperature to 600 °C and 800 °C while keeping all the other conditions constant). Previous studies have shown that the reduction degree of RGO decreased greatly when the annealing temperature decreased, and only weak reduction occurred when the temperature dropped to 600 °C.[92] Unsurprisingly, we found that AuNPs were formed on the 600 °C H_2/Ar reduced GO surface (Figure 4.13A), rather than AuNWs which were formed on 1000 °C H_2/Ar reduced GO, similar to the results on the HZ slightly reduced GO films (Figure 4.1b). When the reduction temperature increased to 800 °C, Au nanorods of $\sim 1 \mu m$ length and 30-35 nm diameter were observed on the H_2/Ar

reduced GO surface (Figure 4.13B), indicating that nanoparticles evolved to 1D nanostructures as the reduction degree of RGO substrates increased from low to a moderate level. The anisotropy of nanorods and nanowires appears to be correlated with medium reduction degrees whilst nanoparticles were formed on RGO with low reduction degrees achieved with either HZ or 600 °C H₂/Ar.

Figure 4.11 Schematic drawing of $-sp^2$ domains (dark areas) and $-sp^3$ domains (blue areas) on GO and RGO surface (left) and the gold nanostructures formed after $AuCl_3$ treatment at room temperature (right). (A) GO: $-sp^2$ domains are isolated by the large quantity of $-sp^3$ carbon atoms. A lot of small AuNPs are evenly formed on the GO surface, as demonstrated in Figure 4.1a; (B) Slightly-reduced GO: After HZ reduction, the original and newly reduced $-sp^2$ domains connect to each other. The remained fewer $-sp^3$ sites (active sites for Au^{3+} reduction) and larger $-sp^2$ domains (the areas which donate electrons) result in fewer and larger AuNPs, as shown in Figure 4.1b; (C) Moderately-reduced GO: After H_2/Ar reduction, most $-sp^3$ carbons are reduced to $-sp^2$ sites. The network of $-sp^2$ domain is well formed, leaving some small areas and pathways of $-sp^3$ carbons. Au nucleus firstly form on the $-sp^3$ sites, and then prefer to grow along the edge of the nearby $-sp^2$ domains and pathways, which provide electrons for the crystal growth. Thus AuNWs are formed, as demonstrated in Figure 4.1c; (D) Highly-reduced GO: After EtH_2 reduction, very few $-sp^3$ sites remain and they are far from each other, surrounded by the network of $-sp^2$ domains. At room temperature, only a few AuNPLs are formed, shown in Figure 4.1d. And at higher temperature ($80\text{ }^\circ\text{C}$), well-defined semicircular-shaped AuNPLs (as shown in Figure 4.1e) are formed due to the change of diffusion and dynamics.

Figure 4.12 Small and dense Au nanoparticles formed on GO surface.

For the highly-reduced GO, we observe anisotropic growth of quasi 2D plate-like AuNPLs, with increasing concentration of the plates as the temperature of the $AuCl_3$ increased from $25\text{ }^\circ\text{C}$ (Figure 4.6) to $80\text{ }^\circ\text{C}$ (Figure 4.1d). With the high reduction degree achieved with the EtH_2 method, only very few $-sp^3$ sites are expected to remain (Figure 4.11D), and they are far from each other and surrounded by a highly-restored $-sp^2$ graphitic environment. With room temperature ($25\text{ }^\circ\text{C}$) $AuCl_3$ immersion, growth is slow and Au^{3+} ions diffuse sluggishly to the Au seeds, resulting in small and irregular plates. At

higher immersion temperature (80 °C), the diffusion of Au^{3+} ions is enhanced, leading to highly regular semicircular nanoplates (Figure 4.1e).[235]

Figure 4.13 SEM images of nanostructures formed on lower temperatures with H_2/Ar reduction method: (A) AuNPs formed on 600 °C H_2/Ar reduced GO film and (B) Au nanorods formed on 800 °C H_2/Ar reduced GO film. Inset of (B) is the AFM image of an Au nanorod.

However, we acknowledge that the mechanism for the formation of anisotropic nanostructures is still unclear, and more experiments are needed to elucidate the details of the mechanism. The Au nanostructures synthesized in this study might be applied in various applications such as transparent conductors, biosensors, surface-enhanced Raman scattering, nanoelectronic devices, *etc.*[236-239] Attempt has been made to transfer the Au nanostructure to another substrate. PET films were cleaned by ethanol and D.I. water before transfer. The RGO film with AuNPLs on quartz substrate was placed on the PET film with the RGO-AuNPLs side facing PET. Then RGO-AuNPLs and PET film were pressed by a laminator heated to 130 °C. The AuNPLs were partially transferred onto the PET film, while most of them remained on the RGO film, as shown in Figure 4.14. The incomplete transfer may due to the weaker interaction between the PET film and AuNPLs,

compared with that between RGO film and the AuNPLs. The study of Au nanostructure transfer is still on for further applications.

Figure 4.14 Optical microscopy images of the AuNPLs before and after dry transfer. Left: on RGO film-quartz substrate (before transfer). Middle: on PET film (transferred). Right: remained on film-quartz substrate (after transfer).

4.4 Conclusion

Through the simple expedient of control of the reduction degree of RGO, control may be exerted over the morphology and dimension of gold nanostructures formed *in situ* to produce various anisotropic gold nanostructures without the use of any contaminating template. Nanoparticles, nanowires (1D) and semicircular-shaped nanoplates (2D) can be formed on, respectively, slightly-, moderately-, and highly-reduced GO surfaces. Since the process employs no template/capping agent or additional reducing agent, the morphologies/dimensions of gold nanostructures depends principally on the reduction degree of RGO and, in the case of the nanoplates, also on the details of Au deposition conditions. Anisotropic gold nanostructures, particularly long nanowires, will have many applications, such as in transparent conductors, biosensing, surface-enhanced Raman spectroscopy, catalysis, *etc.*

Declaration

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5 Ultra-High Purity Facile Sorting of Single Walled Carbon Nanotubes for Electronic Applications by Repulsion Interaction Chromatography

5.1 Introduction

According to Moore's Law, sub-7 nm scale transistors will be needed in the foreseeable future (2020) to cope with the current trend of device miniaturization and intensification of device areal density.[194, 240] It is believed that mono-crystalline Si, the current semiconductor workhorse transistor material and a bulk material, will likely not be useable then because of short channel effects, high power density, high device variability, *etc.* Single walled carbon nanotubes (SWNTs) have been heralded as one of few most promising materials for that ambitious advancement in the semiconductor field because of its intrinsic single-atom layer structure and outstanding ballistic transport and other characteristics such as its mechanical robustness, high thermal conductivity, *etc.* Besides, SWNTs-based thin film is also a strong contender as a printable transistor for printed/organic electronics which has been identified as one of Top 10 emerging technologies by the World Economic Forum.[241]

Since the demonstration of SWNTs as a field-effect transistor in 1998 - nearly two decades ago,[190, 191] many outstanding works have been done to solve various challenges.[13] A key stumbling block in the application of SWNTs as a field effect transistor is the contamination of semiconducting (semi-) SWNTs by metallic (met-) SWNTs since all known nanotube synthesis methods produce mixtures of semi-SWNTs co-mingled with met-SWNTs. In the past decade, a great deal of research effort has been

invested into the problem of sorting SWNTs by electronic structure type. Successful sorting has been achieved by various methods as reviewed in Chapter 2. All the methods are effective but each has one or more intrinsic drawbacks which hinder the technologies from implementation in large-scale industrial processes. The search for an improved method for separating out ultra-high purity semi-tubes cost-effectively and which are also able to make good transistor is still an ongoing intense research topic.[47, 59, 242, 243] Some key obstacles to achieving superior performance with SWNT-based transistors include the inability to obtain ultra-high purity fractions (because of the subtle differences in the properties of met-/semi-tubes and the confounding effects of solvent and surfactants), the shortening of nanotubes after the sorting and the difficulty in removing the surfactants/polymers without excessive defects to nanotubes.[14]

Various recent superior sorting techniques such as DGU and column chromatography are founded on a co-surfactant system of sodium dodecyl sulphate (SDS) and sodium cholate (SC) which has been thought to aggregate differentially around metallic nanotubes versus semiconducting nanotubes due to their different polarizability. The differential surfactant binding results in different buoyant density of semi- and met-SWNTs, and thus they could settle in different gradient layers in DGU process. To the best of our knowledge, until now DGU is the only commercialized technique for electronic structure type sorting. Although high purity (~99%) semi- and met-SWNTs can be achieved, DGU method suffers from the high cost of the density gradient reagent and the intrinsic slowness of the DGU process, which combine to make the price of SWNTs sorted by this method much too high for industrial applications.

In addition, with UV-vis-NIR spectroscopy, the purity beyond 98% cannot be determined accurately and so far, it appears that only single nanotube devices metrology will allow us to measure the target metallic content (0.01% or even 0.0001%) needed for nanoelectronics. The recent works by Tulevski *et al.* showed that the highest purity attained per pass with this surfactant mixture using Sephacryl gel to be 98.3% semiconducting (1.7% metallic content) and the tubes to be relatively short. However, it is still a few orders higher in the metallic content than our acceptable content for nanoelectronics.

Herein, we have developed a chromatography technique based on the intrinsic charge properties of SWNTs and the different sensitivity of the charge on pH for metallic nanotubes *versus* semiconducting nanotubes (Figure 5.1, inset). To exploit the interaction of the intrinsic charge of the nanotubes with the chromatography beads, we employ a somewhat untapped surfactant family - the non-ionic surfactants such as Triton X-405, Brij L23, Brij S100 *etc.* - for the sorting of the nanotubes. Strano and Zheng have shown that SWNTs with different band gaps can be differentially protonated by acid.[46, 244] It has been shown that most solution processed SWNTs possess negative charges.[245] However, as the pH is adjusted from neutral to acidic, metallic SWNTs are easily protonated by acids, followed by small band gap large diameter semiconducting SWNTs and then large band gap small diameter semiconducting nanotubes.[245, 246] By adjusting the pH, we can use functionalized agarose beads to trap the metallic tubes while eluting the semiconducting tubes because of higher repulsion between the functionalized agarose beads and the semi-SWNTs/non-ionic surfactant complex (Figure 5.1). Non-ionic surfactants will not introduce any external charge on the side-wall of the SWNTs so that

the nanotube/surfactant complex interaction with beads will depend on the intrinsic charge of the nanotubes, and not the surfactant, which is a key factor for the sorting to work. From the UV-vis-NIR, Raman spectroscopy and single tube device characterization, the purity of semi-SWNTs can be enriched to >99.9% in a single pass of sorting *via* our RICH method.

Figure 5.1 Schematic of the sorting process *via* repulsion interaction chromatography.

5.2 Experimental Methods

5.2.1 Materials

Triton X-405 solution (70% in H₂O) was obtained from Dow Chemical. Sepharose beads (GE Healthcare), (±)-epichlorohydrin (epichlorohydrin, 99%), sodium hydroxide

(NaOH, 98%), hydrochloric acid (HCl, 36-37%), sodium dodecylbenzenesulfonate (SDBS), sodium cholate (SC), cetyltrimethylammonium bromide (CTAB) and all the solvents were purchased from Sigma-Aldrich and used as received. Arc-discharge SWNTs (P2-SWNT, diameter 1.2-1.6 nm, mean diameter 1.4 nm) were purchased from Carbon Solutions and HiPco SWNTs (diameter 0.8-1.2 nm, mean diameter 1.0 nm) were purchased from Unidym. Ultrapure deionized water (18.2 M Ω ·cm) (D.I. water) from a Milli-Q System (Millipore, Billerica, MA) was used in all experiments.

5.2.2 Synthesis of Functionalized Sepharose Beads¹

20 mL Sepharose 4B was washed with 20 mL D.I. water three times before reaction. The washed beads were suspended in 20 mL of 1 M NaOH. 6 mL epichlorohydrin was added into the suspension of Sepharose 4B. The mixture was transferred into a 50 mL centrifuge tube and rotated with a tumbler in an oven at 40 °C overnight. The beads were then thoroughly washed D.I. water and then suspended in 10 mL methanol : water (1:1). 0.5 mmol functionalizing compound was dissolved in 20 mL methanol : water (1:1) and then mixed with the beads suspension. The mixture was rotated with a tumbler at room temperature overnight. Then the beads were washed thoroughly with D.I. water and 20% ethanol and then finally kept in 15 mL of D.I. water at 4 °C until use.

¹ This sorting method is under patent application now. We are not able to disclose the details of the functionalization and the name of the functionalizing compound. We are sorry for the inconvenience caused.

5.2.3 Carbon Nanotube Dispersion Preparation

Taking Triton X-405 as an example, 70% Triton X-405 dispersion was diluted to 2.8% aqueous solution with D.I. water. The pH of the Triton X-405 solution was adjusted with 0.1 M HCl. 1 mg mL⁻¹ solution of SWNTs in 2.8% aqueous Triton X-405 (pH adjusted) was ultrasonicated by a 130-Watt Ultrasonic Processor (VCX130, Sonics & Materials, Inc., USA) for 1 h with ice bath (60% amplitude, 1 s pulse). The pH of the Triton X-405 solution should be consistent with the eluting solution later used for chromatography. The suspension of SWNTs was then centrifuged at 54000 g for 4 h or at 122000 g for 1 h. The top 80% supernatant was carefully extracted and used for chromatography separation. The dispersion was bath-sonicated for 10 min before use if it had been prepared more than 1 day before separation.

The preparation of SWNTs dispersion in other surfactants was with the same procedure, except for the type and concentration of surfactant.

5.2.4 Chromatography

Again, taking Triton X-405 as an example, 5-10 mL of functionalized Sepharose 4B beads were packed into a glass chromatography column (I.D. 15 mm). The column was flushed with D.I. water with back pressure (compressed air) to make the packing firm. The column was flushed with at least 2 column volumes of 2.8% Triton X-405 in aqueous solution (pH consistent with the eluting condition) before loading the SWNTs dispersion. 2 mL SWNTs dispersion was added into the column and was allowed to pass through the column via gravity (no back pressure applied). When the SWNTs dispersion had almost fully entered the gel column, more 2.8% Triton X-405 solution (acidic) was added to elute

the semi-SWNTs out. Triton X-405 solution was continuously added until no more semi-SWNTs came out (eluent became colorless). Then 2% SDBS aqueous solution or 2.8% Triton X-405 solution (basic) was continuously added into the column to elute all the met-SWNTs until all the met-SWNTs were eluted (eluent became colorless). The column was then flushed thoroughly by D.I. water and was ready to re-use for the next cycle of separation. Typical elution time is 2-5 min for semi-SWNTs fraction and 10-15 min for met-SWNTs. The sorted SWNTs were characterized using a Varian Cary 4000 UV-vis-NIR spectrophotometer and a Renishaw inVia Raman microscope with 633 nm (1.96 eV) laser wavelength in a backscattering configuration.

5.2.5 Electrical Testing

The FETs were fabricated on *p*-type silicon wafer containing 300 nm of thermally grown SiO₂ by photolithography (L=75 μ m, W=25 μ m). Source and drain electrodes were 50 nm Au coated on top of 10 nm Ti, deposited by e-beam evaporator. The electrode patterns were cleaned by Argon plasma (100W) for 2 min (the plasma chamber was cleaned by 300W Oxygen plasma for 5 min before Ar plasma) and immersed in 0.5 vol.% of (3-Aminopropyl)triethoxysilane (APTES) solution in ethanol for 45 min to enhance the adhesion of the SWNTs to be deposited. The devices were annealed in vacuum (10⁻⁶ mbar) overnight at 250 °C to improve hydrophobicity of the surface and remove the solvent residues. The sorted semi-SWNTs were then carefully dropped between the source and drain electrodes with a syringe and fine needle. Before drop-casting, the semi-SWNTs solution was diluted with D.I. water and sonicated for 10 min in a bath sonicator. To avoid the coffee-ring effect, the devices were rinsed with D.I. water when the droplets were about to dry and then were blown dry with compressed air. The devices were placed on a

hot plate (130 °C) for 10 min before the next drop. The drop-casting procedure was repeated until the desired SWNTs density was achieved. The electrical testing of the FET devices was carried on a Keithley semiconductor parameter analyzer Model 4200-SCS in ambient environment.

5.3 Results and Discussion

The Sepharose-X beads are packed into a glass chromatography column and flushed thoroughly with at least 2 column volumes of D.I. water and 2.8% Triton X-405 aqueous solution (pH adjusted) before loading the unsorted SWNTs suspension. Arc-discharge SWNTs (*e.g.*, P2-SWNTs, Carbon Solutions) are dispersed in 2.8% Triton X-405 aqueous solution (acidic) at the concentration of 1 mg mL⁻¹ by probe sonication, and followed by 1 h centrifugation at 122000 g to remove all the bundles. The well-resolved absorption spectrum of the unsorted SWNTs in Fig. 5.2B reveals the individual dispersion of the SWNTs in Triton X-405 solution. The first fraction eluted by Triton X-405 solution is the semiconducting fraction (pink to red in color, Fig. 5.2A right), while the metallic fraction (green in color, Figure 5.2A left) is adsorbed in the column until being eluted out by aqueous solution of ionic surfactant (*e.g.*, SDBS), or simply adjusting pH of Triton X-405 to basic with 0.1 M NaOH aqueous solution. The first fraction eluted is the semi-SWNTs which are repelled by the functionalized Sepharose-X beads. In previous studies of SWNTs sorting *via* gel chromatography,[47, 62] the use of SDS as surfactant has always resulted in the metallic fraction being first to be eluted through the column, and the semiconducting fraction either was eluted later or remained in the column. It is because when dispersed in SDS solution, semi-SWNTs are less covered by SDS molecules, and thus interact stronger with the hydrogel beads. And met-SWNTs would be eluted first with

SDS solution since the higher coverage of SDS on met-SWNTs weakens the interaction between met-SWNTs and the hydrogel beads.

Figure 5.2 (A) Visual appearance of arc-discharge SWNT dispersions in aqueous solution with surfactant: sorted metallic (left), unsorted (middle) and sorted semiconducting (right). (B) UV-vis-NIR spectra of unsorted SWNTs (black), semiconducting (red) and metallic (olive) SWNTs sorted by Sepharose-X beads. (C) Raman spectra (633 nm, red laser) of unsorted (black), semiconducting (red) and metallic (olive) SWNTs sorted by Sepharose-X beads.

Figure 5.2B shows the absorption spectra of the sorted semi- (red curve) and met-SWNTs (olive curve) *via* Sepharose-X column at respective optimum pH. The sorting in this work can only happen in acidic condition, and the optimum pH of acidic Triton X-405 solution differs to achieve the best purity of semi- and met-SWNTs.² The absorption spectra show that the M11 peaks become almost undetectably weak in the semiconducting fraction after one-pass sorting (yield ~10%), and the absorption curve is flat in this region because of the near-zero metallic absorption. The content of semi-SWNTs a sample is usually estimated by the area ratio of the absorption peaks with the equation $S22/(M11+S22)$, however, this method is not applicable here anymore since the M11 absorption is flat. We can only estimate that the purity of the sorted semi-SWNTs is over 99% by the absorption spectra. Meanwhile, in the metallic-enriched fraction, the semiconducting peaks (both S33 and S22) are dramatically reduced relative to M11 and the purity of met-SWNTs is ~90% estimated by the area ratio of $M11/(M11+S22)$.

Raman spectroscopy was also used to further evaluate the purity of sorted semiconducting and metallic SWNTs. A red laser with 1.96 eV excitation energy (633 nm) was used as it can probe both semiconducting and metallic arc-discharge SWNTs. The Raman spectra of unsorted and sorted SWNTs *via* Sepharose-X column are shown in Figure 5.2C. The spectrum of unsorted SWNTs shows both semiconducting ($\sim 155\text{ cm}^{-1}$) and metallic ($\sim 171\text{ cm}^{-1}$ and $\sim 196\text{ cm}^{-1}$) peaks in RBM region. After sorting, the metallic peaks at $\sim 196\text{ cm}^{-1}$ totally disappear. Meanwhile, the semiconducting peak ($\sim 155\text{ cm}^{-1}$) vanishes in the sorted met-SWNTs enriched samples. Moreover, G band ($\sim 1569\text{ cm}^{-1}$) of the sorted semi-SWNTs become much narrower because of the greatly reduced metallic

² This sorting method is under patent application now. We are not able to disclose the working pH. We are sorry for the inconvenience caused.

SWNTs content, while the G^- peak of sorted met-SWNTs is much broader and even much higher than the G^+ peak, which strongly supports the high proportion of metallic SWNTs. In addition, we notice that the intensity of the 2D band ($\sim 2634\text{ cm}^{-1}$) increases dramatically for sorted met-SWNTs, becoming much higher than the G band, while it decreases greatly for the sorted semi-SWNTs. The purer the semi-SWNTs, the lower the 2D peak, *vice versa*. Although the intensity of 2D peak has not previously been used as a criterion to for enrichment of semiconducting or metallic SWNTs, the Raman spectra do show that the 2D peak intensity obviously changes between highly purified metallic and semiconducting SWNTs. Similar results have been shown in previous study of 99% semiconducting and metallic SWNTs purchased from NanoIntegris.[46]

The pH-dependent differential protonation of metallic and semi-SWNTs accounts for the different charges on the metallic *versus* semi-SWNTs at the optimum pH. SWNTs have been reported to have intrinsic negative charges, and the density of the charge is diminished gradually when lowering pH.[141] Water itself is a reducing agent, but in the presence of oxygen, the O_2/H_2O couple oxidise the CNTs. The redox reaction can be represented by:

with the half-cell reactions as follows:

The redox potential of Equation 5.1 is $E^{\circ} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}}$ and when $E^{\circ} > 0$, spontaneous reaction will happen. This also indicates that we need E°_{L} to be small and E°_{R} to be large. At lower pH, the reduction potential of the right half-cell reaction (Equation 5.2) changes by -60 mV pH^{-1} unit to become higher, favouring Equation 5.1. The reduction potential of nanotube oxidation (left reaction, Equation 5.3) increases with increasing band gap, or decreases with decreasing band gap, so that oxidation of the larger semi-tubes or metallic tubes occur first with some decrease in pH, and then smaller tubes as further increase in pH.

The use of non-ionic surfactant is important here to avoid introducing any external ions on the SWNTs side wall. We tried to use ionic surfactants, *e.g.*, SDS, SDBS, SC or CTAB, instead of Triton X-405 solution, to disperse and elute the unsorted SWNTs. Not to our surprise, none of the above gives rise to any separation because the subtle charge differential between semi- and met-SWNTs at certain acidic pH was covered by the external charges. Other non-ionic surfactants, *e.g.*, Brij L23 and Brij S100, are also able to achieve excellent separations.

To study the diameter limitation of the RICH method, we performed sorting of HiPco SWNTs with smaller diameter using the same method, but the pH of Triton X-405 solution was adjusted to a lower value due to the smaller diameter of HiPco SWNTs. Similarly, semi-SWNTs were eluted out first (green in color, shown in Figure 5.3A right), while met-SWNTs (pink in color, Figure 5.3A left) were trapped in the column until later be eluted out by basic Triton X-405 solution. UV-vis-NIR absorption shows clear decrease of M11, while increase of S11 and S22, for the sorted semiconducting fraction (Figure 5.3B, red curve). *Vice versa* for the sorted metallic fraction (Figure 5.3B, blue curve). The

sorting effect was double confirmed by Raman spectra (633 nm). As shown in Figure 5.3C, the metallic peaks ($175\text{-}240\text{ cm}^{-1}$) in RBM region almost disappear for the sorted semi-SWNTs (red curve), but increase apparently for the sorted met-SWNTs (blue curve). The sorting of HiPco SWNTs shows the universality of the RICH method for SWNT sorting, regardless of diameter range. But it should be mentioned that the sorting condition for HiPco SWNTs has not been optimized as it was done for P2-SWNT. The purity of the sorted HiPco SWNTs could be further improved by fine adjusting of the sorting pH.

To demonstrate the excellent electronic properties of our sorted semi-SWNTs, we fabricated network field effective transistors (FET) with the sorted dispersion by drop casting. Source and drain electrodes were fabricated on Si wafer with 300 nm SiO_2 as dielectric layer. The dispersion of sorted semi-SWNTs was carefully dropped between the source and drain electrodes (Figure 5.4A). Figure 5.4B shows an AFM image of the semi-SWNTs network between the electrodes. The length of the sorted semi-SWNTs are 0.8-1 μm . Figure 5.4C&D show the performance of typical FET devices with on/off ratio 10^4 - 10^5 and mobility $15\text{-}30\text{ cm}^2\text{ V}^{-1}\text{s}^{-1}$ (mobility computed using the coupling model mobility equations[48, 216] employed in our previous publications[247]). The good on-off switching ratio confirms the high purity of the sorted semi-SWNTs.

Figure 5.3 (A) Visual appearance of HiPco SWNT dispersions in aqueous solution with surfactant: sorted metallic (left), unsorted (middle) and sorted semiconducting (right). (B) UV-vis-NIR spectra of unsorted HiPco SWNTs (black), sorted semiconducting (red) and metallic (blue) SWNTs. (C) Raman spectra (633 nm, red laser) of unsorted HiPco SWNTs (black), sorted semiconducting (red) and metallic (blue) SWNTs.

Figure 5.4 (A) Schematic drawing of the network FET device (not to scale). (B) AFM image of the semi-SWNTs network between source and drain electrodes. (C) and (D) Typical performance of the FET devices with sorted semi-SWNTs network.

However, obvious hysteresis is observed in Figure 5.4C and 5.4D. The hysteresis of SWCNT-FETs has been studied intensively, and could be attributed to the charge traps in bulk SiO₂, [248] the ambient moisture, [249] the existence of free mobile ions [250] and the molecules adsorbed on the SWCNTs. Triton X-100, which has similar structure to Triton X-405, has been reported to cause ambipolar characteristics and significant hysteresis of SWCNT-FETs. [251] Therefore, the large hysteresis shown in Figure 5.4C and 5.4D could be a combined result of the charge traps in SiO₂ dielectric layer, the moisture from ambient and the existence of the Triton X-405 molecules. The study on

elimination of the hysteresis by removal of Triton X-405[251] and the application of a passivation layer[252] is still on the way.

Since the widely-used estimation of purity by absorption spectra is no longer applicable to the highly pure sorted semi-SWNTs in this work, we have sent the sorted SWNTs sample to IBM Thomas J. Watson Research Center (New York, US) to performed electrical test of more than 4000 single tube FETs to statistically verify the purity.[47] The statistic result shows that the purity of sorted semi-SWNTs by RICH method is higher than 99.9%, which is probably the best result for solution-based SWNT sorting to date.

With this method, the yield of the >99% semi-SWNTs after one-step sorting is ~10%, with respect to the initial amount of SWNTs. Among the 90% weight lost, ~60% of the SWNTs were lost during the centrifuge step (removed as bundles in the precipitant), while another ~30% were lost during chromatography process (remain in the mixture with met-SWNTs). The latter could be recovered and fed to the chromatography columns again. Therefore, the yield could be further improved to 20-30% (the content of semi-SWNTs in initial SWNTs was 80%). This yield is considered to be quite high, keeping in mind that the yield of the commercial technology (DGU) is only 1-5%. The cost of this sorting method is much lower than that of the DGU approach since no expensive chemicals or equipments were used in the process (compared with the high-cost density gradient medium and ultra-high centrifuges required for DGU). The columns with modified beads can be reused for unlimited times with proper operation. And the method is easy to scale up by increasing the volume of the columns.

5.4 Conclusion

We have demonstrated high purity and high yield metallicity-based sorting of large-diameter single walled carbon nanotubes *via* a simple and inexpensive chromatography process. Semi-SWNTs with purity >99.9% can be obtained within a few minutes by simply dispersing and eluting SWNTs through modified Sepharose 4B chromatography columns. The hydrogel beads selectively adsorb met-SWNTs in the column when the SWNTs are dispersed in an aqueous solution of non-ionic surfactant at a certain acidic pH range. After elution of the semi-SWNTs, the met-SWNTs can be eluted by ionic surfactant solution or basic non-ionic surfactant solution. FET devices were fabricated with the sorted semi-SWNTs, and the performance of network SWNT FET devices (on/off ratio $10^4 - 10^5$ and mobility $15\text{-}30 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) confirms the ultra-high purity and excellent electrical property of the sorted semi-SWNTs. The yield of the >99% semi-SWNTs reaches 10% after one-pass sorting and could be further improved to up to 30% by simply re-feeding the lower purity fraction. The cost of the separation is very low and the process is easy to scale up for industrial applications in transistors and other electronic devices.

6 Summary and Future Work

6.1 Summary

Graphene and single walled carbon nanotubes have been studied extensively for printable electronics. Both graphene and SWNTs are considered promising materials for transparent conductors as replacement of ITO resistance ($R_s \sim 30\text{-}80 \, \Omega \, \text{sq}^{-1}$, $T \sim 90\%$) due to their superior electrical conductivity, optical transparency, and excellent flexibility, while semi-SWNTs are reported to be the most promising semiconducting material to replace single crystalline silicon for the new generation high-performance transistors. In addition, graphene oxide and reduced graphene oxide are perfect platforms for nanostructure synthesis due to their abundant functional groups. In this thesis, the properties of single walled carbon nanotubes and graphene-based materials have been engineered towards low-cost and high-performance SWNTs/graphene based transparent conductors, SWNT-based network FETs and other electronic applications.

Firstly, various graphene / SWNTs and Ag hybrid transparent and flexible conducting films have been fabricated on PET substrates in simple, cost-effective, and solution-based processes. While the performance of all the hybrid films (Ag with unsorted SWNTs, met-SWNTs and CVD-grown graphene) are similar in terms of sheet resistance and optical transmittance, those with unsorted SWNTs are the most cost-effective. Such flexible and transparent electrode exhibits sheet resistance down to $\sim 5.8 \, \Omega \, \text{sq}^{-1}$ at $\sim 83.7\%$ optical transmittance. The high $\sigma_{\text{DC}}/\sigma_{\text{Op}}$ (~ 350) of such SWNT-Ag-PET hybrid films is comparable to the best result on rigid substrate reported to date. Meanwhile, the SWNT-Ag-PET films exhibit excellent bendability. In addition, the hybrid films are stable in

ambient conditions due to the stability of SWNTs. The superior performance and the scalable low-cost process of such hybrid films enable their various applications in the printable electronics including photovoltaics, touch panels and OLED.

Further, the reduced graphene oxide thin films were applied as platform for Au nanostructure synthesis. We found that various anisotropic gold nanostructures could be produced *in situ* on the surface of RGO films without the use of any contaminating template by simple controlling of the reduction degree of graphene oxide. Nanoparticles, nanowires and semicircular-shaped nanoplates can be formed on, slightly-, moderately-, and highly-reduced GO surfaces respectively. Since the process employs no template/capping agent or additional reducing agent, the morphologies/dimensions of gold nanostructures depends principally on the reduction degree of RGO, and in the case of the nanoplates, also on the details of Au deposition conditions. The growth of various gold nanostructures could be explained by the electron transfer between Au^{3+} and reduced graphene oxide with different size and distribution of the $-\text{sp}^2$ / $-\text{sp}^3$ domains at each reduction level. The anisotropic gold nanostructures, particularly long nanowires, will have many applications such as in transparent conductors, biosensing, surface-enhanced Raman spectroscopy, catalysis, *etc.*

Finally, we developed a simple and cost-effective chromatography process to sort ultra-pure semiconducting SWNTs for the application of FETs. The functionalized hydrogel beads (Sephacrose-X) selectively adsorb met-SWNTs in the column when the SWNTs are dispersed in an aqueous solution of non-ionic surfactant. After elution of the semi-SWNTs, the met-SWNTs can be eluted by ionic surfactant solution or basic non-ionic surfactant solution. Semi-SWNTs with >99.9% purity and met-SWNTs with >90%

purity are obtained using the functionalized agarose beads after a one-pass sorting process which takes only a few minutes. Network FET devices were fabricated with the sorted semi-SWNTs, and the performance of a typical FET device with on/off ratio $10^4 - 10^5$ and mobility $15\text{-}30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The process is easy to scale up and cost of the separation is only a fraction of today's price which will facilitate the industrial applications of SWNTs in transistors and other electronic devices.

6.2 Directions for Future Research

For the future work on the SWNT / graphene based hybrid transparent conducting films and sorting of semi-SWNT for printable electronics, the following studies are proposed:

- 1) The current SWNT-Ag hybrid films provide excellent conductivity, transparency and flexibility. However, the roughness of the hybrid films is still high due to the fluctuation of the self-assembled Ag grids ($\sim 3 \text{ }\mu\text{m}$). It would be helpful to embed and transfer the Ag grids to another substrate (*e.g.*, resins) to flatten the surface followed by fabricating the SWNT network or graphene film to bridge the Ag lines. The flattened hybrid films will be more suitable for some special applications (which require a flatter conductive layer) such as organic solar cells.
- 2) The synthesis of ultra-long Au nanowires on the surface of RGO films was exciting and the improvement of electrical conductivity of the RGO films was expected. However, it was found that the electrical conductivity of the RGO films was not improved by the Au nanowires network. The reason was not clear in the current study. It is recommended to improve the electrical properties of the AuNWs-RGO hybrid

films in the future research by adjusting the length, diameter and density of the AuNWs.

- 3) Semi-SWNTs with ultra-high purity are sorted with the functionalized Sepharose beads in this study. However, the purity of met-SWNTs is still to be further improved. The functionalizing compounds studied in this thesis were all negatively charged. At the optimal pH, the more oxidized met-SWNTs (with more positive charges) were adsorbed onto the beads while the less oxidized semi-SWNTs (remain negatively charged) were repelled by the negatively charged beads. Met-SWNTs and semi-SWNTs with opposing charges might attract each other in the solution and form small bundles which were also stuck in the column. Therefore, the purity of the met-SWNTs could not exceed 90% no matter how the pH was adjusted. In the future study, positively charged compounds are suggested for beads functionalization towards higher purity of met-SWNTs for the applications of transparent conductors as ITO replacement. With the positively charged beads, met-SWNTs with positive charges will be repelled and thus be first eluted with higher purity, while semi-SWNTs will be adsorbed on the beads together with the small bundles. The eluted semi-SWNTs could be recycled and used on negatively charged beads again to enhance the purity of semi-SWNTs.
- 4) The ultra-pure semi-SWNT is a promising material to replace Si in high performance transistors. However, the performance of SWNT network transistors not only depends on the purity of the semi-SWNTs, but also is affected by the length of the carbon nanotubes. The sorting of semi-SWNTs by length is highly recommended for the future study to get the longer fractions for better electronic performance.

- 5) The sorted semi-SWNTs are dispersed in non-ionic surfactants which are difficult to rinse away from the SWNTs. The existence of surfactant significantly increased the tube-tube resistance of the SWNT network and caused large hysteresis effects in the I_D - V_G curves of the SWNT network FETs. Removal of the surfactants would be a necessary task for the future research on the applications of the sorted SWNTs. Thermal annealing and solvent exchange in aqueous dispersion might be good ideas to start with.
- 6) Due to their high performances, low cost and simple processes, the methods to produce SWNT-Ag hybrid films and ultra-pure semi-SWNTs in the present study hold great potentials for scaling up and commercialization. For the scaling up of SWNT-Ag hybrid film production, it is crucial to study the deposition methods of SWNT thin films on large scale and low cost. For the commercialization of ultra-pure semi-SWNTs, the purity grades, length, and diameter distribution of the sorted semi-SWNTs could be further classified to meet the requirements of different customers better.

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Patents

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2. Chan Bee Eng Mary, Ashok Kumar Sundramoorthy, **Wang Jing**, " Self-Assembly of Calix[4]arene-Dispersed Oxidized Graphene For Transferable Transparent Conductive Thin Films ", US Provisional Patent Application (Registration number: US Prov 62/021,767, filed 2014)

Journal Papers

1. **Jing Wang**, Jintao Zhang, Ashok Kumar Sundramoorthy, Peng Chen, Mary B. Chan-Park, "Solution-Processed Flexible Transparent Conductors Based on Carbon Nanotubes and Silver Grids Hybrid", *Nanoscale*, 6(9): 4560-4565 (2014)
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11. Xiaochen Dong, Jingxia Wang, **Jing Wang**, Mary B. Chan-Park, Xingao Li, Lianhui Wang, Wei Huang, Peng Chen, "Supercapacitor Electrode Based on Three-Dimensional Graphene-Polyaniline Hybrid", *Mater. Chem. Physics*, 134(2-3): 576-580 (2012)
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