CONTROLLED FUNCTIONALIZATION AND ASSEMBLY OF GRAPHENE NANOSTRUCTURES FOR SENSING AND ENERGY STORAGE

by

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Dedication

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CONTROLLED FUNCTIONALIZATION AND ASSEMBLY OF GRAPHENE NANOSTRUCTURES FOR SENSING AND ENERGY STORAGE

Abstract

By

ENOCH NAGELLI

The superior electron carrier mobility, thermal conductivity, and mechanical properties of graphene have led to the rapid development of graphene-based applications for high speed electronics, chemical and biological sensing, optoelectronics, energy storage and conversion. However, the incorporation of graphene into these applications requires the precise connection of individual sheets at the molecular level with other materials where chemical interaction is significant. In this regard, the chemical functionalization of graphene has played a critical role in facilitating the integration of graphene into useful “building-blocks” or functional components in these applications. The functionalization of graphene can alter its electronic band structure, doping, and affinity for other organic, inorganic, and biological materials. The site specific functionalization of graphene is essential to modify the region-specific surface properties to gain specific characteristics required for particular applications and to covalently/non-covalently link graphene sheets of different properties together into various graphene-based devices. Controlled chemical modification could be a very useful approach to various multifunctional systems critical to applications such as nanoelectronics, nanophotonics, nanosensors, and nanoenergy systems.
We describe a simple and effective modification method for functionalizing the two opposite surfaces of individual graphene sheets with different nanoparticles in either a patterned or non-patterned fashion. The asymmetric and patterned functionalization of graphene sheets with each of their two opposite surfaces attached by ZnO and Au NPs can serve as a platform upon which to build high performance electronics and photonic devices. In addition, we develop a novel approach for multicomponent symmetrical patterning metal/metal oxide nanoparticles on graphene involving region-specific plasma treatment, followed by region-selective substrate-enhanced electro-less deposition of Au nanoparticles and solution alkalization formation of Fe$_3$O$_4$ nanoparticles. We demonstrated that metal and metal nanoparticle functionalized graphene can enhance the sensing capability and selectivity for vapors. A miniaturized gas sensor array based on graphene exhibiting great room-temperature sensing properties for various selective vapors and the potential for cost-effective graphene-based sensors was developed. These functionalization methods for spatial micro- and nanopatterning of graphene chemistry in both covalent and noncovalent functionalization schemes can be crucial for further the enhancement of graphene-based devices.

Moreover, there is a pressing need to integrate graphene sheets into multidimensional and multifunctional systems with spatially well-defined configurations. The controlled assembly of graphene films still remains to be a challenge. Self-assembly has been recognized as an effective strategy for the bottom–up synthesis of 3D macrostructures using graphene sheets as building blocks. Here we report a novel, simplistic, and scalable methodology utilizing the Langmuir-Schaefer technique for the controlled transfer and assembly of graphene onto any substrate for hierarchical
organization into large-scale multi-dimensional functional materials for diverse applications. This novel method of graphene assembly can lead to research and development of next generation of high performance materials and structures by providing a scientific rationale that will enable bold innovative concepts for engineered hybrid structures.
Chapter 1

Introduction

Single sheets of exfoliated and reduced graphite oxide sheets were first isolated and characterized by transmission electron microscopy (TEM) and x-ray diffraction (XRD) by Bohem et al\textsuperscript{1} in 1961. Graphite oxide was dispersed and chemically reduced in alkaline media by hydrazine, H\textsubscript{2}S, and iron salts to produce thin flat sheets of carbon.\textsuperscript{1} Later in 1994, the term “graphene” was formally defined in a report to the International Union of Pure and Applied Chemistry (IUPAC).\textsuperscript{2} Since the 1940s, theoretical studies have recommended that individual layers of graphite could possess superior electronic properties.\textsuperscript{3} These theoretical predictions were deemed accurate when isolated graphite layers exhibited other exceptional properties such as charge carrier mobility (>200,000 cm\textsuperscript{2}/V.s), Young modulus (>0.5-1 TPa), and spring constants (1-5 N/m).\textsuperscript{3} These promising properties together with the unique two-dimensional structure and high specific surface area make graphene an excellent candidate for many diverse energy, sensors, and electronics applications.\textsuperscript{3} Despite being termed for a single layer of carbon atoms, isolated structures based on individual layers of carbon atoms are also referred to as “graphene”, although layer numbers are usually specified.\textsuperscript{3} The term “graphene” is also used in conjunction with the term “reduced graphene oxide” (rGO) which is prepared by way of first forming graphite oxide and then further exfoliated to render graphene oxide (GO).\textsuperscript{3} Graphite oxide and graphite intercalation compounds (G-ICs) have been thoroughly investigated as there are reports from the 1840s when scientists
demonstrated the insertion of acid or alkali metals in between graphite layers.\textsuperscript{3} Intercalation of graphite leads to increasing interlayer distance which dissociates the electronic coupling within the graphite layers.\textsuperscript{3} In order to investigate the molecular weight of graphite, Brodie in 1859 used sulfuric and nitric acids together with a strong oxidizing agent to intercalate and chemically oxidize the surface, forming graphite oxide.\textsuperscript{3} This novel chemical oxidation method has led researchers today to materialize the synthesis and isolation of G-ICs, graphite oxide, and GO to ultimately produce single layer rGO sheets.\textsuperscript{3} The intercalation and oxidation of graphite reduces the attractive forces within each graphite plane to eventually exfoliate using ultrasonication, thermal treatment, or other energy input processes.\textsuperscript{3}

Moreover, Morgan et al\textsuperscript{4} hypothesized that the adsorption of organic gas molecules (CO, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}) onto a crystalline platinum surface at high temperature can produce graphitic-like structures.\textsuperscript{3-4} After additional studies were conducted, it was determined that in high temperature conditions carbon dissolved and phase separated to form single or multi-layers on the surface of different transition metal crystal faces.\textsuperscript{3-4} Building on this, van Bommel et al\textsuperscript{5}, discovered single layer carbon flakes with graphene-like structure during the epitaxial sublimation of silicon carbide (0001) at high temperatures and ultrahigh vacuum. The number of layers of the graphene-like structure formed was dependent on the temperature used in the sublimation experiment.\textsuperscript{3,5}

In addition to the chemical and thermal methods, the micromechanical exfoliation of highly ordered pyrolytic graphite (HOPG) by oxygen plasma etching was first achieved by Lu et al\textsuperscript{6} in 1999 to produce multi-layers of graphene. A patterned photolithography substrate was used to selectively etch the HOPG using oxygen plasma
to produce graphitic islands which were then mechanically exfoliated to thin graphene films.\textsuperscript{3,6} However, it was not until in 2004 when Geim and Novoselov et al\textsuperscript{7} used the micromechanical exfoliation method to isolate and characterize single layers of graphene from HOPG.\textsuperscript{3,7} The graphene flakes were produced by physically pressing HOPG surface onto a SiO\textsubscript{2}/Si substrate and removed leaving single layers of graphene.\textsuperscript{3,7} Currently, the micromechanical exfoliation method is the most effective way to produce pristine defect-free graphene but scalability for large quantities remains to be a challenge.\textsuperscript{3,7}

Since the advancement in the science of extracting single-atom-thick crystallites from bulk graphite by Geim and Novoselov in 2004,\textsuperscript{7} the research on graphene has received considerable attention. This single atomic plane of graphite consisting of carbon hexagons is known to be one of the thinnest materials in the universe and one of the strongest ever measured.\textsuperscript{8-10} The charge carriers within graphene exhibit superior intrinsic mobility, zero effective mass, and can travel for micrometers without scattering at room temperature.\textsuperscript{7-11} It can sustain current densities six orders of magnitude higher than that of copper, with breakthrough thermal conductivity and stiffness, impermeability to gases while compensating for contradictory qualities such as brittleness and ductility.\textsuperscript{7-11} Graphene’s unique electronic spectrum consists of quasi-particles that lose their effective mass while propagating through the lattice.\textsuperscript{8-11} In comparison to conventional 2D electronic systems, the electron waves in graphene propagate within a single-atomic-thick layer making them more accessible to scanning probes and sensitive to high dielectric constant materials, semiconductors, and ferromagnetics.\textsuperscript{8-11} The unique charge diffusion properties of graphene include electron mobility of sub-micrometer distances without scattering, even through rough substrate surfaces and adsorbates.\textsuperscript{8-11} Charge carriers with
zero rest mass and lack of scattering together contribute to the quantum effects in graphene, which are evident even at room temperature.\textsuperscript{8-11} Due to the quasi-particles in its 2D membrane, unlike any other material, graphene shrinks with increasing temperature.\textsuperscript{7-11} The single-atom-thick film is also remarkably impermeable to gases, such as helium.\textsuperscript{7-11} Apart from the noteworthy electronic characteristics, graphene has also exhibited excellent mechanical and thermal properties similar to that of carbon nanotubes (CNTs) and graphite, which are both structurally made up of graphene sheets.\textsuperscript{8-11} Graphene exhibits a breaking strength of approximately 40 N/m, a Young’s modulus of 1.0 TPa, and can be elastically stretched 20\% more than any other crystal.\textsuperscript{8} At room temperature, it has a thermal conductivity of 5000 Wm\textsuperscript{-1}K\textsuperscript{-1}.\textsuperscript{8} Moreover, these physiochemical properties make graphene extremely attractive as electron emitters in field emission displays, scanning probe microscopy tips, supercapacitors, batteries, interconnects, nanoelectromechanical systems, reinforcement fillers in nanocomposite materials, as well as actuators and sensors.\textsuperscript{8,12-13} Furthermore, the use of graphene for most of the above-mentioned and many other applications often requires the incorporation of individual graphene sheets into various device elements at the molecular level. Carbon nanomaterials have been the focus for advancements in lithium batteries, supercapacitors, and fuel cells. Recently, Gong et al\textsuperscript{15} and Qu et al\textsuperscript{16} have reported breakthrough advancements in developing carbon-based metal-free electrocatalysts for fuel cells. In addition, Stoller et al\textsuperscript{17} developed innovative graphene-based supercapacitors where graphene sheets move in response to electrolytes resulting in a very high weight-specific capacitance.
References


Functionalization and Assembly of Graphene

1-1.1. Functionalization of Graphene

While being comprised of only a single layer of carbon atoms and being both flexible and transparent, graphene is the strongest, stiffest, and best conductor of heat and electricity to ever have been discovered.$^{1-3}$ The zero band-gap of graphene and lack of reactivity in its pristine state has led to researchers developing numerous functionalization methods.$^{1-3}$ The functionalization of graphene allows for solution processability, selective modification of properties, and incorporation with other nanostructures for device applications. Since graphite is naturally hydrophobic and composed of individually \( \pi-\pi \) stacked graphene layers, it is important to develop functionalization methods to disperse graphene and to alter its properties. Even at room temperature, graphene’s electrical conductivity is unmanageable which can be detrimental for specific sensors and electronics performance.$^1$ In order to increase graphene’s competitive potential in device applications, such as transistors, optoelectronics, sensors, and biomedical applications, there has been a focus on developing functionalization methods to overcome its physical limitations.$^{1-3}$ The deficiency of a band gap in graphene is one of the main problems to address for transistor applications as the on-off ratio is crucial for functionality.$^4$ However, graphene’s band-gap can be tailored through electronic coupling when grown epitaxially on silicon carbide.$^4$ Although externally engineering its band gap through applied gate voltages or substrates is plausible, there still remains limitations to controlling the on-off ratio.$^{3-4}$ Another approach to tailor the band gap of graphene has been the production of
semiconducting graphene nanoribbons with an edge arm-chair conformation. In spite of these efforts, this method of edge modification and structure control still remains a challenge as some of the graphene can adopt a disordered edge structure. Therefore, methods of chemical functionalization of graphene have been employed to control its electronic properties. Moreover, it is also possible to regulate both the type and concentration of charge carriers by doping, which increases the carrier concentration to open the band gap of graphene. Functionalization methods include reactions of graphene and its pre-cursors with organic and inorganic molecules and surface chemical modification of graphene through reactions of numerous covalent and noncovalent interactions. Methods of covalent functionalization include the attachment of organic functional groups such as free radicals and dienophiles (substituted alkenes) onto pristine graphene and through the chemistry of oxygen groups in graphene oxide. In addition, the covalent binding of hydrogen and halogens to graphene has also been demonstrated. Covalently bonding to electron-withdrawing or electron-donating functional groups can induce p-doping or n-doping in graphene, respectively. Thus, a p-n junction can selectively be formed at interface between the selectively modified p-doped and n-doped region of graphene. On the other hand, p-doping can also be induced by bonding to metals with higher electron affinity, such as gold. Alternatively, it has also been demonstrated that graphene can be non-covalently functionalized without effecting the extended π-conjugated surface network. For example, doping with alkaline metals can result in the formation of an ionic bond and the donation of electrons to the conduction band of graphene. These versatile methods of functionalization altering the properties of graphene have been the focus of researchers to incorporate different nanostructures.
with graphene such as metals, metal oxides, quantum dots, and polymers for superior properties and applicability.\textsuperscript{1-4} Therefore, controlled chemical modification could be a very useful approach to various multifunctional systems critical to applications such as nanoelectronics, nanophotonics, nanosensors, and nanoenergy systems.

**Figure 1-1:** Functionalization methods of graphene. (a) edge-functionalization, (b) basal-plane-functionalization, (c) noncovalent adsorption on the basal plane, (d) asymmetrical functionalization of the basal plane, and (e) self-assembling of functionalized graphene sheets. (B) Chemical structure of graphene oxide

1-1.2. Covalent Functionalization of Graphene

The most common methods of synthesis, exfoliation, and dispersability of graphene are in principle based on either a top-down or bottom-up approach for materials design. The exfoliation of graphite, both chemically and mechanically, are examples of the top-down approach where graphite is broken down to its sub-component level, thus
producing graphene (Figure 2-1). On the other hand, chemical vapor deposition and 
expitaxial growth are the most common techniques employed for the bottom-up synthesis 
of graphene. It has been recently shown by Hamilton et al and Bourlinos et al that it is 
possible for the isolation of defect-limited single layer and few-layer graphenes by the 
dispersion of graphite in organic solvents. The dispersion of graphene in various organic 
solvents provides the opportunity of functionalization with different chemical moieties 
and the construction of multi-functional nanocomposites.

**Figure 1-2:** Schematic illustration of the top down approach of the exfoliation of graphite 
to isolate individual graphene sheets. Figure adapted from ref. 2.

Graphene-based nanocomposites have led to the many promising energy and 
environment applications incorporating functionalized graphene as building-blocks for 
materials and device design. In order to selectively functionalize graphene, other 
nanostructures and polymers are a commonly used. Many well-designed multi-
functional nanocomposites have been developed for photovoltaic and electrochemical 
energy storage and conversion devices together with environmental applications such as 
purification and removal of metal ions and pollutants and gas detection. The covalent
bonding of organic molecules onto graphene is generally achieved through the following methods: (1) covalent bonds established between the free radicals or dienophiles and C=C of pristine graphene and (2) formation of covalent bonds between the organic functional groups and the oxygen functional groups in graphene oxide.3

Figure 1-3: Schematic illustration of the covalent attachment alkyl nitrene chains onto C-C bond of graphene. Alkylazides with hexyl, dodecyl, hydroxylundecanyl, and carboxy-undecanyl functional groups can covalently bond to graphene leaving a hydroxylated surface. Figure adapted from ref. 3.

Highly reactive free radicals covalently bond to the sp2 carbon atom in graphene through chemical functionalization with diazonium salts and nitrophenyls to engineer the band gap of graphene.8 Functionalization of graphene with diazonium salts leads to the formation of hydroxylated aryl groups which have been shown to facilitate the polymerization of polystyrene by atomic transfer radical polymerization and the covalently bonded polymer chains on graphene (Figure 2-2).4,8 Photochemically induced reactions with benzoyl peroxide and graphene also produce phenyl radicals which react
with the sp2 carbon atoms to form a covalent bond. In addition to free radical reactions with sp2 carbon atoms of graphene, dienophiles have been shown to covalently bond to the carbon-carbon bond of graphene. The dispersability of graphene in organic solvents is critical to enable the formation of different substituted cycloaddition systems such as those based on azomethineylide and nitrene. The cycloaddition reactions of graphene with dienophiles allows for the covalent linkage of different functional groups and polymers with improved chemical and thermal properties compared to as synthesized graphene oxide.

Furthermore, the most facile solution processing method for covalent functionalization of graphene is the acid oxidation of graphite to introduce oxygenated functional groups such as carboxyl, epoxy, and hydroxyl groups producing graphite oxide. The resultant single sheets of graphene oxide are dispersed through the electrostatic repulsion and solvation from the negatively charged oxygen functional groups. The main disadvantage to the solution oxidation method is that it is difficult to control the degree of oxidation making it further challenging for control of subsequent functionalization to the oxygen groups on the basal plane. The resulting dispersed graphene oxide sheets with oxygen groups on the basal plane are insulating. Graphene oxide has fluorescent properties due to the optical gap arising from the defects altering the π network. The optical properties of graphene oxide can be modified by controlling the degree of reduction or by further functionalization. Due to the potential for scalable mass production of graphene oxide, there have been efforts to remove oxygen and reduce the graphene oxide sheets. The most common methods of reduction include high temperature annealing and chemical routes to rehybridize the sp3 carbon atoms to sp2
carbon without aromatic structure and surface defects.\textsuperscript{3-4} Despite reduction methods, there still remains an acute amount of oxygenated groups and surface defects on graphene.\textsuperscript{3} Properties such as electrical conductivity are effected by the number of surface defects on the graphene sheets.\textsuperscript{3} Therefore, it is often identified which type of graphene is being studied whether its chemically reduced graphene, chemically converted graphene, thermally reduced graphene in order to differentiate it from that of pristine graphene.\textsuperscript{3}

Chemically, the most common method to link moieties to the oxygen functional groups is through the acylation reaction between the carboxylic acid groups of graphene oxide and octadecylamine to incorporate long alkyl chains onto graphene oxide.\textsuperscript{4} Through the acylation reaction, the carboxylic acid groups can also be bonded to the amine-functionalized molecules through either the surface condensation or thiolization reactions.\textsuperscript{3-4} Moreover, nucleophilic ring-opening reactions can occur between epoxy groups of graphene oxide and the amine-terminated molecules.\textsuperscript{4}

\textbf{1-1.3. Non-covalent Functionalization of Graphene}

The non-covalent functionalization of graphene is accomplished through van der Waals forces or $\pi$-$\pi$ stacking of aromatic molecules on graphene without effecting its $\pi$ conjugated structure.\textsuperscript{1-4} As opposed to covalent functionalization methods, non-covalent functionalization eliminates the formation of surface defects on graphene without effecting its electronic structure.\textsuperscript{3-4} Many organic molecules-graphene hybrid structures have been constructed through $\pi$-$\pi$ stacking of both graphene and graphene oxide.\textsuperscript{4} Specifically, pyrene-based molecules have been demonstrated to have strong bonding with graphene’s basal plane through $\pi$-$\pi$ interactions which enables the dispersion of
graphene in aqueous solutions.\(^4\) Similar to how the non-covalent intermolecular interactions arising from \(\pi\) bonding systems stabilize proteins, DNA-protein complexes, enzyme-drug interactions, organic supermolecular structures, and nanomaterials, these \(\pi\) bonding systems are significant to graphene-based nanomaterial design and fabrication.\(^3\) Small changes in the electronic structure of the \(\pi\) bonding systems can impact the properties and function of the graphene-based nanosystem.\(^3\) The types of \(\pi\) bonding complexes formed include nonpolar gas-\(\pi\) interactions, hydrogen-\(\pi\) interactions, \(\pi-\pi\) interactions, cation-\(\pi\) interactions, and anion-\(\pi\) interactions where the strength of these interactions is dependent on the combination of attractive forces comprising of electrostatic, dispersive, and inductive interactions and exchange repulsion interactions.\(^3\) In nonpolar gas-\(\pi\) interactions, depending on the polarity of the counter molecule (gas molecule) either electrostatic or intermolecular dispersion forces predominate.\(^3\) In most cases, the hydrogen-\(\pi\) interactions involve hydrogen bonding that occurs due to the polarization of the \(\pi\)-electron network where dispersion forces are determined by the number of electrons involved in the interaction.\(^3\) The bonding of graphene with other conjugated molecules is governed by \(\pi-\pi\) interactions which form a bond through intermolecular dispersion interactions when both have similar electron densities despite being negatively charged.\(^3\) Nevertheless, when there is a difference in the number of electrons the two components are bonded through induction interactions.\(^3-4\) The \(\pi-\pi\) bond is an important means of non-covalent interactions for utilizing graphene in developing supermolecular self-assembled organic nanostructures.\(^3\) In addition to interactions with organic molecules, metal cations also bond through electrostatic and induction forces to the \(\pi\) network.\(^3\) The interaction of cations with the \(\pi\)-complexes is dominated by a larger
electrostatic energy than that of cation-water interactions which is significant for graphene-based nanomaterial design considering that the total interaction energy makes it viable for dielectrics. Unlike in metal cation-π-complexes, organic cation and anions interact with the π network with much weaker binding energies. Therefore, different donor and acceptor aromatic molecules can bond with graphene through the π-π interaction to engineer the electron density.

1-1.4. Nanoparticle Functionalization of Graphene

The superior inherent properties of graphene when combined with the properties of metal and metal oxide nanoparticles can lead to many promising materials for energy storage and conversion and optoelectronic applications. The large active surface area per unit of mass of pristine graphene makes it an ultimate substrate for dispersing nanoparticles. The incorporation of noble metals such as Pt, Au, Ag, Rh, and Pd onto graphene has led to the development of nanocomposites for catalytic, magnetic, and optoelectronic applications. Generally, the nanoparticles are made starting with a metal salt precursor which are reduced in solution containing dispersed graphene oxide, reduced graphene oxide, or pristine graphene. Luo et al have demonstrated that thermally evaporated gold on graphene can be annealed to form gold nanoparticles (3-30 nm in diameter) (Figure 2-3). Recently, it has been shown by Granatier et al that palladium has the higher inclination to interact and bind to graphene than gold and silver through a covalent bond. Meanwhile, Muszynski et al confirmed that increasing concentration of graphene sheets in solution led to the deposition of more uniform gold nanoparticles on the graphene surface. Simultaneous reduction of graphene oxide and
HAuCl₄ to form gold nanoparticles on the surface of graphene was achieved by Vinodgopal et al. through high-frequency ultrasound treatment of graphene oxide dispersed with poly (ethylene glycol) generating highly reactive organic free radicals to reduce both graphene oxide and gold ions in solution. Hassan et al. developed a general approach to the simultaneous reduction of graphene oxide and deposition of metal nanoparticles with multiple reducing agents by microwave irradiation where the differences in the dielectric constants of the reactants and the solvent creates a transfer of energy and heat generation upon irradiation.

Figure 1-4: Scanning electron microscope (SEM) images of gold nanoparticles deposited on (a) graphite and (B) single layer graphene. The size and shape of the gold nanoparticles varied with graphene layer thickness. Figure adapted from ref. 11.

Moreover, metal oxide nanoparticles have also been incorporated in nanomaterial device design for catalytic, energy storage and conversion, optoelectronics, and flexible electronics applications. Metal oxides such as tin oxide (SnO₂), manganese oxide (Mn₃O₄), cobalt oxide (Co₃O₄), and titanium oxide (TiO₂) dispersed on carbon supported
substrates have shown high charge capacity and cyclic performance as anodes in Li-ion battery systems.\textsuperscript{2-3} The insertion of graphene sheets between SnO\textsubscript{2} nanoparticles prolongs the life time of the anode during the charge-discharge cycles by minimizing the volume increase during intercalation and the physical wear.\textsuperscript{3} Bain et al\textsuperscript{16} showed the alkaline hydrolysis of SnCl\textsubscript{4} with reduced graphene oxide to render SnO\textsubscript{2} nanoparticles on reduced graphene oxide sheets to marginally decrease in charge capacity as a Li-ion battery anode after 30 cycles.\textsuperscript{3,16} An important factor in enhancing the charge capacity is the dispersion and loading of metal oxide nanoparticles on graphene.\textsuperscript{3} Zhang and coworkers\textsuperscript{17} showed that the oxygen groups can serve as supports for Sn\textsuperscript{4+} cations through electrostatic interactions upon dispersion of graphene oxide in SnCl\textsubscript{4}.\textsuperscript{3,17} Nanocomposites with other metal oxides such as MnO\textsubscript{2}, CuO, Co\textsubscript{3}O\textsubscript{4}, CoO, Fe\textsubscript{3}O\textsubscript{4}, TiO\textsubscript{2}, and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and graphene or reduced graphene oxide have shown improved Li-ion battery anode performance.\textsuperscript{3} Additionally, graphene/TiO\textsubscript{2} nanocomposites have received considerable attention for energy storage and photocatalysis applications.\textsuperscript{3-4} Wang et al\textsuperscript{18} conveyed that surfactant-assisted self-assembly of graphene and TiO\textsubscript{2} nanoparticles improve the Li ion insertion/extraction kinetics even at high charge-discharge rates.\textsuperscript{3,18} This demonstrates the effectiveness of using functionalized graphene sheets as a conductive electrode material for energy storage.\textsuperscript{18} Likewise, TiO\textsubscript{2}-supported reduced graphene oxide has been investigated for photocatalytic water splitting properties, specifically to reduce the recombination of photogenerated electron-hole pairs.\textsuperscript{3} As shown by Zhang et al\textsuperscript{19}, the increased conductivity of reduced graphene oxide enhances the photocleaving of water while disrupting the recombination of the photogenerated electrons from TiO\textsubscript{2} holes leading to higher water splitting efficiency.\textsuperscript{3,19} Utilizing its
photocatalytic properties, TiO$_2$ nanoparticles deposited on graphene act as charge carriers upon UV irradiation to reduce graphene oxide as evidenced by a color change from dark brown to black.$^{3,20}$ Lightcap et al.$^{21}$ demonstrated graphene functionalized with TiO$_2$ can also serve as a conduction pathway for the formation of silver nanoparticles.$^{21}$ The photogenerated electrons upon UV irradiation of TiO$_2$ conduct through graphene before reducing Ag$^+$ to Ag$^0$ nanoparticles.$^{21}$ Along with TiO$_2$, researchers have examined other semiconducting metal oxides such as ZnO nanoparticles which exhibit photocatalytic properties upon UV irradiation when functionalized with graphene oxide.$^{3-4}$ The UV irradiation of the ZnO/graphene oxide nanocomposite partially reduces the graphene oxide when the photogenerated electrons from the excited state of ZnO nanoparticles are transferred to the graphene oxide.$^{22}$ Furthermore, magnetic nanoparticles such as magnetite (Fe$_3$O$_4$) are deposited on graphene oxide by the coprecipitation of Fe$^{3+}$/Fe$^{2+}$ through the addition of ammonia solution to aqueous FeCl$_3$, FeCl$_2$, and graphene oxide.$^{3,23}$

1-1.5. Assembly of Graphene

The site-selective functionalization of graphene is important for the region-specific connection of graphene sheets into self-assembled systems with well-defined structures for practical applications.$^{24-25}$ The controlled functionalization of graphene sheets at the molecular level still remains a big challenge. There is a pressing need to integrate graphene sheets into multidimensional and multifunctional systems with spatially well-defined configurations. One focus of researchers today has been fabrication of three-dimensional (3D) architectures comprising graphene sheets with inherent
excellent intrinsic properties. However, there remains difficulty of integrating two-dimensional graphene sheets into macroscopic structures with precise connection of individual graphene sheets at the molecular level.\textsuperscript{24-25} Self-assembly has been recognized as an effective strategy for the bottom–up synthesis of 3D macrostructures using graphene sheets as building blocks. Common methods of micro-scale graphene-based uniform film assembly include layer-by-layer (LBL) assembly, vacuum assisted flocculation (VAF), and spin-coating.\textsuperscript{26} The most facile technique of assembly remains to be the consecutive LBL technique through either electrostatic interactions, hydrogen bonding, van der Waals forces, or electron exchange attractive forces of the different components (Figure 2-4).\textsuperscript{26} In addition to these techniques, spray-coating, Langmuir-Blodgett (LB) assembly, dip-coating, and solution blending have been demonstrated to develop layered graphene films.\textsuperscript{26} Nevertheless, the shortcoming of these graphene solution based assembly techniques is that it is difficult to selectively control thickness of the assembled graphene sheets.
Figure 1-5: (a) Crystal structure of graphene, (b) Schematic of the LBL assembly technique showing the sequential electrostatic self-assembly of oppositely charged structures onto the surface to construct multi-layered films, and (c) Chemical structure of graphene oxide. Figure adapted from ref. 26.

With increasing demand to produce large areas of high-quality layer-controlled graphene films, researchers have developed various methods of synthesis including the epitaxial growth on silicon carbide (SiC) and chemical vapor deposition (CVD) on metal substrates such as nickel (Ni) and copper (Cu). Current technology includes polymer assisted transfer and assembly of graphene films by the removal of the underlying growth substrate through chemical etching and selectively transferring the polymer/graphene...
composite film onto any substrate before the removal of the polymer. This technique enables for easy processing and handling of uniform graphene films for assembly. Bae and coworkers\textsuperscript{29} used a polymer coated adhesive layer on the graphene/Cu in a roller technique to produce high quality 30 inch transparent graphene films. Similarly, Martins et al\textsuperscript{28} demonstrated a polymer assisted lamination technique to selectively transfer and assembly graphene onto arbitrary substrates (Figure 2-5). The polymer assisted transfer and assembly of graphene has been critical for optoelectronics and microelectronics research since it enables the controlled deposition of monolayer graphene onto selective substrates for device incorporation. However, the disadvantage of this technology is the susceptibility for chemical contamination of graphene therefore altering its intrinsic properties. The chemical etching of copper and the lack of complete removal of the polymer residue without high thermal treatment can change the electronic properties and band gap structure.\textsuperscript{27} Recently, Lin et al\textsuperscript{27} was first to develop a non-polymer assisted transfer technique to assembly graphene onto substrates by dilution of the copper etchant solution before lowering the free-standing graphene film to ultimately deposit on substrates. Therefore, both the polymer-assisted and non-polymer assisted transfer and assembly of graphene are both advancements in graphene-based device fabrication as they act as a platform to fully utilize the excellent inherent properties of graphene in a controlled and selective manner.
Figure 1-6: Schematic of polymer-assisted roller process of graphene/Cu films where graphene/Cu samples are physically adhered through two rollers before the copper is chemically etched away rendering graphene on a polymer support film. Figure adapted from ref. 29.

References


Energy and Sensing Applications

1-2.1. Carbon Nanomaterials for Energy Applications

Energy remains to be the primary focus to address the challenges of finite fossil fuels and global warming.\textsuperscript{1-4} The development of carbon nanomaterials is the key for advancements in energy conversion and storage.\textsuperscript{1-4} Their unique mechanical, electrical, and optical properties have attracted a vast interest as potential energy storage and conversion devices.\textsuperscript{1-4} Moreover, utilizing properties such as high surface area and surface-to-volume ratio, carbon-based electrocatalysts and electrodes for lithium batteries, fuel cells, and supercapacitors are the most promising candidates in terms of energy and power densities.\textsuperscript{1-4} New multifunctional materials provide a scientific rationale that will enable innovative concepts for engineered carbon-based nanostructures to be fabricated and characterized for energy storage and conversion applications. Carbon-based nanomaterials have optimized supercapacitor performance by increasing the surface area and enhancing electrolyte accessibility thus leading to increased capacitance and power delivery. Moreover, carbon nanomaterials can also reduce the use of precious metal catalysts by functioning as nanocatalysts with enhanced activity and performance in fuel cell applications. A strong fundamental understanding in the design, synthesis, and assembly of new carbon nanostructured materials is critical in underpinning the development of novel technologies as well as providing opportunities
for exploiting new scientific principles. With the demand of clean and sustainable energy sources, new nanostructured materials are being developed to provide cost-effective and environmentally safe solutions to the world’s energy problems. Developments in the area of alternative fuels and energy storage technologies such as advanced batteries, fuel cells, supercapacitors, and biofuels are emerging as strong potential replacements for petroleum-based sources. Furthermore, carbon nanomaterial research will strengthen the capability for the development of new, cost-efficient, and environmentally friendly energy conversion and storage systems to address the current challenges of energy demands, finite resources, and ecological concerns.

Figure 1-7: Schematic representation of the operational principle of a (a) supercapacitor and (b) lithium ion battery for energy storage.
1-2.2. Energy Storage

Compared to that of traditional rechargeable batteries such as lead acid and Ni-Cd batteries, lithium-ion batteries are a new technology in small rechargeable batteries due to higher voltage, higher energy density, and longer cycle life.\textsuperscript{2} Despite being commercially successful, there are performance limits for the electrode and electrolyte system in lithium batteries.\textsuperscript{1} Commercial batteries consist of micrometer-sized electrode materials which are restricted by kinetics, lithium-ion intercalation capacities, and structural stability.\textsuperscript{2} In order to address these performance limits, nanomaterials are being considered to develop a new generation of rechargeable lithium batteries for clean energy storage.\textsuperscript{1} Nanostructured anode and cathode materials for lithium-ion batteries have been the recent focus to further understand the nanometer-size effects on energy capacity and storage.\textsuperscript{2} The first example of lithium storage in a carbon-based material was lithium-intercalated graphite.\textsuperscript{3} It consists of a lithium-ion intercalated negative electrode (graphite) and a lithium-ion intercalated positive electrode (lithium metal oxide, LiCoO\textsubscript{2}) which are separated by a lithium-ion conducting electrolyte such as a solution of LiPF\textsubscript{6} in ethylene carbonate-diethylcarbonate.\textsuperscript{1} Upon charging, Li ions are evoked from the cathode and inserted into the anode.\textsuperscript{2} While discharging the Li ions are released by the anode and absorbed again by the cathode.\textsuperscript{2} Using nanoelectrodes for lithium batteries can better accommodate the strain produced from lithium insertion and removal, thus improving cycle life.\textsuperscript{1} The higher electrode/electrolyte contact area leads to higher charge/discharge rates while eliminating the production of new reactions with bulk materials.\textsuperscript{1} The nanoelectrodes facilitate short path lengths for electronic and Li\textsuperscript{+} transport allowing for battery operation at low electronic and Li\textsuperscript{+} conductivity or at
higher power. In nanometer-sized systems, the distances over which Li\(^+\) must diffuse are decreased therefore, many lithium ions are absorbed and stored without deteriorating the electrode. Since the electroactivity for Li insertion is increased, the rate capability is enhanced resulting in higher power density due to the shorter transport distances for e\(^-\) and Li\(^+\) and larger electrode/electrolyte contact area. Moreover, the stability of the nanoelectrode is dependent on the structural transition to thermodynamically undesirable structures. In order to eliminate these transitions, nanoparticles with radius (r\(_p\)) larger than the crucial nucleation radius (r\(_c\)) should be used. Therefore, these nanoparticles can more readily cope with the structural changes that accompany during the insertion and extraction of Li. The charge accommodation in nanoparticles occurs at or near the surface and the smaller the particle size, the more the number of atoms at the surface. As a result, there is less of a need for Li\(^+\) diffusion in the solid phase which as a result increases the charge and discharge rate of the cathode and lessens the volumetric changes and lattice stresses caused by the cyclic insertion and extraction of Li. The development of nanoelectrodes can lead to novel Li-storage mechanisms resulting in high capacities, rechargeability, and applicability to a variety of battery systems. The mechanisms are associated with the reversible in situ formation and decomposition of Li\(_\gamma\)X (where X = O, S, F, or N) is described by the following equation:

\[
MX + \gamma\text{Li}^+ + \gamma\text{e}^- \leftrightarrow \text{Li}_\gamma \text{X} + M
\]

Where M = Fe, Co, Ni, Cr, Mn, Cu. In addition to the conversion mechanism, the interfacial Li storage mechanism model elucidates the extra storage capacity in nanoscale
transition metal oxides at low potential. A charge separation is formed from Li⁺ ions being stored on the ionic conductive side of the interface (LiₓX) while the electrons (e⁻) are confined on the metallic side (M). Since the interfacial area of LiₓX/M is very large, the storage mechanism can be applicable to both supercapacitors and battery electrodes without compromising rate and capacity. On a nanometer scale, Li surface storage may directly correlate with overall capacity since the overall mechanism is more energetically favorable for nanoparticle insertion rather than bulk.

1-2.3. Li-ion Batteries

Numerous anode and cathode materials have been considered for different types of lithium-ion batteries. The desired characteristics for anode materials include a high capacity for lithium, high chemical potential of the lithium in the lithiated compound, fast kinetics of Li insertion and extraction, and low volume or structural changes during Li insertion and extraction. Metals and semiconductors based on tin alloys, silicon, and inter-metallic compounds are the most common Li storage anode materials. Since the use of metallic lithium anodes in batteries was proven to be unsafe as dendrite formation can cause short circuits, lithium-intercalated-graphite as a new alternative anode for lithium storage in a carbon-based material was discovered. These lithium-intercalated-graphite materials with strong covalent bonds, large bandwidths, and low ionicity can weakly bind lithium for large capacities at high lithium chemical potentials. The carbon-based lithium materials also offer enhanced electron and lithium ion mobility leading to a high chemical diffusion coefficient of lithium. The high electronic in-plane conductivity of carbon is attributed to its delocalized π-bonds. As a result, the transport of electronic
carriers from the current collector to the Li\textsuperscript{+} contact electrolyte is fast, thus reducing the solid state diffusion distance of Li.\textsuperscript{3} The strength of the sp\textsuperscript{2} type C-C bonds from the strong orbital overlap in the first octet allows for the accommodation of stable nanostructures.\textsuperscript{3} Different carbon-based materials including fullerenes, nanotubes, diamond, and graphene have been investigated as lithium storage materials.\textsuperscript{3} For example, it has been reported that carbon-based structures with a large number of graphene units have a large capacity for Li.\textsuperscript{3} Li can be incorporated into all carbon-based structures by addition or substitution reactions.\textsuperscript{3} Furthermore, carbon-based materials have become the focus as anodes for lithium batteries due to its characteristics of storage capacity, charge and discharge performance, high electronic conductivity, and extensive lithium diffusion capabilities.\textsuperscript{3} Specifically, graphene has been the recent focus for energy storage applications due to its high theoretical surface area of 2630 m\textsuperscript{2} g\textsuperscript{-1}.\textsuperscript{5} The specific capacity of lithium batteries was shown to increase to 540 mA hg\textsuperscript{-1} from 372 mA hg\textsuperscript{-1} when graphene sheet-based electrodes were used instead of the standard graphite-based electrodes with intercalated Li\textsuperscript{+} in the graphite lattice.\textsuperscript{5} Incorporating carbon nanotubes (CNTs) or C\textsubscript{60} molecules as spacers to prevent aggregate stacking of graphene sheets increased the specific capacity even more to 730 mA hg\textsuperscript{-1} and 784 mA hg\textsuperscript{-1}, respectively.\textsuperscript{5} It has also been reported that the high-rate-discharge capability of lithium ion battery anodes is attributed to the nano-sized pores in graphene sheets.\textsuperscript{5}

1-2.4. Supercapacitors

Supercapacitors support increased loads of voltage in various systems such as portable equipment and electric vehicles.\textsuperscript{1} Similar to a battery, these devices consist of
two electrodes, a separator, and electrolyte. A typical unit cell of a supercapacitor
consists of two porous carbon electrodes which are isolated from electrical contact by a
porous separator. Metal foil current collectors or carbon-based polymer composites are
used to conduct current from the electrodes. With the electrodes and separator immersed
in a electrolyte, ionic current flows between the electrodes without discharging the cell.
Despite sacrificing energy density, supercapacitors are designed for high power and long
cycle life of about a thousand fold of a typical battery. The advantages of
supercapacitors compared to conventional energy storage devices include high power,
prolonged cycle life, wide thermal operating range, low weight, package flexibility, and
low maintenance. Supercapacitors can be categorized into either electrical double-layer
capacitors (EDLC) or redox supercapacitors. EDLCs are non-faradic electrical energy
storage devices which store and release energy by charge separation at the
electrochemical interface between an electrode and electrolyte. The cycle-life of EDLCs
is unlimited because it only operates on electrostatic surface-charge buildup. These
supercapacitors have a very high energy density compared to regular dielectric capacitors
since the amount of energy stored is inversely proportional to the double-layer thickness.
EDLCs store and deliver a larger quantity of charge at higher power than that of
rechargeable batteries. However, redox supercapacitors involve a large pseudo-
capacitance from rapid faradic charges and redox reactions using conducting polymer
electrode materials and metal oxides. The amount of charge stored in redox capacitors
is proportional to the voltage. In theory, redox supercapacitors have greater energy
density than EDLCs, however, faradic changes from the phase changes within the
electrode hinder cycle life and power density. The focus in developing supercapacitor
materials has been on nanostructured carbons and the development of high-surface-area activated carbon electrodes to increase overall capacitance and conductivity.¹ Specifically, activated carbon, aerogels, CNTs, mesoporous carbon, nanotemplates, and carbon-derived carbons have all been explored as porous carbon electrode materials in supercapacitors.¹,⁶,⁷ For example, carbon aerogels have been investigated to replace standard carbon fiber electrodes.¹ The low ionic and electronic charging resistance in carbon aerogel electrodes improves the overall capacitance and cyclability.¹ In addition to aerogels, carbon nanotubes have also been studied as new supercapacitor electrode materials. Generally, properties such as high specific surface area and pore-size distribution of the carbon nanomaterials make them ideal for use as supercapacitor electrode materials with high capacitance and high electrolyte accessibility, respectively.¹ Recently, graphene has emerged as an ideal material for supercapacitor electrodes because of its high theoretical surface area.⁵ It has been reported that exfoliated graphene has a higher specific capacitance and energy density than that of CNTs.⁷ For instance, Stoller et al. showed that properties such as large and accessible surface area and high conductivity of chemically modified graphene (CMG) make it a hopeful candidate for EDLC supercapacitors.⁶ The weight-specific capacitance of chemically modified graphene was reported to be 1352 F g⁻¹.⁵ An advantage for supercapacitors incorporating CMG-sheet based electrodes is that graphene sheets adjust their position based on the electrolyte instead of depending on the highly porous structure of activated carbon in a sold stationary support for electrolyte transfer.⁵ CMG sheets can physically move to adjust depending on the size and spatial distribution of the electrolyte.⁶ Since incorporating CMG sheets eliminates the need for any conductive fillers, CMG-based
electrode materials can be made thicker than commercial electrodes. As a result, this improves the electrode to collector/separator ratio, thus increasing the overall energy density of the supercapacitor. In order to develop graphene-based electrodes for supercapacitors, it is important to control the aggregation of graphene sheets which can lead to a loss of surface area for energy storage. Correspondingly, recently it has been shown that using CNTs to physically separate the graphene sheets can preserve the surface area. In addition, self-assembly of multi-walled carbon nanotubes (MWNTs) and modified graphene sheets can be used to develop hybrid carbon films with well-defined nanoscale pores for supercapacitors. These hybrid interconnected carbon structure films facilitate fast ion diffusion through the nanoscale pores, thus increasing the specific capacity.

1-2.5. Fuel Cells

The demands for portable power sources have consequently increased research in the distribution and remote generation of electrical energy in fuel cells. Recent focus has been on the development of nanomaterials for applications in low temperature (T < 200 °C) fuel cells, the development and dispersion of valuable and non-valuable catalysts, fuel reformation and hydrogen storage, and the fabrication of membrane-electrode assemblies (MEA). The most active catalyst materials for low-temperature fuel cells fed with hydrogen and methanol are platinum-based catalysts. However, the continuing challenge for fuel cell performance is to reduce noble metal catalysts such as Pt, Au, and Ru loading and develop processes for high-volume MEA fabrication without effecting the MEA performance in order to lower the overall cost. In general, chemical energy is
converted directly into electricity in a fuel cell when hydrogen gas is purged onto the anode causing hydrogen to split into electrons and protons.\textsuperscript{9} The protons diffuse through the cell towards the cathode while the electrons flow out of the anode generating electrical power.\textsuperscript{9} Both the protons and electrons combine at the cathode with oxygen to form water.\textsuperscript{9} Despite the favorable H\textsubscript{2} oxidation kinetics reducing the amount Pt catalyst at the anode, the slow oxygen reduction reaction (ORR) on the Pt cathode is the main step that determines the energy conversion efficiency of a fuel cell.\textsuperscript{9} The ORR controls the performance of a fuel cell through either (a) a four electron process involving combining oxygen with electrons and protons together with the oxidation on the anode and producing water as an end-product or (b) a less efficient two electron process producing hydrogen peroxide ions as intermediates.\textsuperscript{10} In essence, noble metals catalysts are used in fuel cells to accelerate the ORR at the cathode.\textsuperscript{9} Nevertheless, metal based catalysts have many competitive disadvantages other than cost such as low selectivity, inadequate durability, and damaging environmental effects from catalysts residues and unfavorable products from side reactions.\textsuperscript{9} For instance, despite being the best catalyst for ORR, Pt-based electrodes are limited by their vulnerability to time-dependent drift and carbon monoxide (CO) deactivation.\textsuperscript{11} The high cost and scarce natural reserves of Pt have prevented large-scale production of fuel cells for commercial applications.\textsuperscript{9} Therefore, it is advantageous to develop cost-effective and high-performance metal-free catalysts.\textsuperscript{9} Due to their surface properties, environmental compatibility, and corrosion resistance, carbon nanomaterials can function as metal-free catalysts with enhanced performance.\textsuperscript{9} Incorporating surface heteroatoms such as nitrogen into these carbon
nanomaterials can manipulate and alter electrons to form advantageous electronic structures for catalytic reactions.9

1-2.5.1: Carbon Electrocatalysts

Nitrogen-containing precursors can be used for in-situ doping or post-treatment doping of carbon nanostructures.9 Post-doping of carbon nanomaterials results in surface functionalization without changing their bulk properties.9 However, in-situ doping during the synthesis of carbon nanomaterials homogenously incorporates nitrogen atoms within the carbon structure.9 N-doped carbon nanomaterials from in-situ doping are high-surface-area porous carbon nanomaterials with high nitrogen concentration.9 N-doped carbon nanomaterials can be synthesized by isothermal cyclotrimerization reactions of carbonitriles.9 Arc-discharge, laser ablation, or chemical vapor deposition (CVD) can be also used to produce N-doped CNTs or carbon nanofibers (CNFs).9 Using substrate-assisted growth with and without a template, ordered N-doped CNTs and CNFs have been developed to facilitate electron conduction and mass transport as metal-free catalysts for processes such as for ORR at the cathode of fuel cells.9 Recently, research focused mainly on reducing or replacing Pt-based electrodes in fuel cells has led to the development of novel ORR Pt alloy electrocatalysts, transition metal chalcogenides, CNT-supported metal particles, enzymatic electrocatalytic systems, and poly(3,4-ehylenedioxythiophene) (PEDOT)-coated membranes.9 In addition, aligned CNTs have also been reported to have ORR electrocatalytic activity due to the FeN2-C and/or FeN4-C active sites within their structure.9 It has also been reported that N-doped CNF electrodes have electrocatalytic activity for ORR through a two-step two-electron
pathway. ORR activity was also observed in noble-metal free catalysts due to the presence of Fe-N_4/N_2 active sites bound to the carbon support and/or exposed edge plane defects combined with N-doping to influence the adsorption of intermediates. Despite N-doping improving ORR activity in these materials, they are less electroactive than Pt catalysts. Contributing to the efforts to replace Pt-based electrodes, a recent breakthrough reported by Gong et al. showed that vertically aligned N-doped CNTs (VA-NCNTs) could function as very effective metal-free ORR electrocatalysts. The metal-free VA-NCNTs catalyzed the four electron ORR process without CO poisoning with much higher electrocatalytic activity and long-term operational stability than that of commercial Pt-based electrodes in alkaline electrolytes. Characteristics such as high surface area with good electrical and mechanical properties and exquisite thermal stability of aligned CNTs promote their application as fuel cell electrodes in ambient and extreme conditions. The enhanced catalytic performance is attributed to the net positive charge formed on the adjacent carbon atoms as a result of the electron-accepting ability of nitrogen atoms in the carbon plane of the VA-CNTs. This nitrogen-induced charge delocalization can alter the O_2 chemisorption mode from the conventional end-on adsorption at the nitrogen-free CNT (NCNT) surface to an side-on adsorption onto the NCNT electrodes. The ORR potential could be lowered due to the N-induced charge transfer from adjacent carbon atoms. As a result, this can weaken the O-O bonding and facilitate ORR at the VA-NCNT electrodes. Furthermore, Qu et al. reported N-doped graphene (N-graphene) films to also have excellent ORR performance similar to that of VA-CNTs with the same nitrogen concentration in alkaline electrolytes. Graphene sheets with a two-dimensional (2D) geometry offer enhanced electron transport
as electrode materials.\(^9\) Both graphene and N-graphene metal-free catalysts for ORR can be produced by multiple low-cost and large scale methods such as CVD, chemical reduction of graphite oxide, exfoliation of graphite, microplasma reaction, and atmospheric pressure graphitization of silicon carbide.\(^9\) N-graphene was also found to be a better electrocatalyst with long-term operational stability and more tolerant to CO poison effects than commercial Pt-based electrodes.\(^{11}\) Therefore, the discovery of this new ORR mechanism in N-doped CNT and graphene electrodes can be applied towards the development of other efficient metal-free catalysts for fuel cell applications.

![AFM images of graphene sheets synthesized via chemical vapor deposition (CVD).](image)

**Figure 1-8:** AFM images of graphene sheets synthesized via chemical vapor deposition (CVD). (A) An optical image and (B and C) AFM images of a CVD-deposited graphene thin film, along with the corresponding height analyses of graphene sheets from AFM image (C).
1-2.6. Graphene Gas Sensors

Being comprised of mainly surface atoms within its 2D structure, graphene’s exceptional properties make it an excellent candidate for chemical sensing applications. Its high surface-to-volume ratio combined with its excellent electrical, optical, and mechanical properties has led researchers to explore incorporating graphene into various chemical, electronic, biological, mechanical, and optoelectronic sensors. Specifically, the highly reactive surface atoms of graphene make it a viable candidate for gas sensing applications. The interactions of molecules with the surface of graphene can be detected by measuring the changes in conductivity arising from charge transfer or changes in electron mobility. The charge transfer can occur through the interaction of either electron-donating or electron-withdrawing gas molecules with graphene leading to a change in carrier concentration, respectively. Some gas molecules can dope graphene with electrons and while others can dope graphene with holes. The interaction of molecules with the surface atoms of graphene can range from weaker Van der Waals to strong covalent bonding depending on the adsorbate. Schedin et al demonstrated that the sensitivity of graphene can reach to the single molecule limit. This sensitivity arises from graphene being a low-noise material without electron scattering within its 2-D plane making it possible to detect the slightest change in carrier concentration. Therefore, graphene sensors can be used for real-time sensing exhibiting great room-temperature sensing properties for various selective stimuli and the potential for cost-effective graphene-based sensors.
References


Materials Characterization

2-1. Raman Spectroscopy

Raman spectroscopy is a characterization instrument to identify samples through molecular vibrations. The principle of the technique is based on inelastic scattering or Raman scattering of a monochromatic light (visible, near infrared, or near ultraviolet range from a laser source) on a sample and then detecting the scattered light. Although a large portion of the scattered light is of the same frequency as the excitation source, otherwise known as Rayleigh or elastic scattering, a minimal amount of the scattered light (5 – 10% of the intensity of the incident light) is shifted in energy from the laser frequency due to molecular interactions from the sample. Therefore, plotting the intensity of the shifted light against frequency results in a Raman spectrum of the sample. This phonon spectroscopic characterization tool was used to confirm the graphitic structure as well as the functionalization of both graphene and carbon nanotubes. An inVia Renishaw Raman Spectrometer was used in this study.

2-2. X-ray Diffraction

X-ray diffraction (XRD) was used to characterize the atomic and molecular crystallography structure of all organic and inorganic materials. X-rays of known wavelength illuminate materials while moving the sample and detector to measure the intensity of the diffracted x-rays as a function of beam and sample orientation. Due to the penetration depth of x-rays into matter, it is possible to obtain the three-dimensional density of electrons within any crystal through which the mean positions of the atoms are
determined. A typical x-ray diffractometer consists of a source of radiation, a monochromator to specify wavelength, apertures to control the beam shape, and a detector. The x-rays produced from the source are scattered when impinging on the sample causing a portion of its intensity to re-radiate as a spherical wave. Typically, in a crystal, the symmetrical arrangement of atoms with a separation distance of $d$ causes these spherical waves to be homogeneously in directions where their path-length difference $2dsin\theta$ equals the wavelength ($\lambda$). Therefore, an x-ray diffraction spectrum plots the diffraction radiation intensity versus the respective angle of each sample. This materials characterization tool was used to verify the crystallinity and atomic make up of as-synthesized and functionalized carbon nanomaterials. A Rigaku desktop x-ray diffractometer was utilized for all atomic crystallographic studies of materials.

2-3. Atomic Force Microscopy

Atomic force microscopy (AFM) is a type of high resolution scanning probe microscopy used to characterize surface topography. The AFM consists of typically a silicon or silicon nitride cantilever with a sharp tip used to probe or scan the surface. When the tip approaches the sample surface, the forces between the tip and the sample cause deflection of the cantilever governed by Hooke’s law. The forces measured in AFM include mechanical contact forces, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, Casimir forces, and solvation forces. Moreover, the deflection of the cantilever is measured using a laser spot reflected from the top surface into photodiodes. AFM can be conducted in various modes divided into two main categories: static or contact mode and dynamic (tapping) or non-contact mode. This surface topographical imaging tool was used for surface imaging and topography of
pristine and functionalized carbon nanomaterials. The non-contact or tapping mode was employed for all materials characterization. An Agilent Technologies AFM was used for all surface imaging and topography of all pristine and functionalized carbon nanomaterials and inorganic nanostructures.

2-4. Scanning Electron Microscopy

Scanning electron microscope (SEM) produces surface morphological images through the interaction of a focused beam of electrons with the sample. An electron beam (0.2 – 40 keV) is formed by applying thermal energy to a tungsten filament and then emitted to a localized spot (0.4 nm – 5 nm diameter) from an electron gun. Electrons interact with atoms in the sample producing signals which contain information of surface topography and composition of a sample. The different methods of energy exchange occurring between the electron beam and the sample surface are detected by specialized detectors. These energy dissipation interactions can arise from the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering, and the emission of electromagnetic radiation. The most common method of scanning is the detection by secondary electrons emitted by atoms excited by the incident electron beam. During operation, the SEM uses scanning coils to create a magnetic field using a voltage differential to manipulate the electron beam back and forth in a defined section of the sample surface with increased magnification. Furthermore, this materials surface imaging characterization tool was used to image the conductive surfaces of carbon materials and other inorganic nanostructures. The differences in regional conductivity of functionalized carbon nanomaterials was advantageous for SEM characterization as a facile image processing technique. A Tescan Vega-3 SEM and Hitachi S4800-F high
resolution SEM were used to study the morphology of the pristine and functionalized nanostructures developed.

2-5. UV/Vis Spectroscopy

Ultraviolet-visible spectrophotometry (UV/Vis) is the absorption or reflectance spectroscopy in the ultraviolet-visible spectral region. A light source, diffraction grating in a monochromator or prism to separate the different wavelengths of light, and a detector are the essential components of the spectrophotometer. The absorbance or reflectance in the visible region is related to the perceived color of the chemicals in the sample or system of interest. Molecules undergo electronic transitions within the uv/vis spectral region where molecules containing π electrons or non-bonding electrons can absorb the ultraviolet or visible light energy are excited to higher anti-bonding molecular orbitals. Therefore, the smaller the energy band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) the longer the wavelength of light it can absorb. The ratio of the intensity of light passing through the sample \( I \) to the intensity of light before it passes through the sample \( I_0 \) is the transmittance \( %T \). The absorbance \( A \) can be found from the \(-\log(\%T/100\%)\). The electronic states and transmittance/absorbance of the different nanostructures were measured using the UV/Vis spectrophotometer. The band gap energy levels and the surface plasmon resonance of nanostructures were measured. A Horiba UV/Vis Spectrophotometer was used for all the measurements of the nanomaterials.
2-6. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface spectroscopic quantitative measurement technique that provides elemental composition, empirical formula, chemical state, and electronic state of elements within a material. A beam of x-rays at either high vacuum or ultra-high vacuum irradiate a sample and a spectra is obtained by measuring the kinetic energy and the number of electrons displaced within a penetration depth of 10 nm of the material. The photogenerated electrons ejected from the sample into the vacuum before reaching the detector have to travel through the sample before doing so. The spectra portrays the number of electrons detected versus the binding energy of the electrons detected. Elements produce characteristic set of peaks relating to their configuration of electrons at specific binding energies to identify each element within the sample. The number of electrons detected in each characteristic peak is proportional to the amount of the element within the sampling volume of the material. Thus, this characterization tool was essential in determining the elemental makeup, electronic structure, oxidation state, and surface functional groups of the carbon nanomaterials as well as inorganic nanostructures. The elemental composition characterization of all the nanostructured materials were conducted on a VG Microtech ESCA 2000 using a monochromatic aluminum X-ray source.

2-7. Contact Angle Goniometer

The contact angle is measured through a static water sessile drop method through which a contact angle is obtained using an optical high resolution camera and software by extracting the profile of the liquid on a surface. The contact angle is comprised of the angle at the liquid/solid interface and the liquid/vapor interface. The contact angle
quantifies the wettability of a solid by a liquid through Young’s equation. A system consisting of solid, liquid, and vapor at a given temperature and pressure has an equilibrium contact angle relative to the strength of the liquid, solid, and vapor molecular interactions. The wettability of all samples were measured to verify the changes in hydrophilicity or hydrophobicity of pristine and functionalized nanostructures. The contact angle was used as a materials characterization technique to gain a more in-depth understanding of surface molecular interactions resulting from functionalization and assembly of the carbon materials. A dataphysics OCA 20 contact angle measuring goniometer was used for all wettability characterization of all nanostructured materials.

2-8. Electrochemical Measurements

A three electrode setup was applied for all electrochemical experiments. Cyclic voltammetry was used in all electrochemical characterization of the carbon-based nanomaterials. The working electrode consisting of the carbon-based nanostructured material is swept linearly versus time for electrode performance studies in electrolyte solution. During the potential sweep, current is recorded at all the different voltages rendering a rectangular shape plot of current versus potential where depending on the working electrode pseudocapacitance, electric double layer effects, and redox peaks can arise. The reference electrode was an Ag/AgCl redox couple (E=+0.241 V vs SCE) placed 2 cm away from the cathode to keep the ohmic drop constant. A platinum wire serves as the counter electrode. All electrochemical experiments were performed with a potentiostat/galvanostat (CH760E, CH Instruments) and data were collected using the EC-lab software.
3-1. Introduction

Multicomponent micropatterned hybrid nanostructures arranged in a controllable manner have attracted significant amount of attention due to synergistic properties arising from spatially well-defined different components.\textsuperscript{1,2} Complex multicomponent nanostructures, compared to that of simple single component systems, have novel multifunctionality through the integration of different functional components into designed complex structures.\textsuperscript{2} The production of large-scale graphene films with patterns is essential in the development of graphene-based nanodevices.\textsuperscript{3} Unique properties such as stable crystal structure, optical transparency, and superior electronic properties form high electron mobility make graphene a nanomaterial with promising applications.\textsuperscript{4,5} Among the many methods employed for producing graphene films, mechanical cleavage of HOPG\textsuperscript{6} or exfoliation of graphite crystals\textsuperscript{7,8} are the most widely recognized and used methods to produce single- and few-layer pristine graphene. However, the graphene films prepared by these methods can be removed easily by solvent washing or sonication since they are physically adsorbed and randomly dispersed on a substrate.\textsuperscript{3} Randomly dispersed or physisorbed graphene are not ideal for graphene-based device fabrication because of limitations in size, easy removal, lack of site specificity placement of the graphene film on substrates.\textsuperscript{3} Therefore, it is vastly desirable to assemble graphene at designated locations and patterns for the design and fabrication of graphene-based devices on a
larger scale. Different methods have been employed to develop micropatterned graphene films, including contact printing using a HOPG stamp made by O$_2$ reactive ion etching, chemical vapor deposition through a mask, and electron beam lithography through a hydrogen silsesquioxane mask. Moreover, with the potential of graphene for novel electronic applications, the ability to control the electronic properties of graphene on a nanometer length scale is imperative. This has been accomplished through electrostatic gating and chemical doping. Specifically, the interaction of oxygen with graphene can dramatically affect its electronic properties by increasing hole and electron mobility. Here, we report a simple, effective, novel, and reproducible method for multicomponent micropatterning of graphene films with metal nanoparticles. The fabrication of patterned graphene films consists of three simple steps as illustrated in Figure 3-1.
Figure 3-1: (A) Fabrication of multicomponent metal-nanoparticle patterned-graphene films: (1) chemical vapor deposition (CVD) synthesized graphene on 300 nm sputtered Ni catalyst on a SiO₂/Si substrate, (2) oxygen RF plasma (0.04 mbar, 10 W) was used to functionalize the exposed areas of the graphene with oxygen groups through the TEM grid as a physical mask for 20 s, (3) Fe₃O₄ nanoparticles are formed on the O₂-plasma functionalized areas of graphene via the hydrophilic–hydrophilic interaction, followed by the alkalization of ferrous chloride tetrahydrate in the presence of ammonia, and (4) after
removal of the TEM grid mask, 5 mM aqueous solution of HAuCl₄ was used for SEED of Au nanoparticles.

Solid-state sensor arrays attain selectivity by having characteristic features or components for a specific analyte derived from the combined response of the sensors contained within the array. The high sensitivity for surface adsorption in combination with large specific surface area make graphene promising candidates for incorporation into solid-state gas sensors to detect a variety molecules. Changes in electrical conductivity due to the charge transfer between the adsorbed acceptor or donor molecules and graphene is the underlying principle for the solid-state sensor where a few extra electrons can elicit relative changes in carrier concentrations. Recent theoretical studies on molecular gas adsorption on graphene have showed that physically adsorbed molecules can act as donor or acceptors on surface dangling bonds and vacant sites. The high sensitivity of the two-dimensional graphene arises from its whole volume comprised of a single layer of carbon with every atom on its surface being exposed to adsorbates. The charge transfer at the location of the adsorbate on the surface of graphene occurs due to changes in the Fermi level, carrier density, and electrical resistance of graphene. Similar to that of carbon nanotubes (CNTs), the intrinsic property of chemical sensitivity has made graphene an ideal material for incorporation into the design of chemical sensors. For example, it has been recently reported that the use of aligned-CNTs (a-CNTs) in either patterned or non-patterned form, without the need for direct manipulation of individual nanotubes can be collectively addressed through a common substrate to enhance the sensitivity and detection of analytes.
Similar to that of CNTs and a-CNTs, the reduced dimensionality of the graphene sheets together with the exceptionally high surface area, composed of almost entirely surface atoms, have vast potential as chemical gas sensing applications. The enhanced conductivity and active defect sites make chemically reduced graphene oxide a potential candidate for vapor sensors. Electron transport through this two-dimensional material can be highly sensitive to adsorbed molecules enabling the development of sorption-based sensors which detect small levels of vapor using low-power electronics. Moreover, decoration of graphene with metal or semiconducting particles can increase sensitivity. For example, Penza et al. reported that Au- and Pt-decorated CNTs elicited a response (ΔR/R₀) to NO₂ and NH₃ which was six to eight times larger than that of pristine CNTs due to a spillover effect at the metal nanoparticles.

Moreover, chemiresistive materials have been employed to detect toxic chemicals and explosives and have been shown to be suitable for gas sensing applications. For example, toxic chemicals such as formaldehyde (CH₂O) can exist in building infrastructure materials and in the combustion gas of organic materials. Despite the efforts of many research groups in developing gas sensors, challenges still remain related to selectivity, sensitivity, and stability. In order to achieve chemical selectivity and stability for multiple gas sensing applications, graphene sheets can be decorated with catalytic metal and metal oxide nanoparticles specific for targeted surface interaction. A graphene-metal nanoparticle array was fabricated with plasma etching, a conventional technology in the semiconductor industry for producing graphene patterns on a large scale, and the substrate enhanced electroless deposition (SEED) technique on graphene for production of graphene-metal nanoparticle hybrids. Oxygen plasma etching was used
pattern and etch graphene through a TEM grid. The substrate enhanced electroless deposition (SEED) technique\textsuperscript{22} was used to deposit gold nanoparticles in the areas of non-plasma-etched graphene. Using the SEED technique, metal ions with a redox potential lower than that of graphene can be readily reduced into metal nanoparticles onto the graphene sheet-support.\textsuperscript{22,23} The deposition of metal nanoparticles is achieved via a redox reaction of a galvanic cell, in which the graphene sheets act as a cathode for metal deposition from the reduction of metal ions in solution, while the metal substrate serves as an anode where metal atoms are oxidized followed by dissolution.\textsuperscript{22,23} The SEED process allows for the electroless deposition of any metal nanoparticles on conducting graphene as long as the redox potential of the substrate metal is lower than that of the metal ions in solution.\textsuperscript{22,23} Here, we report a simple and effective SEED method for electroless deposition of metal (Au) nanoparticles on graphene in the absence of any additional reducing or capping reagents in a patterned form.\textsuperscript{22,23} The Au-pattern decorated graphene is further functionalized through an alkalization reaction of ferrous ions with ammonium hydroxide (NH\textsubscript{4}OH) to form Fe\textsubscript{3}O\textsubscript{4} nanoparticles in the plasma etched areas of graphene. From a crystalline point of view, increasing the surface area with Fe\textsubscript{3}O\textsubscript{4} and Au on graphene can produce more activity sites for adsorption and desorption of gas molecules. The Au and Fe\textsubscript{3}O\textsubscript{4} nanoparticle-decorated graphene hybrid device can be used for chemical vapor sensing through monitoring conductivity changes caused by the charge-transfer interaction with gas molecules. Moreover, a patterned graphene-metal and metal oxide nanoparticle hybrids for selective multifunctional vapor sensing capabilities is developed.
5-2. Experimental Methods

Synthesis of Graphene

Chemical vapor deposition was used to develop graphene films by sputtering a thin layer of nickel film (300nm) on a SiO$_2$/Si substrate, which was then heated up to 1000°C within a quartz tube under a high purity argon atmosphere. Thereafter, a hydrocarbon rich reaction gas mixture (CH$_4$:H$_2$:Ar, 50:65:200 standard cubic centimeters per minute) was introduced into the quartz tube and kept flowing for 5 min, followed by purging with a flow of Ar only for another 5 min. The sample was then rapidly moved out from the furnace center (1000°C) under Ar protection.

Oxygen Plasma Functionalization

Plasma functionalization was carried out on a custom-built plasma apparatus powered at 13.56 MHz, 200 W (Cesar 133 RF power generator) and a pressure of 100 Pa with O$_2$ flow. The plasma was applied for less than 10 s on the exposed areas of the graphene film through the hexagonal TEM grid in order to avoid possible surface damage.

Multicomponent Metal and Metal Oxide Deposition

SEED was used to deposit Au nanoparticles on the Ni-supported patterned graphene films by depositing aqueous solution of HAuCl$_4$ (5mM) on the surface of the patterned graphene. The nanoparticle growth process is controlled by diffusion of AuCl$_4^{-}$ from the bulk solution to the non-plasma-etched areas of graphene/solution interface.$^{16,17}$ Since this is a diffusion controlled process, smaller particles often gain a faster growth than larger particles due to relatively more surface-receiving sites for the metal ions.$^{16,17}$ In addition, nanoparticles of Fe$_3$O$_4$ were synthesized by hydrolysis of an aqueous solution containing iron salts and a base at room temperature in ambient atmosphere.$^{18}$ Ferrous
chloride (FeCl₂·4H₂O, 0.05M) is used as the iron salt and ammonium hydroxide (NH₄OH, pH=12) was used as the base for the reaction. After using SEED to deposit Au nanoparticles, the patterned-graphene film was immersed in the iron salt (ferrous chloride) solution mixed with an aqueous solution of ammonium hydroxide, a precipitate was immediately produced. The pH value of the reaction bath was 12. The precipitate was washed with ultra-pure water several times to remove excess amine molecules.

Vapor Sensor Measurements

The patterned-graphene hybrid sensors were developed by thermally evaporating 2mm strips of ca. 5 mm apart from each other across the patterned-graphene surface for electrical contacts. The patterned-graphene sensor was the exposed to chemical vapors (i.e. ethanol) in one-neck flask containing a chemical solvent for resistance measurements with a two-probe dc resistance meter (Dual Display Multimeter, Fluke 45) under ambient conditions. To verify, four-probe dc surface resistance measurements were carried out under the same conditions as above. There were no obvious differences between the two-probe and four-probe results, which indicates that good contacts were made with the patterned-graphene film. The resistance of the external wires is insignificant due to their relatively short length. As a control, the patterned-graphene hybrid sensors used were on SiO₂/Si substrates for measuring dc surface resistances in response to chemical vapors to be investigated. The pressure of the chemical vapor in the three-necked bottle was adjusted through a valve, while the compressed air inlet was used to introduce the air to maintain the total pressure at 1 atm. The partial pressure in ppm was then calculated by: [Vapor Pressure (Pa)/1 atm (101325 Pa)]×1000000.
5-3. Results and Discussion

The sensor chips were fabricated using CVD graphene grown on nickel consisting both single layer and multilayer graphene areas deposited on Ni catalyst (Figure 3-2A, E-F). The Raman spectra and mapping of the G and 2D bands of both single layer and multilayer graphene as observed in Figure 3-2B. Raman mapping of the G band and 2D band of the graphene clearly shows the homogeneity of the grapheme film grown on nickel (Figure 3-2C and D).
Figure 3-2: AFM and SEM images and Raman Spectra of the CVD graphene. (A) AFM image of pristine graphene, (B) Raman Spectroscopy of graphene showing the G peak and 2D band features characteristic of single-layer and multi-layer graphene with the $G$ band at $1582 \ \text{cm}^{-1}$ and a symmetric 2D band around $2700 \ \text{cm}^{-1}$ which is consistent with the reported single layer graphene spectra.\cite{25,26} (C) Raman mapping of the G Band of the graphene film, (D) Raman mapping of the 2D Band of the graphene film, and (E and F) SEM images of the smooth pristine graphene film grown on Ni/SiO$_2$/Si.

The multicomponent graphene sensor chips were fabricated by treating the exposed areas of the graphene film through the hexagonal windows of the TEM grid to oxygen plasma for 10 seconds introducing carbonyl, epoxy, and carboxylic groups into the crystal structure of graphene (Figure 3-3A and B). The plasma functionalization time was kept short on the exposed areas of the film in order to avoid possible surface damage in a custom-built plasma apparatus powered at 13.56 MHz, 200 W (Cesar 133 RF power generator) and a pressure of 100 Pa with pure oxygen (99.999%) flow where oxygen gas is exposed to a radio frequency (RF) potential to partially ionize the oxygen gas to react with the graphitic C-C and C=C bonds which can be confirmed with the changes in the graphene surface wettability (Figure 3-3C and D). The static contact angle decreased after the plasma functionalization indicating the presence of surface oxygenated groups on graphene. The oxygen plasma functionalization can be confirmed by the increase in the D-band of Raman spectra of the graphene film indicating a higher crystal disorder due to the oxygenated groups (Figure 3-3E and F).
Figure 3-3: Plasma functionalization through a custom built (A) RF-plasma reactor system, (B) Schematic of the RF plasma reaction mechanism where the RF power is applied around the chamber to excite the carrier gas molecules (in this case O₂) and dissociate into chemically active atoms or radicals, Static surface contact angle measurement of the (C) pristine graphene and (D) oxygen plasma treated graphene, and Raman spectra of graphene before and after plasma functionalization (E) showing an increase in the D band intensity arising which is evident from the change in the I_D/I_G ratio.
Upon removal after the TEM grid from graphene, the O₂ plasma functionalized areas serve as sites for the selective deposition of the Fe₃O₄ nanoparticles. In a typical synthesis, the aqueous solution of FeCl₂·4H₂O was added to the oxygen-plasma-etched graphene to complete the ion exchange and form a Fe³⁺/Graphene composite. In the second step, NH₄OH solution was added dropwise (until pH=12) to the aqueous solution of FeCl₂·4H₂O/graphene thus, leading to the conversion of Fe³⁺/graphene into Fe(OH)₃/graphene and finally reduced into Fe₃O₄/graphene (Figure 3-4). Moreover, after the selective area deposition of Fe₃O₄ nanoparticles (Figure 3-5), SEED was used to deposit Au nanoparticles via spontaneous reduction on the non-plasma-functionalized areas to render multicomponent micropatterned graphene films (Figure 3-6). The Ni catalyst used for the CVD growth of graphene serves as the metal support of a redox potential lower than that of the Au⁺ ions to be reduced into nanoparticles. The deposition of the Au nanoparticles is achieved via the redox reaction of a galvanic cell, in which the graphene acts as a cathode for Au deposition from the reduction of the Au⁺ ions in solution, while the Ni catalyst serves as an anode where Ni atoms are oxidized into Ni⁺ followed by dissolution. (Figure 3-7)
Figure 3-4: Scheme of the co-precipitation reaction of Fe₃O₄ nanoparticles. Aqueous ferric chloride is mixed with ammonium hydroxide solution which acts a precipitation agent to form ferrous hydroxide suspensions through which Fe₃O₄ nanoparticles are precipitated out. The optimum reaction conditions of controlled oxidation in a pH range 8-14 can lead to a concentration ration of Fe³⁺/Fe²⁺ is 2/1.
Figure 3-5: AFM images of (A) plasma treated graphene and (B-D) Fe$_3$O$_4$ nanoparticles (~50 nm from the topographical inset) deposited in the plasma functionalized areas of graphene with increasing resolution. The increased roughness of the plasma treated graphene is an indication of the surface modification from the short plasma treatment introducing oxygenated groups to the graphene surface (as confirmed with Figure 3-3F).
and increase of \( \frac{I_D}{I_G} \) ratio in the Raman spectra). The AFM images clearly show the formation of nanosphere-like \( \text{Fe}_3\text{O}_4 \) nanoparticles on graphene.

The resulting micropatterned and multicomponent graphene films were analyzed using SEM and energy dispersive x-ray spectroscopy (EDX) to confirm the region specific deposition of \( \text{Fe}_3\text{O}_4 \) and Au nanoparticles (Figure 3-7 A-F). The EDX elemental mapping images clearly shows the deposition of \( \text{Fe}_3\text{O}_4 \) within the hexagonal framework (Figure 3-7G) and Au deposited in the outer hexagonal framework (Figure 3-7H) of the graphene. The EDX elemental analysis spectrum confirms the presence of Fe and Au on the patterned graphene film (Figure 3-7I).

**Figure 3-6:** AFM image and SEED mechanism of Au on Graphene. The AFM image clearly shows the Au particles (~10 nm from topography inset) deposited on graphene.
The SEED mechanism is the reduction of Au ions to Au nanoparticles via the electroless deposition and electron transfer from the Ni substrate to graphene to ultimately reduce the Au ions into nanoparticles on the surface of graphene.

**Figure 3-7:** AFM Images of Au nanoparticles on Graphene. (A-C) The AFM images with increasing resolution clearly shows the Au particles (~10 nm from topography inset) deposited on graphene. The Raman spectra shows the characteristic G band and 2D Band of graphene after the multicomponent functionalization. The increase in the D band is an
indication of the disorder arising from the Fe₃O₄ and Au nanoparticles affecting the phonons of graphene.

**Figure 3-8:** SEM and EDX images of multicomponent-patterned graphene. (A - F)

Hexagonally patterned graphene with Fe₃O₄ nanoparticles within the hexagon and Au nanoparticles deposited in the outer border; enlarged views of the Fe₃O₄ nanoparticle deposited areas (B and C) and Au nanoparticle deposited areas (E and F) on the multicomponent graphene hexagonal pattern in panel. The EDX images clearly depict
region-specific elemental mapping of (G) Fe within the hexagon framework where the Fe₃O₄ were deposited and (H) Au in the outer hexagon framework via SEED.

The phase structure during functionalization of the graphene sensor chips is obtained by X-ray diffraction (XRD). Figure 3-6 shows the representative XRD patterns of pristine CVD graphene grown on Ni, single component Fe₃O₄ functionalized graphene after O₂ plasma treatment, and the multicomponent Fe₃O₄/Au/graphene. The positions and relative intensities peaks match well with the standard Fe₃O₄ and graphene patterns.²⁷-²⁹ The broad reflection of the carbon (002) peak in the pattern suggest the turbo static nature of graphene. The peaks for the Fe₃O₄ nanoparticles is used as reference and three characteristic peaks at 27.65°, 39.35°, and 51.5°, corresponding to the (220), (311), and (422) planes of the magnetite spinel structure of Fe₃O₄ observed in both graphene-Fe₃O₄ and graphene/Fe₃O₄/Au spectrums. The major crystalline Au peak for (111) occur at 37.5°, (200) at 46.3° and (220) at 63.95. The characteristic peak from sputter deposited Ni (111) is evident in all three spectra.
Figure 3-9: XRD patterns of graphene on Ni, graphene/Fe₃O₄ (bottom curve), and graphene/Fe₃O₄/Au was recorded at 25°C shows a broad reflection of d spacing corresponding to the (002) and (001) planes. The peaks for the Fe₃O₄ nanoparticles is used as reference and three characteristic peaks at 27.65°, 39.35°, and 51.5°, corresponding to the (220), (311), and (422) planes of Fe₃O₄ observed in both graphene-Fe₃O₄ and graphene/Fe₃O₄/Au spectrums. The Au peak for (111) occur at 37.5°, (200) at 46.3° and (220) at 63.95. The characteristic peak from sputter deposited Ni (111) is evident in all three spectra.

The X-ray photoelectron spectroscopy (XPS) is used to further confirm the formation of Fe₃O₄ and Au nanoparticles by verifying the oxidation state of Fe and Au, respectively (Figure 3-7 A-B). The penetration depth of XPS provides elemental surface
information and can differentiate through the specific elemental binding energy the presence of Fe$^{2+}$ and Fe$^{3+}$ cations. The peaks at 710 and 723.5 eV in the high resolution Fe2p scan can be attributed to the levels of Fe2p3/2 and Fe2p1/2 in the multicomponent graphene film, respectively (Figure 3-7C). XPS analysis is also sensitive to Au displaying a doublet for 4f5/2 and 4f7/2 with peaks at 87.8 and 83.4 eV, respectively (Figure 3-7D). It is also in agreement with the literature that the peaks shift to higher binding energy and broaden for Fe$_3$O$_4$ due to the appearance of Fe$^{2+}$(2p3/2) and Fe$^{2+}$(2p1/2). The XPS pattern also reveals that Fe$_3$O$_4$ has been generated after being reduced. The peak located at 286.2 eV can be attributed generally to surface-adsorbed hydrocarbons and their oxidative forms (e.g. C-OH and epoxide). The peak at 284.5 eV in the C1s spectrum (Figure 3-7E) is assigned to the carbon element in association with oxygen in the carbonate ions. The predominant peak at 531.8 eV is attributed to O1s which belongs to the lattice oxygen of Fe$_3$O$_4$ (Figure 3-7F). The remaining smaller peaks at higher binding energies (785.6, 788, 802.1, and 805.2 eV) are satellite shake-ups of the assigned components.
Figure 3-10: XPS survey spectra of (A) graphene/Fe$_3$O$_4$ and (B) multicomponent patterned graphene/Fe$_3$O$_4$/Au, along with the high-resolution spectra of (C) Fe 2p, (D) Au 4f, (E) C 1s, and (F) O1s. The higher binding energies shifts of the high resolution fits for Fe 2p confirm the presence of Fe$_3$O$_4$. The presence of Au is further confirmed due to the binding energies.
The enhanced conductivity and active defect sites make graphene a potential candidate for vapor sensors. Electron transport through this two-dimensional material can be highly sensitive to adsorbed molecules enabling the development of sorption-based sensors which detect small levels of vapor using low-power electronics. Moreover, the resultant multicomponent hexagonally patterned graphene with Fe$_3$O$_4$/Au can be used for region specific adsorption of analytes from vapor. The vapor sensor tests were performed at room temperature using ethanol, methanol, and formaldehyde as probe molecules. Figure 3-8 shows the response-recovery curves of the Fe$_3$O$_4$/Au patterned graphene gas sensor. It can be seen that the sensor responses increase with increasing vapor concentration. The sensor shows very fast response and recovery. In four cycles, the sensor shows only a slight decrease in response amplitude, indicating the perfect reproducibility of Fe$_3$O$_4$/Au patterned graphene sensor. A comparison in the sensor performance and sensitivity shows that the patterned multicomponent sensor is more than two times response than the single component sensor due to the increased active surface in the patterned multicomponent sensor. The enhanced sensor properties can be related to two factors such as the structure of Fe$_3$O$_4$ nanoparticles or the catalytic activity of the Au nanoparticles. Moreover, figure 3-9 shows the selectivity of Fe$_3$O$_4$/graphene and Au/graphene sensors to formaldehyde and ethanol, respectively. The higher magnitude in the resistance response of the Au-modified and Fe$_3$O$_4$-modified graphene sensors is caused by the catalytic effects of the Au and Fe$_3$O$_4$ for specific vapors. Generally, the gas sensing mechanism is related to the surface-adsorbed oxygen species, which can trap electrons from the conduction band of the metal oxide and simultaneously result in the formation of electron exhausted layers on the oxide surface.
Figure 3-11: Dynamic response–recovery curves of gas sensors based on Fe$_3$O$_4$/Au patterned graphene to (A) ethanol, (B) methanol, and (C) formaldehyde. Relative variations of the resistance, $\Delta R$, for reduced graphene oxide with deposited metal nanoparticles via SEED on copper upon exposure to vapor with time intervals “on” and “off”. $\Delta R = (R_{\text{vapor}} - R_0)/R_0 \times 100\%$, where $R_0$ and $R_{\text{vapor}}$ are the resistances of the patterned sensor before and after exposure to ethanol, methanol, and formaldehyde vapor, respectively. The sensor performance was also tested in various concentrations of methanol vapor at room temperature. The resistance increased with concentration (ppm).
of methanol vapor demonstrating the sensitivity rapid response of the sensor even at low concentrations.

Figure 3-12: Dynamic response–recovery curves of gas sensors based on Fe₃O₄/graphene and Au/graphene to (A) ethanol and (B) formaldehyde demonstrating selectivity. Relative variations of the resistance, ΔR, for reduced graphene oxide with deposited metal nanoparticles via SEED on copper upon exposure to vapor with time intervals “on” and “off”. ΔR = (Rᵥapor – R₀)/R₀ x 100%, where R₀ and Rᵥapor are the resistances of the patterned sensor before and after exposure to ethanol and formaldehyde vapor.

In addition, there are two types of gas or analyte adsorption that occurs during the surface sensing mechanism. Physisorption is the first step of the association of the gas species with the sensor surface and chemisorption involves exchange of electrons between the adsorbed species and the material surface. Physisorption is exothermic while chemisorption is endothermic an activated process whose activation energy can be supplied by thermal or non-equilibrium which leads to the fact that physisorption
predominates in low temperature range whereas chemisorption dominates in higher temperature range. The sensing characteristics of metal oxides are widely considered to be related with chemisorbed oxygen and water, which can act as intermediates catalyzing the charge transfer processes between gas species and the bulk through fluctuations in the concentration and the charges of oxygen vacancies. The charge transfer that occurs at the interface of the metal nanoparticle and graphene due to the work function differences leading to the formation of a dipole.\textsuperscript{33} As a result, the Fermi level of graphene is shifted due to the interface potential step (Figure 3-10).\textsuperscript{33} The metal nanoparticles deposited on graphene act as a platform for charge transfer between the gas molecules and graphene.\textsuperscript{33} Reducing gases donate electrons to the metal nanoparticle creating an electric field at the interface between graphene which facilitates the electron doping of graphene and a decrease in the hole current.\textsuperscript{33} On the other hand, oxidizing gases accept electrons from the metal nanoparticles increasing the hole conductivity.\textsuperscript{33}
Figure 3-13: Band gap diagram of the metal nanoparticle and graphene. (A) The equilibrium band gap of graphene/metal nanoparticle sensor (inset optical image) interface clearly showing the changes in the Fermi level ($\Delta E_F$) of graphene creating a dipole and a potential change ($\Delta V$) due to charge transfer from the differences in the work function of graphene ($\phi_G$) and work of function of metal nanoparticle ($\phi_M$). (B) Band gap schematic with the interaction of the gas molecule by donating electrons to the metal nanoparticle changing the Fermi level of the nanoparticle/graphene interface decreasing the hole transport. Figure adapted from ref. 33.
3-4. Conclusion and Future Work

A facile region-specific micropatterned functionalization of graphene with two components was developed. Without any complicated processing methods, the region selective deposition of different nanoparticles in a patterned fashion was demonstrated. The metal and metal oxide nanoparticle functionalized graphene sensor chips can enhance the sensing capability and selectivity for low concentration vapors at room temperature. A miniaturized gas sensor based on graphene exhibits sensing properties for various selective vapors and the potential for cost-effective graphene-based sensors. Ethanol, methanol, and formaldehyde are reducing gases and can act as an electron donors by feeding electrons back into the metal oxide in the sensing reaction, thus causing quantifiable changes in sensor resistance. In the process of sensing reactions catalyzed by Au nanoparticles, the vapor is first oxidized via oxidative dehydrogenation eventually into CO₂ and H₂O by dissociated oxygen species. Graphene increases the active surface area and provide more adsorption–desorption sites for the analyte. In addition, the active Au nanoparticles can serve as promoters for catalyzing the sensing reactions between reducing vapor and surface oxygen species thus further enhancing sensor performance. However, the performance of the sensor chip needs to be measured after being exposed to many more vapors. The recovery of the sensor may be improved upon desorption of the interacting molecules.
3-5. References


As an atomically thin sheet of carbon atoms packed in a two-dimensional (2D) honeycomb lattices with excellent electronic, thermal, and mechanical properties, graphene has shown great potential for a wide range of applications. Examples include the use of graphene and its derivatives as transparent conductive electrodes or active materials in solar cells, counter electrodes in dye-sensitized solar cells, electrocatalysts for oxygen reduction in fuel cells, high-performance electrodes in supercapacitors, batteries, and even actuators.\textsuperscript{1-15} There is now a pressing need to integrate graphene sheets into multidimensional and multifunctional systems with spatially well-defined configurations, and hence integrated systems with a controllable structure and predictable performance.\textsuperscript{1-15} This requires controlled functionalization of graphene sheets at the molecular level, which is still a big challenge.

The recent availability of solution-processable graphene by exfoliation of graphite into graphene oxides (GOs), followed by solution reduction,\textsuperscript{16-19} has allowed the functionalization of graphene sheets via various solution reactions.\textsuperscript{20-22} However, there is still no report on the asymmetric functionalization of graphene sheets with each of their two opposite surfaces attached by different chemical functional groups. The asymmetric functionalization of graphene should significantly advance the self-assembling of graphene sheets into many new multidimensional and multifunctional systems with a
molecular level control. A simple but effective asymmetric modification method for functionalizing the two opposite surfaces of individual graphene sheets with different nanoparticles in either a patterned or non-patterned fashion is demonstrated. The resultant asymmetrically-modified graphene sheets with ZnO and Au nanoparticles (NPs) on their two opposite surfaces be pivotal in material design of 3D architectures where individual graphene sheets can be connected or bond selectively with other nanomaterials for applications such as optoelectronics, actuators, and sensors.

4-2. Experimental Methods

Synthesis of graphene

An aqueous dispersion of chemically derived graphene sheets were synthesized by a modified Hummer’s method as described in the literature. Graphite oxide (GO) was first synthesized from the chemical oxidation of natural graphite flakes (Sigma Aldrich). The GO was readily suspended in water to form a stable and yellow-brown dispersion. 10 mL of GO suspension (0.2 mg/mL) was then mixed with 10 mL of water, 10 µL of hydrazine monohydrate and 40 µL of ammonia solution (28 % in water), and the reaction mixture was heated in an oil bath (~95°C) for 1 h. After the completion of the reduction reaction, excess hydrazine in the resulting suspension was removed by dialysis to produce a stable graphene suspension. The chemical reduction of GO into graphene is confirmed by high resolution C1s XPS spectra, as shown in Figure 4-1.
Figure 4-1: AFM Image and XPS of graphene. The AFM image shows the dispersed graphene sheets with an approximate thickness of ~1 nm. The high resolution fits for the C 1s XPS spectra confirms the formation of (a) graphene oxide and (b) reduced graphene oxide.

Synthesis of spherical ZnO nanoparticles

As previously reported in literature\textsuperscript{24}, ZnO colloidal suspension was obtained by dissolving 110 mg (0.5 mmol) of Zn(Ac)\textsubscript{2}.2H\textsubscript{2}O in 25 mL ethanol with sonication for 5 min at 0 °C. To the above solution, 21 mg (0.5 mmol) of Li(OH)·H\textsubscript{2}O was then added and continuously sonicated for another 5 min at 273 K to produce a stable and optically transparent ZnO nanoparticles suspension. (Figure 4-2A)

Synthesis of cubic Au nanoparticles

Cubic Au nanoparticles were prepared via a gold seed growth reaction according to the previously reported procedure.\textsuperscript{25} First, the Au seed was prepared by the following procedure: HAuCl\textsubscript{4}.3H\textsubscript{2}O (2.5 \times 10^{-4} M) was reduced with ice-cold NaBH\textsubscript{4} (6.0 \times 10^{-3} M), followed by dilution with water and subsequent sonication for 15 min.
4M) in the presence of cetyltrimethylammonium bromide (CTAB, 7.5 x 10^{-2} \text{ M}). After the addition of NaBH_{4} to the aqueous solution (10 \text{ mL}) containing CTAB and HAuCl_{4}, the reaction mixture was stirred for 2 min. Therefore, this procedure resulted in Au seeds less than 2 \text{ nm} in diameter. In order to shape-specific Au nanoparticles, the prepared seed solution was added to a growth solution. The cubic Au nanoparticle growth solution consisting of 0.40 \text{ mL} of HAuCl_{4} solution (5 \times 10^{-3} \text{ M}) was added to 4.75 \text{ mL} of CTAB solution (0.10 \text{ M}) followed by the addition of 0.03 \text{ mL} of AgNO_{3} (0.01 \text{ M}), 0.034 \text{ mL} of Lascorbic acid (0.10 \text{ M}), and 0.01 \text{ mL} of Au seed solutions. The solution was gently mixed by inverting the solution immediately after the addition of every component. The resulting sample was examined by SEM. As shown in Figure 4-2B, the obtained Au particles are mostly cubic with an average size of around 60 nm.

Figure 4-2: AFM of ZnO nanoparticles, SEM of cubic Au nanoparticles, and UV/vis of the pyrene functionalization of Au nanoparticles. The AFM and SEM images clearly
show the difference in the spherical shape of ZnO nanoparticles and cubic shape of the Au nanoparticles. The UV/Vis spectra confirms the functionalization of the cubic Au nanoparticles with pyrene-CH$_2$NH$_2$ for further graphene functionalization.

**Synthesis of 1-pyrenemethylamine (Pyrene−CH$_2$NH$_2$) modified Au nanoparticles**

Typically, 10 µL of 0.5 M NaOH was firstly added to 5 mL of the Au nanoparticle solution to make the solution pH=8.5. Afterwards, 100 µL of 10$^{-3}$ M of 1-pyrenemethylamine hydrochloride (95%, Aldrich) in ethanol was added to the Au particle solution and stirred for 30 min to produce the Pyrene−CH$_2$NH$_2$ modified Au nanoparticles. The UV-vis absorption spectra was used confirm the functionalization of the Au nanoparticles, pyrene-CH$_2$NH$_2$, and Pyrene−CH$_2$NH$_2$ modified Au solution were examined. As shown in Figure 4-2C, the absorption spectrum of pure Pyrene−CH$_2$NH$_2$ in ethanol shows three vibronic bands at 310, 325, and 342 nm, respectively. The as-prepared Au nanoparticles exhibited a surface plasmon resonance absorption band (SPR) at around 520 nm. Upon attachment of Pyrene−CH$_2$NH$_2$ to Au in water, the absorption spectrum exhibits obvious change and the strong and sharp vibronic features of the Pyrene−CH$_2$NH$_2$ molecules with a significant decrease in absorbance intensity. A slight red-shift was observed for the SPR absorption band of the Au nanoparticles. Therefore, results indicate the attachment of Pyrene−CH$_2$NH$_2$ onto the Au surface through the specific interaction between its alkylamine substituent and Au.

**Asymmetric modification of graphene sheets with ZnO and Au nanoparticles on two opposite surfaces**
In a typical procedure, well dispersed graphene sheets (0.05 mg/mL) were firstly spin-coated (900 rpm, 2 min, Spin-coater, KW-4A, CHEMAT TECHNOLOGY) onto a silicon substrate. The deposited graphene sheets were treated by the acetic-acid plasma with a custom-built plasma apparatus powered at 250 kHz, 30 W, and a monomer pressure of 0.1 Torr for 1 min. This step will introduce the carboxylic groups on the exposed side of the graphene sheets. Then the substrate was dipped into a ZnO colloidal solution to attach ZnO nanoparticles through a carboxylate group linkage with oxide nanoparticle surface. Subsequently, a thin-layer poly(methyl methacrylate) (PMMA) was coated onto the silicon substrate by spin-coating from a 10 wt % chloroform solution at a rate of 2000 rpm for 2 min, followed by heating the coated substrate at 120 °C for 5 min. After having cooled up to room temperature, the silicon substrate was removed in a diluted HF solution (5 wt%). By using this process, the ZnO anchored graphene surface only was transferred onto a PMMA substrate and the bare graphene surface was exposed for subsequent modification. The PMMA-supported graphene sheets were then dipped into Pyrene-CH2NH2 modified Au nanoparticle solution to adsorb Au nanoparticles onto the bare graphene surface through π-π stacking interaction with Pyrene-CH2NH2 as the interlinker. Finally, the PMMA supporting layer was removed by sonication in chloroform to release of the asymmetrically-modified graphene sheets with ZnO and Au nanoparticles attached onto the opposite sides of the same graphene sheets.

PMMA-assisted Micropatterning

The PMMA micropatterns on a Si substrate were fabricated as follows: a Si substrate with well-dispersed graphene sheets was first coated with 300 nm thick of PMMA by spin-coating a 10 wt % chloroform solution at a rate of 3000 rpm for 2 min, and then
exposed through a quartz photomask to DUV (λ=254 nm) on an OAI photolithography system. Subsequent development of the exposed regions by using MIBK (methyl isobutyl ketone)/IPA (isopropanol) (1:1, v/v) mixture solution resulted in the formation of PMMA micropatterns.

Micropatterned asymmetric modification of graphene sheets with ZnO and Au nanoparticles

In a typical experiment, graphene sheets were firstly deposited on a silicon substrate by spin-coating a diluted graphene solution (0.05 mg/mL), and a PMMA pattern was formed on the graphene-deposited substrate according to the previously reported procedure. The substrate was then treated by the acetic-acid-plasma at 250 kHz, 30 W, and a monomer pressure of 0.1 Torr for 1 min. Subsequently, the micropatterned substrate was dipped into a ZnO colloidal solution to attach ZnO nanoparticles into PMMA-free areas of the graphene surface through a specific interaction between the carboxylate groups and oxide nanoparticles. Upon completion of the ZnO attachment, the PMMA pattern was removed in chloroform to release the plasma-untreated regions of the ZnO-predeposited graphene surface for subsequent region-selective adsorption of the Pyrene-CH$_2$NH$_2$ modified Au nanoparticles through the specific π-π stacking interaction between the Pyrene-CH$_2$NH$_2$ linkage and bare graphene surface.
4-3. Results and Discussion

**Figure 4-3**: AFM images of (a) graphene sheets, (b) spherical ZnO NPs, (c) a graphene surface attached with the spherical ZnO NPs, (d) a graphene sheet with the ZnO-attached surface coated by PMMA and the bare surface exposed, (e) cubic Au NPs, (f) an asymmetrically-modified graphene sheet with the Au-modified surface exposed. Inset of (e) shows the SEM image of the cubic Au NPs. Note that the images shown in (c) and (f) were not taken from the same graphene sheet due to technique difficulties.

Building on a polymer-masking technique for asymmetric functionalization of carbon nanotube sidewalls by sequentially masking vertically-aligned carbon nanotubes (VA-CNTs) with only half of the nanotube length being modified each time, a new polymer-masking technique for sequentially masking individual graphene sheets twice
with only one side of the surfaces being modified each time was employed. A dilute aqueous solution of well-dispersed graphene nanosheets were deposited onto a silicon substrate by spin-coating (Figure 4-3a). Individual graphene sheets on the substrate were then treated by acetic-acid-plasma to introduce the carboxylic groups on the exposed surface of the graphene sheets (Figure 4-4b) while their opposite surface was protected by the silicon substrate without any exposure to plasma functionalization. Subsequently, spherical ZnO NPs (~10 nm in diameter, Figure 4-2a) were attached onto the plasma-treated graphene surface (Figure 4-4b) through the interaction of carboxylic groups with ZnO particles according to previously published procedures. This was followed by spin-coating with a thin-layer PMMA from a CHCl₃ solution to mask the ZnO-attached graphene surface (Figures 4-3d and 4-4c). The PMMA-coated, ZnO-attached graphene sheets were then separated from the silicon substrate by immersing into a HF aqueous solution to expose the bare surface of graphene (Figure 4-4d) for subsequent functionalization with cubic Au NPs (Figure and inset 4-3e) grafted with pyrene-derivative (1-pyrenemethylamine) for π-π stacking onto the bare graphene surface (Figures 4-3f and 4-4e). Subsequent removal of the PMMA supporting layer by ultrasonication in chloroform led to the release of the asymmetrically-modified graphene sheets with the spherical ZnO and cubic Au NPs on their two opposite surfaces (Figure 4-4f).
Figure 4-4: Schematic representation of the steps for asymmetrical functionalization of the two opposite surfaces of individual graphene sheets with ZnO and Au NPs, respectively. Among many functional entities that can be asymmetrically attached onto individual graphene sheets through the scheme above, we chose the ZnO and Au NPs of different sizes and shapes for characterization with AFM, and SEM. As expected, the AFM image of the resultant ZnO-attached graphene given in Figure 4-3c clearly shows many spherical ZnO particles having been deposited onto one side of the graphene sheet. In contrast, Figure 4-3f reveals an asymmetrically-modified graphene sheet with one side of the graphene sheet attached by the cubic Au NPs while the ZnO-attached surface of the same graphene sheet was protected by the PMMA coating.

Further evidence for the asymmetric functionalization comes from the scanning transmission electron microscopy (STEM), in conjunction with the energy dispersive X-ray (EDX) measurements. While the STEM image in the inset of Figure 4-5 shows only the cubic Au NPs on one side of an asymmetrically-functionalized graphene sheet, the
corresponding EDX spectrum (Figure 4-5) from the same side surface of the same graphene sheet reveals the presence of Zn and O signals in addition to Au and C. The Zn and O signals are originated, and detected by the X-ray, from the ZnO NPs attached onto the graphene surface opposite to the Au NP-attached side, unambiguously indicating a success for the asymmetric functionalization corresponding with STEM image. Note that the Cu signal comes from the copper TEM grid.

Figure 4-5: Energy-dispersive X-ray (EDX) spectrum of an asymmetrically-modified graphene sheet with ZnO and Au NPs attached onto two opposite surfaces. Inset shows grid used in this study (EDX analysis area is indicated by white circle).

Due to its penetration depth and surface-sensitivity to provide elemental information, X-ray photoelectron spectroscopy (XPS) is used further investigate the
interaction between the nanoparticles and graphene. As for the chemically-derived graphene sheet, the C1s spectrum (Figure 4-6b) consists of three components: a strong peak at 284.5 eV corresponding to the C-C bond, and two weak components at 286.5 and 288.1 eV attributable to the C-O bond and the C=O bonds, originating from residual oxygen-containing functionalities on the graphene oxide sheets after hydrazine reduction.

After the attachment of ZnO NPs, the C1s peak position (Figure 4-6c&d) shifts to higher binding energy (from 284.5 to 284.9 eV), as previously observed in the ZnO coated carbon nanotubes. Meanwhile, the O1s peak (Figure 5-3c) becomes more prominent and the intensities of the C-O and C=O components in the C1s spectrum (Figure 5-3d) significantly increase relative to the chemically-derived graphene (Figure S7b), indicating the attachment of ZnO on graphene via the formation of strong covalent single and double bonds between carbon and oxygen atoms. However, the acetic-acid-plasma-pretreatment could also introduce the surface carboxylic and hydroxyl groups. It is noticeable that the O1s peak position (the inset of Figure 5-3c) shifts to lower binding energy (from 532.5 to 531.4 eV). Such peak shift lies in the fact that both the oxygen in the attached ZnO (530.6–531 eV) and in C=O groups (about 531.3 eV) have lower binding energies than the oxygen in C-O (about 533 eV). These results confirm the successful attachment of ZnO NPs on the plasma-pretreated graphene surface. For the Au-attached graphene sheet, the XPS spectrum in the Au region (the inset of Figure 5-3e) presents two peaks at 83.9 and 87.5 eV, corresponding to the Au-4f7/2 and Au-4f5/2 bands, respectively. However, these two peaks slightly shift toward low binding energy relative to bulk Au atom (84.0 eV for Au 4f 7/2 and 87.7 eV for Au 4f 5/2).[S12] This could be a consequence of the presence of 1-pyrenemethylamine absorbed on the Au NP
surface. Generally, the Au-4f core-level energy is very sensitive to the chemical environment around Au core such as the strength of the interaction between the Au core and surrounding ligand. Therefore, the shift implies that there exists a strong interaction between Au and 1-pyrenemethylamine. On the other hand, the appearance of the weak N1s peak at around 399 eV (the inset of Figure 5-3c) confirms that 1-pyrenemethylamine has indeed been immobilized on the graphene surface to serve as an effective linker for anchoring Au NPs onto graphene.
Figure 4-6: XPS analysis of the asymmetrically functionalized graphene. (a,b) graphene: a strong peak at 284.5 eV (C-C bond), two weak peaks at 286.5 and 288.1 eV (C-O bond and the C=O bonds) from residual oxygen-containing functionalities on the graphene oxide sheets after hydrazine reduction (c, d) ZnO-graphene: C1s peak position (shifts to higher binding energy (from 284.5 to 284.9 eV), the O1s peak is more prominent and the intensities of the C-O and C=O components in the C1s spectrum significantly increase
indicating the attachment of ZnO on graphene. (e, f) Au-graphene: in the Au region has two peaks at 83.9 and 87.5 eV, corresponding to the Au-4f7/2 and Au-4f5/2 bands which slightly shift toward low binding energy due to 1-pyrenemethylamine absorbed on the Au NP surface.

Having successfully demonstrated the asymmetric modification of the two opposite surfaces of individual graphene sheets with different nanoparticles in a non-patterned fashion, the region-specific modification of the graphene surface with different nanoparticles in a controlled manner remains to be a challenge. As shown in Figure 4-3a, from a dilute aqueous solution (0.05 mg/mL) of well-dispersed graphene nanosheets were deposited onto a silicon substrate by spin-coating. Individual graphene sheets on the substrate were then covered by PMMA micropatterns photo-lithographically produced according to a previously reported method. Due to the random distribution of the graphene sheets on the substrate surface, one can anticipate that some graphene sheets may be partially masked by the PMMA micropatterns (Step 1, Figure 4-7a). Subsequent acetic-acid-plasma treatment allowed for the attachment of ZnO NPs onto the PMMA-free graphene surface through the specific interaction between the plasma-induced carboxylic groups and oxide particles (Step 2, Figure 4-7a), as mentioned above. The deposition of ZnO NPs on the plasma-treated PMMA patterns can be readily removed by dissolving the PMMA patterns in a CHCl₃ solution, leading to the graphene sheets region-selectively attached with ZnO NPs (Figures 4-7a and 4-9a). Furthermore, Au NPs pre-functionalized with 1-pyrenemethylamine could be selectively adsorbed onto the ZnO-deposited graphene surface in the ZnO-free regions untreated by the plasma through
the π-π stacking interaction between the pyrene linkage and bare graphene surface (Step 3, Figure 4-7a), as confirmed by Figures 4-7c and 4-9b. This is further supported by the pattern of small spherical ZnO with relatively big cubic Au NPs in the TEM image (inset of Figure 4-8) and the co-existence of Au, Zn, O, and C peaks in the corresponding EDX spectrum (Figure 4-8).

**Figure 4-7:** (a) Schematic illustration for the patterned functionalization of graphene with spherical ZnO and cubic Au NPs. (b) AFM image of a modified graphene sheet with small spherical ZnO NPs region-specifically deposited on the plasma-treated area. (c)
AFM image of a graphene sheet modified with small spherical ZnO NPs deposited in the plasma-treated area and big cubic Au NPs attached in the ZnO/plasma-free region on the same graphene surface. (Scale bars: (b) 1 µm; (c) 2 µm).

**Figure 4-8:** EDX spectrum and TEM image (inset) of the patterned asymmetrically-modified graphene sheets with ZnO and Au nanoparticles attached on different regions of the same graphene surface through a photolithographic patterning combined with the π-π stacking and plasma treatment.
Figure 4-9: (a) AFM image of a modified graphene sheet with small spherical ZnO NPs region-specifically deposited on the plasma-treated area. (b) AFM of a graphene sheet modified with small spherical ZnO NPs deposited in the plasma-treated area and big cubic Au NPs attached in the ZnO/plasma-free region on the same graphene surface. (c-e) The corresponding height profiles: c) for the Line A-B in a), d) for the Line C-D in b), and e) for the Line E-F in b) (Scale bars: (a) 1 µm; (b) 2 µm).

4-4. Conclusion and Future Work

Owing to the highly generic nature characteristic of the plasma technique, together with the versatile $\pi-\pi$ stacking interaction between the pyrene-grafted entities
and graphene surface, the methodology developed in this study could be regarded as a general approach toward the fabrication of multidimensional and multifunctional integrate graphene sheets with configurations controllable at the molecular level. Furthermore, the patterned and non-patterned asymmetric functionalization concepts reported in this paper are applicable to graphitic films with more than one graphene sheets and even many other non-graphitic films. Thus, the novel methodology demonstrated in this study will have great impact on both the fundamental and applied research in the field of materials science and engineering. The dissimilar functional groups deposited in a region-specific or surface-specific manner on graphene can be joined together to form novel nanostructures with unique electronic, magnetic, nonlinear optical, and mechanical properties. However, for the effective incorporation of graphene into devices, individual sheets need to be micropatterned or assembled into 3D structures with desirable features similar to that of silicon. Therefore, it is essential to selectively modify surface properties of graphene to gain specific characteristics for particular applications and to covalently or non-covalently link or assemble graphene sheets together into various devices. The asymmetric functionalization of graphene can be incorporated into functional macromolecular structures with region-specific defined characteristics for energy storage and conversion, sensing, and optoelectronics. Utilizing this novel functionalization method, it can be possible to develop miniaturized nanosensors, nanophotonics, nanoelectronics, and nanoenergy systems with multi-dimensional predetermined macromolecular structure.
4-5. References


Chapter 5

Electroless Metal Nanoparticle Functionalization of Graphene

5-1. Introduction

The exceptional inherent properties of graphene make it advantageous for metal nanoparticle functionalization for advanced catalytic systems applications through the electrochemical reactions governing energy conversion in fuel cells. The functionalization of graphene with metal nanoparticles has received a substantial attention recently since the hybridization of graphene with functional nanomaterials enhances the electrical, thermal, chemical, and mechanical properties of each of its components. Moreover, various methods have been employed for both the covalent or non-covalent attachment of metal nanoparticles on graphene sheets. Methods of metal nanoparticle deposition include electrochemical methods which require external stimuli from power sources for the reduction of metal ions onto graphene\(^1-^2\), external reducing agents such as light\(^3\) or microwaves\(^4\). Moreover, metal nanoparticles have also been formed and adsorbed on graphene by the chemical reduction of metal salts in the presence of reducing agents.\(^3\) However, these methods involve the need for external stimuli sources and the use of harsh reducing agents. A more facile method of functionalization is the electroless deposition of metal nanoparticles through a spontaneous galvanic displacement reaction to produce graphene-nanoparticle hybrids. The electroless deposition technique is of particular interest due to its simplicity for large
scale production of the hybrids without an external reducing agent since the reducing electrons originate from the substrate. The process involves the formation of metal nanoparticles onto graphene through differences in reduction potential involving metal ions of a redox potential higher than that of graphene can be reduced into nanoparticles on the graphene support. The reduction potential of the underlying or supporting substrate is the determining factor in governing which metal ion can be reduced to nanoparticles onto graphene (Figure 5-1). Concentration of the metal salt solution and the reaction or exposure time of the graphene/substrate in solution determine the formation, size, and density of the metal nanoparticles on graphene. For example, given that a copper has a redox potential of +0.34 V vs SHE (standard hydrogen electrode) and since Pt (PtCl₄²⁻/Pt, +0.775 V vs SHE) has a redox potential higher than that copper, Pt nanoparticles spontaneously form by via a galvanic displacement reaction without the aid of a reducing agent. Moreover, metal ions even with a redox potential lower than that of graphene can be readily reduced into metal nanoparticles if the redox potential of the supporting substrate is even lower than that of the metal ions, a process which Qu et al previously reported as Substrate-enhanced electroless deposition (SEED) (Figure 5-2). Although demonstrated with single-walled carbon nanotubes (SWNTs), this process can be applied to graphene also as the deposition of metal nanoparticles is achieved via a redox reaction of a galvanic cell, in which the graphene sheets act as a cathode for metal deposition from the reduction of metal ions in solution, while the metal substrate serves as an anode where metal atoms are oxidized followed by dissolution. The electroless deposition of any metal nanoparticles on conducting graphene is a facile and scalable process of the fabrication of the metal nanoparticle/graphene hybrids.
5-2. Experimental Methods

Synthesis of Graphene

Graphene films were primarily grown on 25-μm thick Cu foils (Alfa Aesar, cut into 1 cm strips) in a hot wall furnace consisting of a 22-mm ID fused silica tube heated in a split tube furnace; several runs were also done with 12.5- and 50-μm thick Cu foils (Alfa Aesar). A typical growth process flow is: (1) load the fused silica tube with the Cu foil, evacuate, back fill with hydrogen, heat to 1000 C and maintain a H₂(g) pressure of
40 mTorr under a 2 sccm flow; (2) stabilize the Cu film at the desired temperatures, up to 1000 C, and introduce 35 sccm of CH\(_4\)(g) for a desired period of time at a total pressure of 500 mTorr; (3) after exposure to CH\(_4\), the furnace was cooled to room temperature.

*Electroless Deposition on Graphene*

Platinum (Pt) nanoparticles were electrolessly deposited on Cu-supported graphene by dipping or contacting the graphene/Cu in an aqueous solution of K\(_2\)PtCl\(_4\) (5mM). The nanoparticle growth process is controlled by diffusion of PtCl\(_4\)^{-1} from the bulk solution to the areas of graphene/solution interface. Since this is a diffusion controlled process, smaller particles often gain a faster growth than larger particles due to relatively more surface-receiving sites for the metal ions. After the deposition process, the graphene-on-Cu is coated with poly(methyl methacrylate) (PMMA) and dried in air. The PMMA/Pt-graphene/copper is suspended in a copper etchant (1M of FeCl\(_3\)) to remove the copper leaving a free standing composite film to be transferred to desired substrates such as SiO\(_2\)/Si to render Pt deposited graphene films. The PMMA is selectively removed or washed away in boiling acetone solution thus, isolating Pt-graphene films on substrates.
**Figure 5-2:** Schematic of the electroless deposition of Au nanoparticles onto Ni-supported CVD graphene film. The redox potential of Ni is -0.257 V vs SHE, graphene +0.34 V vs SHE, and Au is +1.002 V vs SHE. The formation of Au nanoparticles occurs through a redox reaction of a galvanic cell where the graphene is the cathode and Ni serves as an anode in the reduction of $\text{Au}^{m+}$ ions to Au and oxidation of Ni to $\text{Ni}^{n+}$. Figure is adapted from ref. 6.

*Layer-by-Layer (LBL) Metal Nanoparticle/Graphene Hybrid Film Transfer*

A large area Cu-supported single layer graphene film serves as a template for LBL stacking of individual graphene films to build a variable thickness stairs-like graphene film. For graphene film transfer, polymethyl methacrylate (PMMA) (6 wt% solution in anisole) was drop casted on the graphene thin films lying on copper foil. The PMMA/graphene supported substrate was suspended in copper etchant solution of 1M FeCl$_3$ to etch away the copper foil and render a free-standing PMMA film with the synthesized graphene adhered to it. The PMMA/graphene film was transferred to adhere on top of the larger area Cu-supported single layer graphene film and then hot acetone was used to dissolve the PMMA residues in hot acetone and leave clean stacked graphene films. This step is repeated to build LBL stairs-like stacked graphene films varying from one to four layers thick using the Cu-supported single layer graphene as the template for stacking.
5-3. Results and Discussion

Figure 5-3 depicts atomic force microscope (AFM) images of the platinum nanoparticles deposited on the graphene/Cu substrate. Interestingly, the particles spontaneously deposited in a hexagon pattern form which can be due to the influence of the grain boundaries of graphene and copper influencing the growth by serving as nucleation sites for the Pt nanoparticles (~ 10 nm). The copper grain boundaries influence the growth the CVD graphene film. Although the detailed mechanism of the spontaneous non-template assisted formation of the Pt nanoparticles on graphene is yet to be confirmed and may need more investigation, a simple conclusion can be drawn from the experimental results is that the particle size of the Pt nanoparticle comprised of the hexagonal pattern increases with increasing graphene layer number. Therefore, this suggests the possibility to tune the patterned deposition of the Pt nanoparticles by altering the grain boundaries of the underlying Cu substrate. If the grain boundaries of the copper are regulated, then the crystal growth of graphene can be controlled to develop ordered patterns of hexagonal Pt nanoparticles.
Figure 5-3: Atomic force microscope (AFM) images (A-C) and topography (D) of the Pt-graphene on a copper substrate (used for CVD growth). The hexagonal Pt nanoparticles of (~ 10nm) patterns (D) are continuous on the graphene-Cu film as evident through the wide-area image (A) and high resolution images (B-C).

Moreover, it is imperative to assemble the metal nanoparticle-graphene hybrids onto to other substrates to assess potential applications such as electrocatalysts for fuel cells or sensors. Figure 5-4 (A) shows an AFM image of Pt-graphene after being
transferred onto a SiO$_2$/Si substrate upon chemically etching away the underlying copper substrate. The image shows the consistent large area patterned spherical Pt nanoparticles spherical on graphene indicating a successful transfer process. In order to confirm the formation of the Pt nanoparticles, x-ray diffraction (XRD) studies were performed to assure the crystallinity of the Pt nanoparticles deposited on the graphene surface (Figure 5-4 (B)). The XRD Spectrum of the Pt-graphene film transferred on SiO$_2$/Si clearly shows broad C (002) peak of the graphene at a 2θ value of 17° and a characteristic x-ray fcc platinum lattice peak at 30° for Pt (111).

**Figure 5-4:** AFM (A) and XRD (B) spectrum of the Pt-graphene film after transferred to a SiO$_2$/Si substrate. As evident from the AFM image, the Pt-graphene hybrid is successfully assembled and transferred from the homogeneity in the wide 20 x 20 um
area scan. The crystal peak of both carbon and Pt are evident thus further indicating the successful transfer of the Pt-graphene hybrid.

**Figure 5-5:** Schematic of the LBL of graphene films for electroless deposition. A LBL stacked graphene-Cu substrate (as described in the experimental methods section) was immersed in an aqueous solution of 5mM of K$_2$PtCl$_4$ for 10 seconds to render an electrolessly deposited Pt nanoparticle-graphene hybrid.

In order to investigate whether the nucleation rate or growth of the patterned nanoparticles on graphene changed based on the thickness of graphene on copper, PMMA-assisted LBL transfer of graphene films was used to have region specific thickness of graphene films onto one single layer graphene-Cu substrate for electroless deposition of Pt with uniform reaction conditions (Figure 5-5). Using scanning electron microscopy, it was apparent that the Pt nanoparticle size increased with increasing layer number of graphene (Figure 5-6). The Pt nanoparticles formed larger cluster-like networks in both two layers (Figure 5-7) and three layers graphene regions (Figure 5-8). However, the single layer graphene region mainly consisted of spherically shaped Pt nanoparticles without cluster formation. According to previous reports$^{7-9}$, the
equilibrium formation of Pt nanoparticles on thin graphene films differs strongly from that of the Pt nanoparticles grown on thick graphene films which also suggests that the interactions mediating the nucleation and growth differ. The larger particles grow on thick graphene by the Ostwald ripening process which is directed by the interaction of bulk cohesive energy and surface interactions.\textsuperscript{7} The morphological differences of the Pt nanoparticles in the different layer number regions of graphene are due to the impact of a new long range interaction which increases in magnitude with decreasing graphene film thickness.\textsuperscript{7,8}

**Figure 5-6:** SEM image of the single and two layers Pt-graphene region after transfer and removal of copper and Raman spectrum depicting the LBL stacking of graphene films. The SEM image clearly shows the cluster-like formation of Pt nanoparticles in the 2 layers region while only single spherical particles in the 1 layer region. The Raman spectrum shows a 2D/G ratio of 1.9 for single layer, 1.5 for two layers, and 1.3 for three
layers of graphene. The increase in the D band is due to the disorder state arising from the presence of Pt nanoparticles on the surface of graphene.

Several reports\(^8,9\) propose that electrostatic interaction within graphene is thickness dependent and play a significant role in mediating size of the metal nanoparticle. Due to the mismatch in work function \(\Delta \Phi\) between graphene (~4.66 eV\(^17\)) and Pt (~5.65 eV), there is a transfer of electrons from the graphene to the nanoparticles when the Pt nanoparticle is adsorbed which results in negative charged particles with an interfacial charge density producing a dipole.\(^8,9\)
**Figure 5-7:** SEM images of the Pt nanoparticles deposited on the single layer graphene-Cu with different reaction times after transferring from Cu. Images A and B of the single layer graphene region of the LBL stacked sample clearly shows the formation of spherical nanoparticles after immersing LBL graphene-Cu substrate in the 5mM K₂PtCl₄ (aq) solution for 10 seconds. Image (C) shows the spherical Pt nanoparticles on single layer graphene after 60 seconds showing increased density and size of the particles with reaction time.

![Figure 5-7](image)

**Figure 5-8:** SEM images of the Pt nanoparticles deposited in the two layer graphene region of the LBL stacked graphene sample after transferring. The images clearly show the formation of cluster-like nanoparticles after immersing LBL graphene-Cu substrate in the 5mM K₂PtCl₄ for 10 seconds.

![Figure 5-8](image)

Since the reaction time and concentration of the Pt salt solution was kept constant to immerse the LBL stacked graphene film, the nucleation size of the deposited
nanoparticles can be compared and analyzed. It was found that the hexagonal-like patterned deposition of nanoparticles formed across the LBL stacked graphene film. AFM was used to image the different regions of the LBL stacked film to obtain a cumulative size distribution based on volume (Figures 5-8A and 5-9A). From the cumulative size distribution curve, D-values can be obtained which signify the diameter which all particles are arranged in order of ascending mass therefore dividing the total mass into specified percentages (Figures 5-8C and 5-9C). For example, D_{0.9} is the diameter at with 90% of a samples mass is comprised of larger particles. D_{0.5} is the median diameter. The volume distribution of the Pt particles in a given section of the hybrid film is given by the percentage of the total sample volume, while the cumulative volume curve provides the total volume of all size ranges as they approach 100%. From analyzing the distribution curves, it is evident that the particle size increased with the layer number of graphene. This can be due to the increased charge transfer taking place in the reduction of the metal ions.
Figure 5-9: AFM image (A), topography (B), and cumulative size distribution curve relating to the AFM image (C) Pt nanoparticles in the single layer graphene region of the LBL stacked graphene. The AFM images clearly shows the hexagonal-like patterned deposition of Pt nanoparticles in the single layer region of the LBL graphene sample. The topography indicates the roughness of the Pt-single layer graphene film. The cumulative size distribution curve plotting the cumulative volume percent vs the size of the features with \( D_{0.9} = 155 \) nm, \( D_{0.5} = 101 \) nm, and \( D_{0.1} = 52.3 \) nm.
**Figure 5-10**: AFM image (A), topography (B), and cumulative size distribution curve relating to the AFM image (C) Pt nanoparticles in the two layer graphene region of the LBL stacked graphene. The AFM images clearly show the hexagonal-like patterned deposition of Pt nanoparticles in the two layer region of the LBL graphene sample. The topography indicates the roughness of the Pt-single layer graphene film. The cumulative size distribution curve plotting the cumulative volume percent vs the size of the features with $D_{0.9} = 203$ nm, $D_{0.5} = 165$ nm, and $D_{0.1} = 115$ nm.
5-4. Conclusion and Future Work

Furthermore, a facile, versatile, and scalable method of metal nanoparticle functionalization of graphene is demonstrated. The electroless deposition of metal nanoparticles on graphene can be used to produce many different hybrid materials without the use of any reducing agents or other external sources. It is shown that particle size can increase with increasing layers of graphene films. The LBL technique can be used to build three-dimensional hybrid materials with controlled structure and design. Further studies on the grain boundaries, surface energy, and nucleation mechanism need
to be conducted to understand the underlying principle of the spontaneous non-template patterned deposition of metal nanoparticles on graphene. It may be important to study different metal substrates used in the CVD of graphene and grain boundaries effect the grain size of the graphene grown. The simple method of electroless deposition to form metal nanoparticle/graphene hybrids can be used for many potential energy or sensing applications.

5-5. References


Chapter 6

Assembly of Graphene and Metal/Metal Oxide Nanoparticle Three-Dimensional Hybrids Thin Film Supercapacitors

6-1. Introduction

In recent years, graphene has received considerable attention for its unique physical, electrical, and mechanical properties. Being a two-dimensional sheet-like structure, graphene and bilayers containing graphene are zero-gap semiconductors that exhibit larger aerial overlap than carbon nanotubes. The hybridization of graphene with functional nanomaterials usually enhances the electrical, thermal, chemical, and mechanical properties of each of its components. Previous methods to develop graphene hybrids involved mixing a graphite oxide dispersion followed by the reduction of metal precursors and vacuum filtration of reduced graphene oxide film followed by spontaneous formation of metal nanoparticles. The challenge in self-assembly is the control of the periodic structures of the hybrid graphene materials over large areas which is essential for functional nanomaterial applications that require the integration of the properties of the materials. The high conductivity and large specific surface area of graphene make it an ideal material for energy storage and conversion.\(^1\) It has been recently reported that the high theoretical specific surface area of completely exfoliated graphene sheets can result in a theoretical specific capacitance of 550 F/g according to the intrinsic capacitance of graphene.\(^1\) However, restacking graphene sheets has impeded the performance of supercapacitors of the graphene materials.\(^2,3\) Therefore, the success of
the utilizing the high surface area and conductivity of graphene based supercapacitors relies on the fabrication process of active materials and electrodes to avoid restacking.\textsuperscript{2,3} Lately, graphene has been investigated as an active electrode material in two ways. First, graphene-based active (pristine graphene, graphene oxide (GO), and active graphene) materials were used without any other electroactive materials.\textsuperscript{4-6} The specific capacitance for aqueous based graphene systems such as graphene and reduced graphene oxide by hydrazine reduction,\textsuperscript{1,7} hydrothermal treatment,\textsuperscript{8,9} vacuum-promoted exfoliation,\textsuperscript{10} and chemical activation of exfoliated graphite oxide.\textsuperscript{6,11,12} developed from is in the range of 90 – 264 F/g. However, the restacking of graphene will diminish the ultra-high specific area of graphene to close to that of bulk graphite (\textasciitilde10m\textasciicircum{2}/g) of graphite and as a result reduce conductivity. In addition to solely graphene-based materials, metal oxides and conducting polymers have also been investigated as active materials for supercapacitor applications. Hybrid graphene materials consisting of metal oxides or conducting polymers to utilize their pseudocapacitance has been studied by a variety of groups resulting in a wide range of performance (e.g., specific capacitance from hundreds to \textasciitilde1000 F/g).\textsuperscript{13-15} An effective method materials design of graphene based supercapacitor electrodes is to physically separate individual graphene sheets with metal/metal oxide nanoparticles to utilize both asymmetric basal planes of graphene thus maximizing the electroactive surface area together with synergistic catalytic effects from the metal/metal oxide nanoparticles.\textsuperscript{15-17} In this study, we have developed a new method for the layer-by-layer (LBL) assembly of gold nanoparticle-decorated and nickel hydroxide deposited graphene thin films. Moreover, we have also developed a new method for the layer-by-layer (LBL) assembly of gold nanoparticle-decorated graphene
thin films. Importantly, the technique does not require the use of added agents for the reduction of gold ions on graphene sheets, a distinct disadvantage over previously developed procedures. In this technique, we study the shape controlled formation of gold nanoparticles via chemical synthesis is deposited on graphene to build a 3D hybrid thin film electrode.

6-2. Experimental Methods

Preparation of Graphene Film

Graphene films were primarily grown on 25-μm thick Cu foils (Alfa Aesar, item No. 13382, cut into 1 cm strips) in a hot wall furnace consisting of a 22-mm ID fused silica tube heated in a split tube furnace; several runs were also done with 12.5- and 50-μm thick Cu foils (also from Aesar). A typical growth process flow is: (1) load the fused silica tube with the Cu foil, evacuate, back fill with hydrogen, heat to 1000 C and maintain a H₂(g) pressure of 40 mTorr under a 2 sccm flow; (2) stabilize the Cu film at the desired temperatures, up to 1000 C, and introduce 35 sccm of CH₄(g) for a desired period of time at a total pressure of 500 mTorr; (3) after exposure to CH₄, the furnace was cooled to room temperature. The experimental parameters (temperature profile, gas composition/flow rates, and system pressure) are shown in Fig. S1. The cooling rate was varied from > 300 C/min to about 40 C/min which resulted in films with no obvious differences.

Layer-by-Layer (LBL) Graphene Film Transfer

A larger area Cu-supported single layer graphene film serves as a template for LBL stacking of individual graphene films to build a variable thickness stairs-like graphene film. For graphene film transfer, polymethyl methacrylate (PMMA) (6 wt% solution in
anisole) was drop casted on the graphene thin films lying on copper foil. The PMMA/graphene supported substrate was suspended in copper etchant solution of 1M FeCl$_3$ to etch away the copper foil and render a free-standing PMMA film with the synthesized graphene adhered to it. The PMMA/graphene film was transferred to adhere on top of the larger area Cu-supported single layer graphene film and then hot acetone was used to dissolve the PMMA residues in hot acetone and leave clean stacked graphene films (Figure 1).

![Figure 6-1: Raman Spectroscopy LBL stacked graphene film. Raman spectra with the D (1300 to 1400 cm$^{-1}$), G (1560 to 1620 cm$^{-1}$), and 2D (2660 to 2700 cm$^{-1}$) bands, respectively. The I$_{2D}$/I$_G$ ratio increases with decreased graphene layer number.](image)
Figure 6-2: NiOH$_2$-graphene Three dimensional Hybrid. A) Step-by-step fabrication of 3D layer-by-layer Graphene/Ni(OH)$_2$ hybrid film: (1) chemical vapor deposition (CVD) synthesized graphene on copper foil, (2) single layer of graphene is separated and transferred via PMMA onto ITO, (3) Ni(OH)$_2$ nanoparticles are electrodeposited onto the graphene film at 0.85V vs SCE, and (4) stacking of a single layer graphene film onto the Ni(OH)$_2$/graphene hybrid film. Steps (3) and (4) are sequentially repeated to build the LBL 3D hybrid Ni(OH)$_2$/graphene film.

Ni(OH)$_2$-Graphene Three-dimensional Hybrid

The Ni(OH)$_2$-coated graphene electrode was prepared by electrochemical deposition of Ni(OH)$_2$ onto an ITO-supported single layer graphene (1.5mm$^2$). The electrodeposition of Ni(OH)$_2$ was conducted on a Chenhua CHI760 model electrochemical workstation with a three-electrode cell, consisting of a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode, and the ITO-supported graphene as a working electrode. An aqueous solution of 0.2M Ni(NO$_3$)$_2$ was used as the electrolyte. Prior to the electrodeposition, the ITO-supported graphene electrode was immersed into an aqueous 1 M HNO$_3$ for 10-20 min to activate the graphene surface. The electrodeposition was then carried out at a constant potential of 0.85 V versus SCE. To deposit a Ni(OH)$_2$ film of about 0.14 mg, the corresponding deposition charge quantity is approximately 0.24 C, which was estimated by Faraday’s law. After deposition, the Ni(OH)$_2$-graphene composite was washed with water several times and used for capacitance measurements. The same one layer Ni(OH)$_2$-graphene on ITO was used as a
template to build a 3D structure with alternating layers of graphene separated with electrodeposited Ni(OH)₂ nanoparticles (Figure 6-2).

![Figure 6-3: XRD of electrodeposited Ni(OH)₂ on graphene supported by ITO.]

6-3. Results and Discussion

*Cyclic Voltammetry of 3D Ni(OH)₂/Graphene film*

Electrochemical properties and capacitance measurements of supercapacitor electrodes were studied by cyclic voltammetry and galvanostatic charge-discharge. A three-electrode cell with a SCE electrode and Pt wire as the reference and counter electrodes, respectively, was employed for electrochemical measurements of the 3D Ni(OH)₂-graphene electrode before and after hybridization with Ni(OH)₂. The measurements were carried out on a CHI electrochemical workstation in a 2M KOH aqueous electrolyte at room temperature. The specific capacitance of the electrode was calculated from cyclic voltammetry (CV) curves for the Ni(OH)₂-graphene in an aqueous solution of KOH (2
M) electrolyte at the scan rates of 10, 20, 50, 100, and 200 mV/s (Figures 6-4, 6-5, 6-6). A pair of strong redox current peaks appeared, arising from the Faradaic reactions of Ni(II) to Ni(III) associated with the Ni(OH)₂ coating.¹⁸ The average specific capacitance of the Ni(OH)₂-graphene electrode was calculated from the CV curves with increasing layer number of the Ni(OH)₂-graphene was obtained. The calculated specific capacitance for one layer of 66 mF/cm², two layer of 133 mF/cm² and 206 mF/cm² for the three layer Ni(OH)₂/graphene film.

**Figure 6-4:** Electrochemical performance of the 3D graphene electrodes measured in 2.0M KOH solution. CV curves of 1 Layer graphene/Ni(OH)₂ composite electrode at scan rates of 10, 20, 50, 100, and 200 mV/s.
Figure 6-5: Electrochemical performance of the 3D graphene electrodes measured in 2.0M KOH solution. CV curves of 2 Layer graphene/Ni(OH)$_2$ composite electrode at scan rates of 10, 20, 50, 100, and 200 mV/s.
Figure 6-6: Electrochemical performance of the 3D graphene electrodes measured in 2.0M KOH solution. CV curves of 3 Layer graphene/Ni(OH)$_2$ composite electrode at scan rates of 10, 20, 50, 100, and 200 mV/s.

Figure 6-7: Electrochemical performance of the 3D graphene electrodes measured in 2.0 M KOH solution. CV curves of 3D graphene and graphene/Ni(OH)$_2$ composite electrodes with increasing layer number measured at a scan rate of 10 mV/s.
Figure 6-8. Galvanostatic charge and discharge curves for (A) one layer, (B) two layer, and (C) three layer Ni(OH)$_2$/graphene electrode at 5mA.

The corresponding galvanostatic discharge curves for the Ni(OH)$_2$/graphene electrode at constant current of 5mA are in a good agreement with the CV measurements, the shape of the charge-discharge curves shown in Figure 6-8 does not show the characteristic of an electric double layer capacitor (EDLC) but mainly pseudocapacitance. Although the graphene layers alone could act as an EDLC but with a low specific capacitance at a scan rate of 10 mV/s was found for the single layer graphene on ITO.
Synthesis of Gold Nanostructures

High aspect ratio nanorods were synthesized by using seed mediated approach described by Murphy et al. First, citrate capped seed nanoparticles are synthesized in which 1.4 mg of sodium citrate and 1.9 mg of HAuCl₄·3H₂O was dissolved in 20 mL water. Then 0.6 mL of 0.1 M ice-cold NaBH₄ solution was added while stirring at a high rate. The solution immediately turned brownish-red thus, indicating the formation of seed gold nanoparticles which were immediately used to for the growth of nanorods.

Figure 6-9: UV/vis and corresponding optical images of gold nanoparticles in aqueous solution of different size (a-c) and (d) shape. The gold nanospheres of different size
exhibit different colors based on surface plasmon resonance. The UV/Vis absorption spectra clearly shows the characteristic absorption peak at ~ 950 nm of the gold nanorods due to the high aspect ratio charging the surface plasmon resonance. All gold nanoparticles were synthesized via seed mediated method in the presence of sodium borohydride as a reducing agent and CTAB as a surfactant.

**Figure 6-10:** AFM images of (A) gold nanorods (~ 150 - 200 nm) and (B) gold nanospheres (~ 50 nm) synthesized by H\textsubscript{AuCl}\textsubscript{4} seed mediated growth with citrate as a capping (stabilizing) agent, NaBH\textsubscript{4} as a reducing agent, and CTAB as a surfactant to enable the thermodynamics to form the particles in suspension.
Figure 6-11: XRD spectrum of electrodeposited gold nanospheres on graphene/ITO. The observed peaks corresponding to the (111), (220), and (311) facets demonstrate that the electrodeposited gold is composed of pure crystalline gold with the face-centered cubic (fcc) nanospherical structures.

Nanogold-Graphene Three-dimensional Hybrid

Solution reduced gold nanorod and nanosphere solutions were spin coated on the surface of the graphene/ITO electrode. The 3D bilayer number was increased by alternating gold nanostructure solution in between transferred graphene layers. Using the 3D nanogold/graphene electrode, electrochemical properties and capacitance measurements of supercapacitor electrodes were studied by cyclic voltammetry and galvanostatic charge-discharge. A three-electrode cell with a SCE electrode and Pt wire as the reference and counter electrodes, respectively, was employed for electrochemical
measurements of the 3D Au-graphene electrode before and after hybridization with Au nanostructures. The measurements were carried out on a CHI electrochemical workstation in a 2M KOH aqueous electrolyte at room temperature. As shown in Figure 6-12, the CV plot depicting a single layer graphene (black line), single layer graphene/gold nanosphere hybrid (blue line), and two layer graphene-gold nanosphere (red line) shows an increase in current with increasing hybrid layers throughout the potential window relating to a larger surface area thus capacitance behavior. The current measured single layer graphene is almost negligible compared to that of the three-dimensional hybrid electrodes. The increase in the current in the same potential window after the deposition of gold nanospheres is due to the enhanced surface area and electrocatalytic behavior of the gold nanoparticles arising from the redox peaks. The current increases with increasing hybrid layer number as evident with the comparison of the single layer hybrid to that of the two layer hybrid graphene-gold nanosphere electrodes. The gold nanospheres on graphene lead to an increase in capacitive behavior through the surface pseudocapacitance mediated through redox reactions occurring on the surface of the gold nanospheres. The EDLC is not evident as the rectangular shape is consistent in the potential window with increasing hybrid layers. Moreover, the stability of the graphene-gold nanosphere electrodes showed reproducibility as the hybrid is constantly charged and discharged over time for 50 cycles. In order to demonstrate the applicability of the hybrid graphene-gold nanosphere for macroscopic film structures, the electrochemical performance of the hybrid up to four layers was tested. Figure 6-13 shows the CV curves for the hybrid graphene-gold nanosphere with increasing layers in an aqueous solution of KOH (2 M) electrolyte at the scan rates of 10, 20, 50, 100, and
200mV/s. The anodic current on the hybrid graphene-gold nanosphere electrode increases as a result of the chemical adsorption of OH and the formation of peroxidation species on the surface of AuNPs. Specifically, Au-OH$_{\text{ads}}^{(1-\lambda)^-}$ is formed on AuNPs according to the following reaction path, Au + OH$^-$ → Au-OH$_{\text{ads}}^{(1-\lambda)^-}$ + $\lambda e^-$ where the ads and $\lambda$ are for the chemically adsorbed species on AuNPs. In the second potential range (0.13 - 0.30 V) the surface oxidation where the surface of the Au NPs is oxidized to form gold oxide species is observed. In the third potential range (0.30 - 0.5 V) a gold oxide monolayer is formed. The gold oxide is reduced to form a cathodic current peak at 0.18 V. The reduction peak at about 0.1 V occurs from the desorption OH groups on the surface of the gold nanospheres. A pair of strong redox current peaks arising from the Faradaic reactions of Au$^0$ to Au(I) are consistent in the CV plots for all the hybrid electrodes.
Figure 6-12: Electrochemical performance of the 3D gold nanosphere/graphene electrodes. The gold nanosphere were electrolessly deposited onto graphene/Cu and then transferred to ITO. (A) Cyclic voltammetry (CV) curves for the 1 bi-layer Au-graphene in an aqueous solution of KOH (2 M) electrolyte at the scan rates of 10, 20, 50, 100, and
200 mV/s. (B) CV plot showing single layer graphene (black line), 1 bi-layer of gold nanospheres/graphene (blue line), and 2 bilayers of gold nanospheres/graphene (red line) at 10 mV/s scan rate. The 3D structure of the electrode with Au nanospheres on graphene increasing the electrochemical active surface area for electrolyte diffusion thus higher charge storage capability and increased pseudocapacitance and specific capacitance. The 2 bi-layer 3D gold nanosphere/graphene has a larger CV retangular window and higher charge storage capability. (C) CV stability test for 50 cycles at 100 mV/s. The electrode is constantly charged and discharged to see how the response changes over time.

**Figure 6-13:** Electrochemical performance of the three-dimensional graphene-gold nanosphere electrodes in a wider current window. The gold nanosphere were
electrodeposited onto graphene/ITO and the two steps are repeated to build the bi-layers. CV curves for the (A) 1 bi-layer Au nanospheres-graphene, (B) 2 bi-layers Au nanospheres-graphene, and (C) 3 bi-layers Au nanospheres-graphene in an aqueous solution of KOH (2 M) electrolyte at the scan rates of 10, 20, 50, 100, and 200 mV/s. (D) CV plot of the 1 bi-layer, 2 bi-layers, and 3 bi-layers of Au nanospheres-graphene at 10 mV/s. The electrochemical window of the 3D structure of the electrode with Au nanospheres on graphene increasing the electrochemical active surface area for electrolyte diffusion thus higher charge storage capability and increased pseudocapacitance and specific capacitance. The 3 bi-layer 3D gold nanosphere/graphene has a larger CV retangular window and higher charge storage

In order to evaluate the supercapacitor performance of the three-dimensional hybrid graphene-gold nanosphere electrode it is important to investigate the charge-discharge capability. Figure 6-14 shows the galvanostatic charge-discharge behavior of the single layer graphene electrode (blue) compared to that of the single layer graphene-gold nanosphere hybrid (red) shows that the hybrid electrode takes more time to charge at constant current (5 mA) therefore can store more energy with higher capacitance behavior. The same as observed with increasing hybrid layers to build macroscopic electrodes (Figure 6-15). The shape of the charge-discharge curves shown in Figures 6-15 and 6-18 exhibit pure pseudocapacitance behavior. Although the graphene layers could act as an EDLC but a low specific capacitance of about 110 F/g at a scan rate of 10 mV/s was found for the single layer hybrid graphene-gold nanosphere.
Figure 6-14: Galvanostatic charge and discharge curves for 1 bi-layer gold nanosphere/graphene (blue curve) and 2 bi-layer gold nanosphere/graphene (red curve) at 5 mA. The electrodes are charged at a constant current where the longer it takes for the electrode to charge the more energy it can store with higher capacitance. The 2 bi-layer gold nanosphere/graphene has a higher capacitance than the 1 bi-layer due to a higher charge storage surface area within the 3D structure.
Figure 6-15: Galvanostatic charge and discharge curves of the three-dimensional graphene-gold nanospheres on ITO. Charge-discharge curves of (A) 1 bi-layer Au nanospheres-graphene, (B) 2 bi-layers Au nanospheres-graphene, (C) 3 bi-layers Au nanospheres-graphene, and (D) 3 bi-layers Au nanospheres-graphene in an aqueous solution of KOH (2 M) electrolyte at 5 mA. The 3D electrodes are charged at a constant current where the longer it takes for the electrode to charge the more energy it can store with higher capacitance. The 2 bi-layer electrodeposited gold nanosphere/graphene has the highest charge-discharge cycle time (~40 seconds) indicating that there is higher resistance for electrolyte diffusion with increasing bi-layers.

In addition, three-dimensional hybrid graphene-gold nanorod structures were developed to exhibit supercapacitive behavior. The surface plasmon resonance effect in
shape controlled gold nanoparticles can be advantageous for synergistic electrocatalytic effects when adsorbed onto the sp2 hybridized basal plane structure of graphene. The ability to control the size of gold nanostructures can lead to the development of graphene based hybrid structures with controlled separation distances between individual graphene sheets. The ability to control the shape of the gold nanoparticles to separate individual graphene sheets can lead to the development of hybrids of different electroactive surface with variable basal planes available for electrolyte network diffusion. Figures 6-16 and 6-17 depict the CV curves of the three-dimensional hybrid graphene-gold nanorod with current proportionally increasing with increasing hybrid layers.

![Figure 6-16: Electrochemical performance of the 1 bi-layer gold nanorods/graphene electrodes in a narrow current window to eliminate the influence of the reduction of oxygen in electrolyte at lower currents. The CV curves for the 1 bi-layer Au nanorods-](image)
graphene in an aqueous solution of KOH (2 M) electrolyte at the scan rates of 10, 20, 50, 100, and 200 mV/s. The potential window increases due to the pseudocapacitance of the Au nanorods of the electrode due to the increase in the electrochemical active surface area for electrolyte diffusion thus higher charge storage capability and increased pseudocapacitance and specific capacitance.

Figure 6-17: Electrochemical performance of the 3D gold nanorod/graphene electrodes in a wider current window. The gold nanorods were spin coated from aqueous solution onto graphene/ITO and these two steps are repeated to build the bi-layers. CV curves for the (A) 1 bi-layer Au nanospheres-graphene, (B) 2 bi-layers Au nanospheres-graphene,
and (C) 3 bi-layers Au nanospheres-graphene in an aqueous solution of KOH (2 M) electrolyte at the scan rates of 10, 20, 50, 100, and 200 mV/s. The electrochemical window of the 3D structure of the electrode with Au nanorods on graphene increasing the electrochemical active surface area for electrolyte diffusion thus higher charge storage capability and increased pseudocapacitance and specific capacitance.

The charge-discharge curves of the three dimensional hybrid graphene-gold nanorod electrodes show similar cyclic charging and discharging capability to that of the graphene-gold nanosphere hybrid. However, the single layer hybrid and two layer hybrid had identical charge-discharge cycle time but the cycle time of three layer hybrid electrode decreased due to the increasing charge transfer resistance within the hybrid network.
Figure 6-18: Galvanostatic charge and discharge curves of the 3D Au nanorods/graphene. Charge-discharge curves of (A) 1 bi-layer Au nanospheres-graphene, (B) 2 bi-layers Au nanospheres-graphene, (C) 3 bi-layers Au nanospheres-graphene, and (D) 3 bi-layers Au nanospheres-graphene in an aqueous solution of KOH (2 M) electrolyte at 5 mA. The 3D electrodes are charged at a constant current where the longer it takes for the electrode to charge the more energy it can store with higher capacitance. The 1 bi-layer and 2 bi-layers of gold nanorods/graphene has the highest charge-discharge cycle time (~80 seconds) but the charge-discharge cycle time decreased up increasing the bi-layers.

6-4. Conclusion and Future Work

The controlled assembly of graphene to construct 3D nanoarchitectures with metal and metal oxide nanoparticles in a LBL manner can render ultra-thin and transparent electrodes with controlled structure. The LBL assembly of graphene together with other inorganic nanostructures can be a general approach to develop other 3D composite nanomaterials for energy conversion and optoelectronics. The electro/electroless deposition of metal and metal oxide nanoparticles on graphene can be increase the surface area and modify the conductivity of graphene. The LBL stacking of graphene with metal/metal oxide nanoparticles to physically separate individual graphene sheets to build the 3D nanoarchitectures can be critical in exposing both asymmetric basal planes of individual graphene sheets to increase the available surface area and conductivity for applications. However, in this work it is critical to control the size of the nanoparticles for
homogeneity in the separation distance between individual graphene sheets in order to build precise controlled structures for applications. In addition to size, it is also imperative to control the density of the nanoparticles on the graphene sheets to ensure that the high theoretical surface area of each graphene sheets is utilized to optimally utilize the superior properties of graphene with other materials.

6-5. References


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Chapter 7

Assembly of Graphene and Carbon Nanotube Three-Dimensional Hybrids for Supercapacitors

7-1. Introduction

Exceptional properties such as stable crystal structure, optical transparency, and superior electronic properties form high electron mobility make graphene a nanomaterial with promising applications. Among the many methods employed for producing graphene films, mechanical cleavage of HOPG or exfoliation of graphite crystals, chemical vapor deposition, solvent thermal reaction, and chemical routes via carbon nanotubes (CNTs), graphite intercalation compounds (GIC) or graphite oxide (GO) are the most widely recognized and used methods to produce single- and few-layer pristine graphene. Moreover, the oxidation and reduction of graphite is one of the most used methods for mass production of graphene for industrial applications. However, the reduction of graphene oxide results in a decrease in hydrophilicity which in turn leads to greater aggregation and precipitation thus, losing its unique 2D characteristics. Both chemical functionalization and electrostatic stabilization have been employed to reduce the agglomeration of graphene in order to utilize its unique properties.

Moreover, graphene and carbon nanotubes have been combined to form transparent conductive films, and electrodes for rechargeable lithium ion secondary batteries. Researchers recently designed a computational model recently of the novel 3D structure consisting of parallel graphene layers stabilized by vertically aligned CNTs in between...
the graphene planes. However, experimental fabrication of the 3D graphene/VA-CNT hybrid structure via the transfer assembly process remains challenging. In addition, on the basis of previous work by Du et al on the tunable 3D pillared VA-CNT/graphene architectures through intercalated growth of VA-CNTs into thermally expanded highly ordered pyrolytic graphite (HOPG) by the pyrolysis of iron phthalocyanine, we report a novel strategy to prepare 3D graphene/VA-CNT hybrid structures by a contact film transfer process for assembly utilizing attractive inter-surface forces e.g., van der Waals of graphene and VA-CNTs. For the first time, we demonstrate a novel yet facile technique to develop three dimensional hybrid graphene/VA-CNT nanostructure via free-standing film transfer through the hydrophobic-hydrophobic interactions.

7-2. Experimental Methods

Synthesis of Graphene Film

Graphene films were primarily grown on 25-μm thick Cu foils (Alfa Aesar, item No. 13382, cut into 1 cm strips) in a hot wall furnace consisting of a 22-mm ID fused silica tube heated in a split tube furnace; several runs were also done with 12.5- and 50-μm thick Cu foils (also from Aesar). A typical growth process flow is: (1) load the fused silica tube with the Cu foil, evacuate, back fill with hydrogen, heat to 1000 C and maintain a H₂(g) pressure of 40 mTorr under a 2 sccm flow; (2) stabilize the Cu film at the desired temperatures, up to 1000 C, and introduce 35 sccm of CH₄(g) for a desired period of time at a total pressure of 500 mTorr; (3) after exposure to CH₄, the furnace was cooled to room temperature. The experimental parameters (temperature profile, gas composition/flow rates, and system pressure) are included in the supplementary
information. The cooling rate was varied from > 300°C/min to about 40°C/min which resulted in films with no obvious differences.

**Synthesis of Vertically Aligned Carbon Nanotubes (VA-CNTs)**

The vertically-aligned multiwalled carbon nanotube (VA-CNT) arrays were synthesized by low pressure chemical vapor deposition (CVD) on 4×4 mm² SiO₂/Si wafers. A 10-nm thick Al layer was coated on the wafers before the deposition of 3-nm Fe film in order to enhance the attachment of grown nanotubes on the Si substrates. The catalyst coated substrate was first inserted into the quartz tube furnace and remained at 450°C in air for 10 min, followed by pumping the furnace chamber to a pressure less than 10 mTorr. Thereafter, the growth of the VA-CNT arrays was achieved by flowing a mixture gases of 48% Ar, 28% H₂, 24% C₂H₂ at 750°C under 10-100 Torr for 10-20 min. The length of the resultant aligned VA-CNTs could be adjusted by controlling the deposition time and pressure.

**3D Graphene/VA-CNT Hybrid Film**

The graphene/Cu-supported substrate was suspended in copper etchant solution of 1M FeCl₃ to etch away the copper foil and render a free-standing graphene film (Figure 7-1). The free-standing graphene film is then transferred directly to a Si substrate suspended free-standing graphene film. Consequently, a VA-CNT array can etched away from the Si/SiO₂ substrate by immersing the in the dilute aqueous HF (1 wt %). Upon absorption of the graphene film on Si, the free standing VA-CNT array is transferred onto the graphene film by contacting the graphene film via dry adhesive force resulting in a 3D layer of VACNT/graphene. Furthermore, a free-standing graphene film is adsorbed on
the resultant 3D structure to give a hybrid bilayer graphene/VA-CNT/graphene as the steps are repeated to increase the layer numbers in the 3D structure.

**Figure 7-1:** Optical images of free-standing graphene in copper etchant, FeCl₃ (top images) and in water upon removal and dilution of the copper etchant (bottom images). CVD graphene grown on Cu is placed to float in 1M FeCl₃(aq) to chemically etch away the copper substrate over time. The Fe³⁺ is a strong oxidizer and Cl⁻ is a strong complexing agent for Cu²⁺ ions forming [CuCl₄]²⁻ in solution. In order to remove the copper etchant and the byproducts of reaction in solution, the solution is diluted repeatedly with deionized water until removing all the impurities leaving only free-standing graphene in water.
3D Graphene/VA-CNT Supercapacitor

A gel solution containing PVA powder (1.0 g) and H₃PO₄ (1.0 g) in water (10.0 mL) was used as the electrolyte for supercapacitors. The as-prepared 3D graphene/VA-CNT composites were connected with a copper wire using silver paste, then the gel electrolyte was coated over the most part (90% length) of the, followed by drying in the air at room temperature for several hours. Then, two such electrolyte-coated VA-CNT electrodes were assembled into a supercapacitor by pressing them together.

**Figure 7-2:** Langmuir-Schaefer Transfer method. A horizontal lifting technique where substrate at very low speed of typically until contact with the monolayer is made and then lifting it up at low speed, until the substrate and water are separated.

7-3. Results and Discussion

The Langmuir-Schaefer assembly of graphene (Figure 7-2) from water facilitates for the facile and scalable integration of two-dimensional graphene sheets into three-dimensional macroscopic structures on arbitrary substrates (Figure 7-3). The AFM image and Raman spectrum confirm the successful transfer of a continuous few layer graphene
film onto a glass substrate (Figure 7-4). This facile and scalable transfer and assembly technology can be critical for the development of multidimensional and multifunctional graphene based applications. However, the realization of these applications requires hybrid graphene systems consisting of two or more components to capitalize on the synergetic properties of each individual component. Therefore, it is significant to study the interfacial surface properties of graphene to develop three-dimensional hybrid networks.

Figure 7-3: Optical images and Raman spectra of transferred and assembled both single layer and multilayer graphene onto hydrophilic and hydrophobic substrates via the
Langmuir-Schaefer method. Optical images of multi-layer graphene (~10 layers) on (a) flexible PDMS and (b) glass. Optical images of single layer graphene on (c) gold patterned SiO$_2$/Si and (d) on flexible PDMS. The Raman spectra correlate with the thickness of the graphene films as the 2D/G ratios correspond accordingly as for the single layer graphene (2D/G > 3) and the multi-layer graphene (2D/G < 1).

**Figure 7-4:** AFM image (topography inset) and Raman spectra of two layer graphene transferred to glass. The AFM image shows large area (24 x 25 um) graphene film with double layer topographical thickness (~1-4 nm) transferred by the Langmuir-Schaefer method onto glass. The Raman spectra confirms with the 2D/G ratio = 3.1 correlating to double layer graphene.
Since the surface of a material determines its compatibility with its surroundings\textsuperscript{18}, it is important to examine and understand the surface properties of graphene. Graphene-based nanocomposites have superior mechanical properties due to the combination of high specific surface area, strong nanofiller-matrix adhesion, and excellent mechanical properties of the sp\textsuperscript{2} carbon bonding network. In general, even though the bulk properties are compatible for a specific application, surface modification and engineering can still be desired to form composite materials.\textsuperscript{18} For example, surface modification is important in for materials used in hybrid materials, coating, and biological media due to factors such as surface charge, hydrophillicity, and wettability which determine cell adhesion, cell proliferation, and immune response.\textsuperscript{18} Specifically, the wettability of a solid surface depends on chemical composition and surface roughness (geometric structure).\textsuperscript{19} Surface properties such as chemical structure, homogeneity, crystallinity, physical shape, and the level of cohesive attractions between atoms and molecules, provide information regarding its interaction with its surroundings.\textsuperscript{18} Correspondingly, the surface properties of graphene are important in device fabrication for multifaceted applications.\textsuperscript{18} For example, understanding the surface properties of graphene is pivotal because contact deposition is critical to device performance and functionality, but the hydphobicity of graphene hinders contact deposition.\textsuperscript{20} During contact deposition on top of graphene, the process can be unsuccessful due to the surface energy and surface roughness. Furthermore, there have been limited studies investigating the surface properties of graphene, specifically the wettability and surface energy of graphene (Figures 7-5 and 7-6).
Figure 7-5: Wettability of various solvents of different polarity on graphene with increased layer number. The relationship with graphene layer number and wettability is based on the surface chemistry of graphene and the polarity of the solvent.

Properties such as its high thermal conductivity compared to that of CNTs and negative thermal expansion coefficient and thermal contraction makes the use of graphene viable in many potential applications.\textsuperscript{18} For example, there has been reported use of graphene in organic solar cells, field-effect transistor (FET), hydrogen storage, and supercapacitors.\textsuperscript{18} Surface properties such as surface wetting and roughness are important in graphene-based device fabrication. Since limited research has focused on the surface properties of graphene, Wang et al\textsuperscript{18} examined the wettability and surface-free energy of graphene by contact angle measurements. Wang et al\textsuperscript{18} assembled graphite, graphene oxide, and graphene (chemically reduced graphene oxide) into a thin film by the filtration process previously reported\textsuperscript{21} to test the wettability of the films by measuring the static
contact angle with water. The presence of non-polar carbon atoms in graphite contribute to its hydrophobic nature as a static contact angle of 98.3° between the graphite film and water was measured. However, the static contact angle for graphene oxide film prepared from oxidized and isolated graphite was measured to be 67.4° exhibiting hydrophilic properties. FTIR characterization revealed the presence of polar hydroxyl and epoxy groups on the graphene oxide surface confirming a hydrophilic structure. Upon chemical reduction of graphene oxide by hyrdrazine, FTIR results revealed the elimination of the polar hydroxyl and epoxy groups making the surface more hydrophobic. The static contact angle on the graphene surface was measured to be 127°, which is larger than that of the graphite film. The wettability properties of different polar organic solvents on graphene were also tested. On the graphene oxide film, the static contact angle was measured to be less than 90° for all the polar solvents. However, the graphene film was wetting with all of the polar solvents except glycerol. For all of the organic solvents, a larger static contact angle was measured on the graphene film compared to the graphite film indicating that graphene has less wettability than graphite. Wang et al postulated that isolating graphite to few- or single-layers of graphene can decrease its wettability. Using Young’s equation, the contact angle can be obtained,

\[ \gamma_s = \gamma_{sl} + \gamma_l \cos \theta \]

where \( \gamma_s \) represents the solid surface free energy, \( \gamma_l \) represents the liquid surface free energy, \( \gamma_{sl} \) represents the solid-liquid interfacial energy, and \( \theta \) is the contact angle.
between the solid surface and liquid. In addition, the work of adhesion between graphene-based materials and selected solvents can be calculated.\textsuperscript{18}

The work of adhesion of the graphene oxide and solvent interface is significantly larger in comparison to the graphite and graphene layers due to the polarity of the covalently bonded hydroxyl and epoxy groups.\textsuperscript{18} The isolated graphene layers exhibited smaller work of adhesion to the solvents compared to graphite which is consistent with the contact angle measurements.\textsuperscript{18} Wang et al\textsuperscript{18} also suggested that reducing the dimensions of a material from 3D to 2D can reduce the wettability and decrease the interfacial adhesion with liquids. The work of adhesion of a solid surface and liquid ($W_{sl}$) can be expressed as,

$$W_{sl} = \gamma_s + \gamma_i - \gamma_{sl}$$

Thus, combining Young’s equation with the above expression for the work of adhesion we obtain an expression for work of adhesion as a function of the surface energy of the liquid and contact angle,

$$W_{sl} = \gamma_i (1 + \cos \theta)$$

Moreover, surface energy values can be obtained from the wettability measurements. Methods such as Zisman and Satio approximation, geometric and harmonic mean approximation, Berthelot’s approximation, Fowkes approximation, acid-base approximation can be used to characterize the surface energy of a solid through contact
angles. Nonetheless, most of these methods depend on the liquids used for wetting. Wang et al\textsuperscript{18} used Neumann’s proposed equation of state theory to determine the surface free energy of graphene.\textsuperscript{22-24} Using the equation of state theory, the contact angle between the solid and liquid is given by the following expression, \textsuperscript{22-24}

$$
\cos \theta = -1 + 2 \frac{\gamma_s}{\sqrt{\gamma_i}} e^{-\beta (\gamma_s - \gamma_i)^2}
$$

where $\gamma_s$ represents the solid surface free energy, $\gamma_i$ represents the liquid surface free energy, and $\beta$ is a constant coefficient related to a specific solid surface. Rearranging the above expression results in the following,

$$
\ln \left[ \frac{\gamma_i}{\gamma_s} \left( \frac{1 + \cos \theta}{2} \right)^2 \right] = -2\beta (\gamma_s - \gamma_i)^2 + \ln (\gamma_s)
$$

Plotting the left side of the equation as a function of $\gamma_i$ followed by second-order polynomial fitting, will help determine the parameters $\beta$ and $\gamma_s$.\textsuperscript{18} Wang et al\textsuperscript{18} performed regression analysis by the equation state theory to determine the surface energy of graphite, graphene oxide, and graphene for different solvents. The surface energy of graphene at room temperature was measured to be 46.7 mJ/m$^2$ while the graphene oxide exhibited a surface energy of 62.1 mJ/m$^2$.\textsuperscript{18} These measured values confirm the notion that isolated graphene sheets are more difficult to wet than graphite and that the work of adhesion between graphene and liquids is smaller.\textsuperscript{18}
Figure 7-6: The surface energy of graphene with increasing layer number. The components of surface energy with dispersive interactions and polar interactions are computed from Young’s relation which relates the contact angle to the surface energies of the solid and liquid and to the surface tension.

Table 7-1: Surface energy and the force components of graphene films with increasing thickness.
Utilizing its superior electronic characteristics, graphene has been investigated for applications such as FETs and logic devices.\textsuperscript{20,25} The development of large-area graphene has further enhanced the prospects of graphene-based electronic applications for the post-silicon era.\textsuperscript{20} It is important to study the surface hydrophobicity behavior of graphene in order to understand the role of contact deposition in determining device performance and functionality.\textsuperscript{20} In efforts to elucidate this characteristic of graphene, Shin et al.\textsuperscript{20} investigated the wettability of epitaxial graphene (EG) on SiC as well as the relationship of wettability on the number of graphene layers by contact angle goniometry. Contact angle measurements were made on a SiC substrate, highly ordered pyrolytic graphite (HOPG), single-layer EG, and plasma-etched graphene on SiC.\textsuperscript{20} Despite the SiC substrate having only a single monolayer of graphene, a dramatic difference was evident in the contact angle of the water droplet with graphene on SiC (92.5°) compared to that of plain SiC (69.3°).\textsuperscript{20} The contact angle of a HOPG surface (91°) suggests its hydrophobicity is similar to that of graphene on SiC.\textsuperscript{20} Upon etching a monolayer of graphene via oxygen plasma, the contact angle (70°) reduced to a similar value of SiC.\textsuperscript{20} As indicative of the contact angle measurements, the surface of graphene is hydrophobic in nature or non-adhesive where using oxygen plasma treatment adhesion properties of graphene can be improved, making the surface more hydrophilic.\textsuperscript{20} Moreover, Shin et al.\textsuperscript{20} also examined the contact angle as a function of the number of graphene layers. As opposed to Wang et al.\textsuperscript{18} who previously reported a contact angle of 127° on graphene films\textsuperscript{19}, it was determined that the wettability of graphene is independent of the layer thickness.\textsuperscript{20} Shin et al.\textsuperscript{20} attributed this contradiction to the surface roughness resulting from the integration of multiple microscale and dissimilar layers of graphene. This is
consistent with the fact that the hydrophobicity increases when a hydrophobic surface is microstructured. The change in the contact angle due to surface roughness can be described by the following relationship,

$$\cos \theta_w = R_w \cos(\theta_0)$$

where $\theta_w$ is the apparent contact angle, $R_w$ is the surface roughness factor, and $\theta_0$ is the contact angle in Young’s mode. Therefore, Shin et al. showed that a monolayer of epitaxial graphene was just as hydrophobic as HOPG and that there was no evident correlation between different layers of graphene and wettability.

Furthermore, the facile and scalable Langmuir-Schaefer assembly technique can be used to develop innovative graphene-based 3-D network structures consisting of parallel graphene layers at variable distance with the empty space between adjacent graphene layers being filled with other nanomaterials to serve as a bridge between two graphene layers to provide additional channels for electrical conduction. Specifically, intercalating vertically aligned CNTs into naturally existing layered graphite and directly forming a layered hybrid nanocomposite consisting of alternate CNT films and graphene sheets can be realized using the scalable Langmuir-Schaefer assembly technique. This scalable technique of assembly allows for the incorporation two different allotropes of carbon nanostructures into an efficient percolating network to obtain high surface area and conductive materials for investigating the synergistic effects between the two components. As shown in Figure 7-7 and 7-8, the Langmuir-Schaefer technique can be
used to build three-dimensional hybrid graphene/VA-CNT structures from free-standing LBL film transfer methods.

**Figure 7-7**: Transfer process to fabricate 3D graphene/VA-CNT. Free-standing graphene and VA-CNT films are assembled together in a layer-by-layer process. (a) Optical image of A-CNT array transferred on silicon. Optical images of 3D graphene/A-CNT on (b)
silicon, (c) paper, and (d) PDMS. Contact angle measurements on (b) VA-CNT and (c) 3D graphene/VA-CNT are shown.

Figure 7-8: Images of free-standing (a) graphene and (b) VA-CNT array. Graphene on PDMS and CNT-graphene on PDMS after Langmuir-Schaefer method. (a) Optical image of graphene transferred and assembled onto PDMS (video in supporting information) and (b) optical image of 3D graphene/A-CNT film after VA-CNT array was transferred and assembled onto graphene.

Raman spectroscopy was used to confirm the formation of the hybrid graphene/VA-CNT structure. As shown in Figure 7-9, the increases in the $I_{2D}/I_G$ and $I_D/I_G$ ratio and the stiffening of the 2D band confirm the formation of the hybrid graphene/VA-CNT structure. XPS was also used to confirm the formation of the hybrid structure with
the LBL deposition and tracking of first the Langmuir-Schaefer assembly of graphene followed by the assembly of nitrogen doped VA-CNTs (VA-NCNTs) array onto the graphene. As portrayed in Figure 7-10, the presence of nitrogen after the deposition of VA-NCNT array onto the graphene to form the hybrid structure is an indication of the successful integration and assembly of the two materials.

Figure 7-9: Raman Spectra showing the LBL building of the 3D graphene-CNT hybrid on PDMS. The change in the 2D/G in the hybrid structure together with the increase in the \( \frac{I_D}{I_G} \) ratio after the transfer of graphene onto the CNT array is an indication of the successful formation of the 3D hybrid on PDMS.
Figure 7-10: XPS Spectra of A) graphene and B) Graphene/N-VACNT. The increase in the nitrogen concentration is due to the successful transfer of the N-doped CNT on graphene.

The SEM images in Figure 7-11 (a-g) show the resultant single and multilayers of the three-dimensional hybrid graphene-VA-CNT structure. The Langmuir-Schaefer technique results in the LBL separation of individual graphene sheets with VA-CNT arrays creating an all carbon hybrid structure. This LBL process can also be applied to produce the graphene/VA-CNT/graphene hybrids as seen in Figure 7-13 (a-c) demonstrating the applicability of the Langmuir-Schaefer assembly for diverse hybrid nanostructures with variable and unique combination of components.
Figure 7-11. SEM images of (A-D) 3D graphene/VA-CNT and (E-G) multi-layer 3D graphene/VA-CNT fabricated through the transfer process.
Figure 7-12: Raman spectra of the VA-CNTs shows the typical spectrum of multi-walled CNTs with characteristic doublet peaks of the D band at ~ 1330 cm⁻¹ and G band at ~ 1550 cm⁻¹. Raman spectroscopy shows that the CVD graphene film has the G peak at 1582 cm⁻¹ and a symmetric 2D band around 2700 cm⁻¹ which is consistent with the reported single layer graphene spectra.¹⁹,²⁰
Figure 7-13. SEM images of 3D graphene/VA-CNT/graphene fabricated by the transfer process.

As a potential application, all-solid-state supercapacitors have been fabricated by using the 3D CNT/graphene composite as the electrode (Figure 7-14a), a piece of Polyvinylidene Fluoride (PVDF) filter membrane and a solution of polyvinyl alcohol (PVA) and H₃PO₄ in water were used as the separator and electrolyte. The electrochemical performance of the supercapacitor was carried out through cyclic voltammetry (CV) curves, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS). Figure 7-14b shows CV curves of the supercapacitor based on the 3D
structure at the scan rate from 0.05 to 1.0 V s\(^{-1}\), which retains perfect rectangular shapes even when the scan rate increased to 1.0 V s\(^{-1}\), suggesting excellent capacitive behavior. Typical galvanostatic charge/discharge curve of a supercapacitor was shown as Figure 7-14c, the symmetric triangular shape indicates nearly ideal capacitive behaviors. From the charge/discharge curve, the specific capacitance of supercapacitors can be calculated using the equation of 

\[ C_{sp} = \frac{2I\Delta t}{S\Delta V} \]

where \( I \) is the applied current, \( S \) is the area of active electrode in supercapacitor, \( \Delta t \) is the discharging time and \( \Delta V \) is the voltage window, respectively. Accordingly, the specific capacitance (vs electrode area) is about 0.9 mF cm\(^{-2}\). The Nyquist plot in Figure 7-14d shows a near vertical shape at low frequencies, suggesting a pure capacitive behavior and a low charge transfer resistance for the adsorption process. The series resistances of supercapacitors is as low as 200 Ω, which represent the low charge transfer resistance at the interface between the electrode and electrolyte. The electrochemical performance is relative low, which can be improved further by introducing conductive polymers or metal oxide in future.
**Figure 7-14:** (a) Schematic illumination of the supercapacitor structure using the 3D CNT/graphene architecture. (b) CV curves of a supercapacitor at scan rates ranging from 0.05 to 1.1 V s⁻¹. (c) Typical galvanostatic charging-discharging curves of a supercapacitor at a constant current of 10 μA. (d) Nyquist plots of a supercapacitor with the frequency range from 10⁻² to 10⁵ Hz.
7-4. Conclusion and Future Work

The Langmuir-Schaffer method demonstrated through this work can be employed to successfully build controlled macromolecular architectures with nanomaterials as building blocks. This facile method of successful assembly and integration of graphene and carbon nanotube arrays has the potential to lead to the construction of new supermolecular systems with defined structure and components. The supercapacitor performance for the one bi-layer 3D graphene/CNT all carbon electrode is promising as further studies can investigate the layer number with the energy storage capability. The Langmuir-Schaefer process can be repeated to build the bi-layer number as demonstrated with the graphene/CNT/graphene composite. The large surface area and all carbon junction between the 2D graphene sheets and 1D CNT array have the potential for diverse applications such as electrocatalysts for energy conversion and thermal interface materials for thermal management. The combination of CNT arrays with graphene into a unique 3D hybrid network have the potential to improve the thermal performance of composite materials by dramatically increasing thermal conductivity. The novel Langmuir-Schaeffer method of assembly for carbon nanomaterials enables the controlled assembly of graphene and CNT arrays at specific locations with all carbon junctions for superior heat transfer in the composite material.

7-5. References


Chapter 8

Summary

8-1. Conclusion and Future Work

Novel and facile methods for controlled functionalization and assembly of graphene for individual nanostructure material system design have been developed. The controlled modification and assembly methods are expected to lead to better quality control procedures at the nanoscale to develop more reliable nano and micro devices with better control of material microstructure and interfacial structure to tailor synergistic mechanical, electrical, and thermal properties. Specifically, the development of new functionalized graphene materials with high-performance properties will increase system component reliability for applications at the junction of materials and chemistry for the development of nanoelectronics, nanosensors, and other nanodevices. However, the incorporation of graphene into these applications requires the controlled modification of the interface to alter its physiochemical properties to optimize interaction with other materials and performance. Therefore, the region-selective chemical modification of graphene is essential for region-specific connection and interaction with individual sheets or other materials into well-defined structures.

Moreover, the new functionalization methods demonstrated for the deposition of multiple chemical moieties on the same side or opposite sides of graphene sheets are general approaches which can be used to selectively modify carbon nanomaterials. This advancement in the science of functionalization of graphene enables selective organization and orientation of individual graphene sheets to induce directional properties
and interaction in systems. The asymmetric functionalization of graphene is critical for the advancement of hybrid systems and supermolecular systems consisting of multiple components to interdependently take advantage of each individual component’s properties. Similarly, the functionalization of multiple components on the same side of graphene sheets serves as a platform for guided directional self-assembly for materials design together with region-specific properties. Furthermore, the combination of these novel functionalization methods demonstrated make it viable for multicomponent functionalization on opposite surfaces of graphene sheets to potentially lead to the development of new class of materials with defined components and structures while maintaining structural integrity.

In addition to controlled functionalization, the novel methodology to selectively assemble graphene films onto any arbitrary substrate in a region-specific manner enables the scalable fabrication and 3D construction of graphene based hierarchical nanostructures. The Langmuir-Schaefer technique employed can be generally applied to selectively assemble graphene of onto any material for device fabrication. Utilizing this new transfer and assembly technology, it is easy to construct 3D hybrid networks based on individual 2D graphene sheets. As opposed to other common polymer-assisted methods, this technique has the potential to assemble defect free as grown graphene onto substrates with intricately small features for miniaturized devices.
Nowadays, electronic devices operate at higher power densities and higher temperatures than ever before. Current and near future military devices can create extremely high heat fluxes of more than 1,000 W/cm². This problem will become even more challenging when coupled with the requirements for low pressure drops, enhanced reliability, compact size, and light weight/lower cost. For developing electric aircraft and other relevant devices, and reducing or perhaps eliminating rotatory power generation systems, it often requires the use of stationary power devices (such as, rechargeable batteries, capacitors, heat exchangers etc.) distributed throughout the vehicle systems, including aircrafts and automobiles.
9-1. Electrostatic Assembly of Graphene/Gold Nanorod Three-Dimensional Thin Film Hybrids for Supercapacitors and Methanol Oxidation

9-1.1. Introduction

Hybrid materials incorporating noble metal nanoparticles dispersed on surface functionalized graphene is a new area of interest due to their unique properties and potential applications as catalysts, optoelectronic devices, and electrochemical energy conversion and storage. Gold nanorods have been the recent focus of researchers because of their novel size- and shape-dependence in the optical, electronic, and catalytic properties. For example, gold nanorods have a strong interaction with visible light through resonance excitation of the collective oscillations of their conduction electrons. The surface plasmon resonance bands of gold nanorods are attributed to the size, shape, aspect ratio, nanoparticle composition, inter-particle distances, and surrounding environment. Moreover, gold nanoparticles have been used as a catalyst for CO oxidation and the water gas shift reaction where reducing the particle size can enhance activity. Specifically, gold nanoparticles have been investigated for the electrooxidation of small molecules such as CO and methanol. Nevertheless, assembling gold nanorods in nanostructured thin films with electronic and ionic pathways for electrochemical applications is challenging. It is advantageous to disperse metal nanoparticles on
electrically conductive supports to reduce ohmic resistance and facilitate charge transfer for electrochemical applications. There have been several reports\(^1\), \(^2\) of the electrochemical properties of layer-by-layer (LBL) thin films consisting of metal nanoparticles and carbon nanotubes (CNTs). For example, a facile method to assemble dispersed CNTs into thin films using the LBL technique consists of the repeated and sequential immersion of a substrate into electrostatically complimentary functionalized materials was demonstrated by Yu et al\(^3\). Implementing this technique can produce ultrathin films and highly tunable surfaces using various nanomaterials on geometric surfaces. The LBL technique was employed to construct ultrathin electroactive multilayer films containing carboxylic acid functionalized-CNTs and chemically reduced graphene oxide (GO) sheets in the presence of poly(ethyleneimine) (PEI).\(^3\) Since it has been demonstrated that both CNTs and graphene can be assembled with a range of polyions using LBL techniques, we extend the idea to the alternating LBL assembly of positively charged gold nanorods and negatively charged PEI modified graphene oxide on an indium tin oxide (ITO) electrode substrate. The electrocatalytic oxidation activity of methanol on the gold nanorod/GO films on the ITO were studied as a function of the number of bilayers.

### 9-1.2 Experimental Methods

In a typical experiment, an aqueous dispersion of GO sheets was stabilized in the presence of PEI. The introduction of the charged soluble polymer chain unit onto the GO plane should result in a well dispersed graphene-based material. The adsorption of the water-soluble cationic PEI chains onto GO sheets could not only render GO sheets to be
dispersible/soluble but also make it possible for controllably fabricating multicomponent hybrid films by sequential self-assembly with positively charged gold nanorods. The PEI-GO surface with abundant –NH₂ groups can be protonated over the range of pH = 2 – 9 after dissolving the PEI-graphene into DI-H₂O. The surfaces of the gold nanorods are covered with positively charged amine functional groups while the negatively charged GO surfaces are covered with (-COO⁻).

9-1.3 Results and Discussion

**UV/Vis Spectroscopy**

UV/vis spectra of the samples were recorded in the range of 350-1000 nm and a quartz cuvette with a 1 cm light path was used. The optical spectra of a piranha treated ITO slide was used for blank and freshly prepared gold nanorod/graphene oxide LBL think film on ITO were recorded by placing the thin films perpendicular to the beam in order to maintain consistent experimental conditions. The optical spectra of the gold nanorod/graphene oxide LBL films developed on the ITO slide is shown below. The spectra show characteristic absorption bands at 400 nm and in the range of 900-950 nm corresponding to the absorption bands of functionalized graphene oxide film and gold nanorods, respectively. The optical spectra curve of the 15 bilayer film is shown in blue while the red curve corresponds to the 3 bilayer film. In addition, the absorbance peaks of graphene oxide and gold nanorods increased with increased bilayer numbers indicating the increased loading amount of gold nanorods on the graphene sheets.
**Figure 9-1:** UV/Vis spectra of the 3D graphene oxide-gold nanorod hybrid film. The blue spectra is that of the 15 bilayer hybrid film and the brown curve is that of the 3 bilayer hybrid film.

*Raman Spectroscopy*

Raman measurements are used as a tool for the characterization of carbon products, especially since conjugated and double carbon-carbon bonds lead to high Raman intensities. Since graphene oxide presents a mostly intact hexagonal carbon lattice, placing chemical groups randomly throughout the 2D sheet instead of the edges, the structure of GO can be modeled accurately. As seen in the Raman spectra of graphene
oxide below, the D band peak at 1450 cm\(^{-1}\) and the G band peak at 1550 cm\(^{-1}\) correspond to the graphite Raman spectra.

**Figure 9-2:** Raman spectra of a single bilayer of graphene oxide-gold nanorod hybrid. The higher I\(_D\)/I\(_G\) ratio is an indication of the disorder from the presence of gold nanorods on the surface of graphene oxide.

*Electrochemical Characterization*
Electrochemical properties and capacitance measurements of supercapacitor electrodes were studied by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge-discharge with a supercapacitance test. All electrochemical experiments were carried out in a conventional three-electrode electrochemical cell by using a voltmaster potentiostat. The working electrode is the hybrid gold nanorod/graphene oxide LBL thin film on a modified ITO glass. An Ag/AgCl (3 M KCl-filled) electrode was used as the reference electrode and a platinum wire as the counter electrode. Cyclic voltammograms (CV) of the gold nanorod/graphene oxide LBL thin film were obtained in 6 M KOH solution at room temperature as a function of bilayers. As seen below, CV studies were performed within the potential range of -0.5 to 0.5 V at scan rates of 0.01-1 V/S for a 15 bilayer film.
**Figure 9-3:** Cyclic voltammetry of the 15 bilayer graphene oxide-gold nanorod film. The increase in current with scan rate is due to the increase in conductivity of the graphene oxide sheets due to the surface plasmon resonance of the gold nanorods.

Glavanostatic cycling of supercapacitor electrodes was performed at constant current density. The discharge curves are linear in the total range of potential with constant slopes, showing nearly perfect capacitance behavior. As seen below, the charge-discharge behavior was studied at three different current (cathodic and anodic) values.
**Figure 9-4:** Galvanostatic charge-discharge curves at constant current. The cyclic performance at variable current density is an indication of capacitance behavior.

**Figure 9-5:** Glavanostatic charge-discharge stability test showing ideal capacitive charging-discharging cyclic behavior up to 1000 s.

Electrochemical impedance spectroscopy (EIS) was performed to study the electronic resistance between the graphene oxide nanosheets and the frequency dependence of ion diffusion in the electrolyte to electrode interface. As seen below, the inconspicuous arc in the high frequency region also known as the Warburg resistance is short indicating that graphene oxide has a short ion diffusion path therefore facilitating efficient access of electrolyte ions to the surface of graphene oxide. The vertical shape at the lower frequency region indicates pure capacitance behavior representing ion diffusion in
structure of the electrode. The more vertical the curve, the more the supercapacitor behaves as an ideal capacitor.

Figure 9-6: EIS plot showing low charge transfer resistance in the high frequency region and pure capacitive behavior in the low frequency region.

Since the surfaces of the gold nanorods are covered with amine functional groups arising from the surfactant terminal chains, it is more than likely that they become protonated (-NH$_3^+$) over an acidic pH range. Moreover, the negatively charged GO surfaces were covered with carboxylate anions (-COO$^-$) in aqueous solution. In order to study the electrocatalytic activity of the gold nanorod/GO LBL thin films, cyclic voltammetry (CV) was used to study the electrocatalytic oxidation of methanol in alkaline media. The CV measurements of the gold nanorod/GO thin film were carried out in 1.0 M CH$_3$OH + 0.05
M NaOH. A large anodic wave voltammetry at -0.15 V was observed for methanol oxidation in a 3-bilayer gold nanorod/GO LBL thin film on the PEI/ITO electrode. It is also confirmed that the gold nanorods are responsible for the electrocatalytic activity for methanol oxidation in the gold nanorod/GO films. The increasing current at voltages greater than -0.6 V can be attributed to enhanced kinetics of methanol oxidation promoted by the adsorption of OH\(^-\) and the formation of surface oxide. However, the methanol oxidation rate was reduced due to the surface oxide with increasing potentials greater than the peak potential (-0.15 V). The surface oxide coverage was reduced in the negative voltage direction sweep thus, leading to increased methanol oxidation current.

**Figure 9-7:** Cyclic voltammetry of the hybrid graphene oxide-gold nanorod film with a scan rate of 10 mV/s in 0.03 M CH\(_3\)OH/0.05 M NaOH solution.
9-1.4. References


9-2. Asymmetric Tip-Functionalization of Non-Aligned Carbon Nanotubes via Self-Assembly on Gold

9-2.1 Introduction

The use of carbon nanotubes as components in nanoelectronic or microelectronic devices could revolutionize the electronics industry in the same manner that microchips have revolutionized the semiconductor industry.\(^1\) However, the use of carbon nanotubes for device applications requires the precise connecting of individual nanotubes at the molecular level into device elements, such as diodes and transistors.\(^2,^3\) Although a wide range of both, horizontally and perpendicularly aligned micropatterned carbon nanotubes have been developed, the hierarchical organization of carbon nanotubes into large-scale and multi-dimensional systems remains a challenge.\(^2,^3\) As a result, various self-assembling techniques have been developed to make large-scale, aligned, and/or micropatterned carbon nanotubes.\(^2,^3\) Site-specific-modification of carbon nanotubes is
essential for the region-specific connection of individual nanotubes into self-assembled systems with defined structures.\textsuperscript{2,3} Various chemical reactions have been employed for the chemical modification of the nanotube tips, the inner, and outer nanotube walls.\textsuperscript{2,3} The arrangement of hexagon rings with a lack of dangling bonds makes the sidewalls of the nanotube unreactive. The fullerene-capped tips of the carbon nanotubes are more reactive than their sidewalls thus, allowing for the chemical tip modification with a variety reagents.\textsuperscript{2,3} It is highly desirable to develop asymmetrically tip-functionalized with two different end-groups for many functional micro-/nano-systems.\textsuperscript{4} The use of vertically-aligned carbon nanotubes for asymmetric functionalization has limited the general applications for modifying non-aligned nanotubes. The asymmetric functionalization of non-aligned nanotubes has not been realized yet. Therefore, we have for the first time developed a chemical modification approach to attach different chemical reagents onto each end of the individual non-aligned nanotubes. The asymmetric modification of the carbon nanotubes will be achieved through end-attached DNA chairs of different base sequences and the self-assembling of these carbon nanotubes asymmetrically end-functionalized with complementary DNA chains into controlled supermolecular structures. DNA chains have been used to create functional structures and devices through sequence-specific pairing interactions.\textsuperscript{1} The biomolecular-recognition principle is applied to carbon nanotubes by DNA-directed placement of carbon nanotubes attached with single-strand DNA chains (ssDNAs) on substrate region-specific functionalized with complimentary DNA chains (cDNAs).\textsuperscript{1}
9-2.2 Experimental Methods

Substrate Preparation.

The gold substrates were prepared by sputter deposition of about 200 nm of gold (99.99% purity) at 1nm/s onto freshly cleaved 1-in. mica sheets containing a pre-coated 3 nm chromium layer to promote adhesion between gold and mica. The gold substrates were cleaned in piranha solution (4:1, H₂SO₄/30% H₂O₂) followed by thorough rinsing with ultrapure H₂O and ethanol and subsequent drying under N₂ flow.

Self-Assembled Monolayers (SAMs).

The gold substrate was soaked in a 1 mM of 2-aminoethanethiol hydrochloride:ethanol solution for 24 h at room temperature. The surface of the electrode was washed with distilled water and ethanol, and was air dried. After these treatments, self-assembled monolayer with primary amino group was formed on the gold substrate. The AFM measurements were performed under ambient conditions using an Agilent 5500 AFM operating in acoustic AC (AAC) mode with a large Multipurpose scanner and PPP-NCH AFM probes (Nanosensors; Kc = 42 N/m, F = 330 kHz). The scan rate was 2 Hz and the scan range was varied from 100 x 100 microns to 1 x 1 microns.

Carbon Nanotubes (CNTs).

Purification of the multi-walled nanotubes (MWNTs) and the single-walled nanotubes (SWNTs) was conducted by refluxing in 1M HCl for 8 hrs. Acid treatment and oxidation of the purified MWNTs and SWNTs were conducted in an aqueous solution of concentrated mixture of concentrated sulfuric and nitric acids (3:1, 98% and 70%, respectively) under ultrasonication for 8 h. The reaction mixture was then diluted with water and allowed to stand overnight for precipitation. The supernatant was decanted, and
the remains were diluted with deionized water and filtered with a 0.45 um diameter pore poly(tetrafluoroethylene)(PTFE) membrane (Gelman) under vacuum. The solid shortened MWNT and SWCNT sample was obtained by washing the remains on the PTFE filter with deionized water until the filtrate pH became nearly neutral.

Figure 9-8: *Surface Condensation via Amide Bond Formation*. The oxidized CNTs can be immobilized on solid surface via amide or ester bond formation. For the surface condensation routes, the CNTs are dissolved in an organic polar solvent, such as N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and the substrates must be pre-modified with amino or hydroxyl groups. The surface condensation reaction was carried out at temperatures ranging from room temperature to 60 - 80°C with DCC or EDC as coupling agents. The oxidized CNTs can be immobilized on the gold surface via amide or ester bond formation.
9-2.3 Results and Discussion

A selected area of the freshly sputtered Au(111) film on mica was scanned. Cross sectional analysis using the AFM was used to measure the variations in surface roughness and changes in thickness between the substrate Au(111) layer and the immobilized amine-terminated thiol functional groups. Figure 9-9 displays topographic images of the freshly sputtered as prepared Au(111) film on mica with fairly homogenous height profile (roughness). As seen, the surface of gold consists of flat Au(111) terraces separated by single atomic steps and dislocations.

**Figure 9-9:** An AFM image of the bare gold surface on a mica substrate and surface topography and height profile of the bare smooth surface.

After 24 hr. immersion in various concentrations of 2-aminoethanethiol in ethanol solution, the AFM images (Figure 9-10) show spikes exhibiting parallel alignment to the scanning direction from weakly physisorbed n-alkanethiol molecules that move with the AFM tip during scanning. It is also evident that the surface roughness increases with
concentration of the alkanethiol solution. Quantitative height measurement is shown in the profile indicating the spike height which approximates the diameter of an alkyl chain. Therefore, we can conclude that the alkanethiol molecules are initially oriented parallel to the surface thus increasing the surface roughness or height with alkylethiol concentration. Upon adsorption of the 2-aminoethanethiol molecules on Au(111) monatomic high islands appeared immediately on the gold terraces. The islands initially increased both in size and number, and then decreased slowly after reaching maximum values with increased thiol concentration. The formation of the islands was attributed to gold atoms on the surface which became highly mobile due to strong binding to the thiols. It was suggested that islands are formed on thiols rather than depressions because the strong attractive intermolecular interactions between the alkyl moieties favors aggregation of the adsorbed alkane molecules (each with a gold atom attached) into islands. However, we were not able to observe the formation of the islands on flat Au-(111) regions by AFM.
**Figure 9-10:** AFM image of surface topography and height profile of self-assembled alkanethiol monolayers on gold. 1mM thiol monolayers and surface height profile.

In addition, water contact angle values are reported in Figure 9-11 for bare gold and gold-thiol monolayers on both Si and mica substrates are shown. The water contact angles are higher with alkanethiol concentration since the substituent chain length increases the contact angle because it is less sensitive to the underlying substrate.

\[
\theta = 24.6^\circ \\
\theta = 27.3^\circ \\
\theta = 37.6^\circ \\
\theta = 41.8^\circ 
\]
**Figure 9-11:** Contact angle (deg) of H$_2$O on the thiol monolayers on sputtered Au.

Contact angle of thiol monolayers from (a) 1mM on mica, (b) 1mM on SiO$_2$/Si, (c) 5mM on mica, (d) 5mM on SiO$_2$/Si, (e) 10mM on mica, and (f) 10mM on SiO$_2$/Si.

$\Theta = 32.2^\circ$  
$\Theta = 39.3^\circ$

**Figure 9-12:** Raman Spectroscopy comparing pristine and oxidized (A) MWNTs and (B) SWNTs.
**Figure 9-13:** Contact angle (deg) of H₂O on the thiol monolayers on sputtered Au.

Contact angle of thiol monolayers from (A) bare Au(111) surface and (B) 1mM of 2-AET from ethanol on SiO₂/Si.

AFM is used to observe the surface adsorption of CNTs on a gold coated substrates. As shown in Figure 9-14, the acid oxidized MWNTs bundles can be clearly observed by AFM indicating the successful linkage of the carboxylic acid functional groups of the CNTs and the amide terminated groups of the SAMs.
Figure 9-14: AFM images and topographic height profiles of self-assembled MWNTs on SAMs of 2-AET on Au (111) via amide bond formation through surface condensation reaction.

In order to achieve asymmetric-tip functionalization of the MWNTs, acid oxidation of the MWNTs is critical to form carboxylic acid groups on both the sidewall and tips. The acid-oxidized MWNTs physisorbed on the surface of the amine terminated alkanethiol SAMs of the substrate. AFM was used to characterize MWNTs physisorbed on the amine terminated alky thiol chain of the SAMs. In summary, we have developed a facile and efficient method to asymmetrically functionalize the random non-aligned carbon
nanotubes with a gold surface assisted method. The obtained asymmetrically functionalized CNTs can self-assemble into various assemblies by controlling the structure of the gold substrate and the SAMs formed, which can be tuned to produce selective or patterned deposition of CNT brushes.

Figure 9-15: AFM images and height profile of MWNTs physisorbed on the surface SAMs via carboxylic tip and amine-terminated thiol interaction.
9-2.4. References


Chapter 10

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