

GRAPHENE SYNTHESIS AND ASSEMBLY FOR GRAPHENE ACTUATORS

By

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To my family and friends

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LIST OF ABBREVIATIONS

CMG	Chemically modified graphene
CNT	Carbon Nano Tube
DI	Deionized
GO	Graphene Oxide
MWCNT	Multi-walled Carbon Nano Tube

Abstract of Thesis Presented to the Graduate School
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In this thesis, we provide an improved method to synthesize graphene and also introduce the assembly of a new kind of graphene actuators. Graphene is an allotrope of carbon with a unique one-atom thick structure. It exhibits many exciting properties such as excellent electrical/thermal conductivity, high surface area, great mechanical strength and inherent flexibility. The synthesis of graphene contained two steps. First graphite oxide was synthesized from nature graphite by a modified Hummer method. Then we exfoliated the graphite oxide into GO using ultra-sonication and reduced GO to graphene by chemical reduction. After using flow-filtration method, we were able to assemble conductive graphene paper, which consisted of parallel graphene sheets. After studying the properties of graphene paper, we developed electromechanical actuators based on two strips of graphene paper with an intermediate dielectric layer. The actuation mechanism of graphene actuators was most likely due to swelling of electrodes originating from dopant intercalations. Graphene actuator strips in the size of 1 mm by 15 mm were assembled. The displacement of actuators under the repeated potential steps between -2 and 2 volts in 1 M NaCl solution was determined to be around 1.2 mm when 10 mm of graphene actuator was immersed in electrolyte.

Actuations of a graphene actuator operated by cyclic voltammetry at a scan rate of 50 mV/s reached almost the same displacement. The actuation didn't die out until 140 cycles.

CHAPTER 1 RESEARCH BACKGROUND

1.1 Graphite

Graphite is an allotrope of carbon. It is a low density, non-expensive material and microcrystalline graphite has been commonly used in pencil manufacturing for years. Graphite has high electrical and thermal conductivity.¹ The conductivity of graphite depends on its structure. A single crystal of graphite has an electrical resistivity from 4 to 6×10^{-5} Ohm-cm,^{2,3} which has the same order of the conductivity of a poor metal. However, polycrystalline graphite has a much higher resistivity due to the crystal boundaries. Graphite has a multi-layer structure and each layer contains hexagonal lattice arrays. As shown in Figure 1-1, graphite is made of parallel layers of graphene which has hexagonal rings.⁴ Each yellow sphere stands for a carbon atom and each blue line stands for the covalent bond between carbon atoms. The dotted line represents the weak Van der Waals forces between the parallel hexagonal rings that allow sliding movement. The angle between the two covalent bonds is 120° . The space between the lattice planes of graphite is 3.37 \AA and every hexagonal lattice in the same plane has a distance of 1.42 \AA between each other.⁵ Each layer of graphite is of sp^2 carbon atoms.

There are three kinds of natural graphite: flake graphite, vein graphite and microcrystalline graphite. Flake graphite is the most common source of graphite used in chemical reactions. It is a natural mineral that is purified to remove heteroatomic contamination.⁶ Vein graphite structure has high electrical conductivity because of its high crystallinity. Microcrystalline graphite is also called amorphous. Besides natural graphite, there are also synthetic graphite such as primary synthetic graphite and

graphite fiber. Based on graphite's unique properties, graphite can be used as carbon brushes, refractory materials, lubricants, friction materials and cathode material in zinc-carbon and lithium-ion batteries.

1.2 Graphite Oxide

Graphite Oxide is a compound of carbon, oxygen and hydrogen. It is nearly amorphous and has the structure of graphene oxide, which is very hydrophilic.⁷ As shown in the Figure 1-2, the structure of graphite oxide contains two kinds of regions, the aromatic region with unoxidized benzene rings and the aliphatic six-membered rings.⁸ The sizes of both regions depend on the degree of oxidation of graphite oxide. The inter-layer distance between the graphene oxide sheets of graphite increases reversibly with increasing humidity in the environment and it varies from 6 Å to 12 Å. Graphite oxide is also the middle product in the process of graphene synthesis since graphite oxide can be fully exfoliated into graphene oxide sheet when it is in the form of aqueous colloidal suspensions. It can be seen that graphite oxide sheets carry a negative charge when they are dispersed in water. Due to the electrostatic repulsion between graphite oxide sheets, graphite oxide can form a stable aqueous suspension.⁷

1.3 Graphene

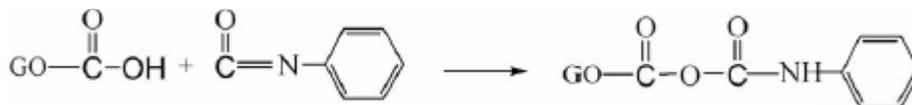
Similar to graphite, graphene is an allotropy of carbon. Graphene has a two-dimensional structure packed in a honeycomb crystal lattice.^{9,10} As shown in Figure 1-3, graphene is a one-atom-thick carbon layer of sp^2 -bonded carbon atoms containing hexagonal lattice arrays. The yellow dots represent the carbon atoms and the blue lines represent the bonds between two carbon atoms. The length of the carbon-carbon bond in graphene is about 0.142 nm. On 2010, Andre Geim and Konstantin Novoselov at the University of Manchester were awarded the Nobel Prize of Physics for “groundbreaking

experiments regarding the two-dimensional material graphene". Graphene has a high value of Young's modulus ($\sim 1,100$ Gpa),^{2,11} great fracture strength (125GPa),² good thermal conductivity ($\sim 5,000$ Wm⁻¹K⁻¹),³ excellent mobility of charge carriers (200,000 cm²V⁻¹S⁻¹)^{4,12} and high specific surface area (calculated value, 2,630 m²g⁻¹).⁵ In addition, graphene also has several transport phenomena (the electron transport is described by the relativistic-like Dirac equation) such as quantum Hall effect. All those significant properties of graphene and chemically modified graphene (CMG) hold great promise for potential application in the area of energy-storage materials,¹³ "paper-like" materials, polymer composites, liquid crystal devices and mechanical resonators⁷. Figure 1-4 is an image of 2-D graphene forming different dimensional carbon materials. As shown in the Figure, graphene can be wrapped up into 0-D buckyball, rolled into 1-D nanotube or stacked into 3-D graphite.⁹ Although the monolayer of nanostructure provides graphene with both chemical and chemical stability, the properties of graphene still depend on the way it is aligned.¹⁴ For example, electrons move faster in the 2-D graphene structure with a mobility exceeding 15,000 m²V⁻¹s⁻¹, while graphene nanoribbon shows semi-conductivity when it has narrow width and smooth edges.¹⁵ The most common method for producing graphene sheets in large quantities is by using a chemical process that involves graphite oxidation, exfoliation and reduction.

1.4 Graphene Oxide

Graphene oxide (GO) is an oxygen-rich monolayer nanomaterial. It is provided by the controlled oxidation of graphite.¹⁶ GO can be prepared by exfoliating or heat expanding of graphite oxide. GO are hydrophilic since the hydroxyl (OH) groups are bonded to the surface of the GO nanosheets,¹⁷ therefore GO is the precursor material

for synthesis of hydrophobic graphene.¹⁸ GO is considered as a new type of macromolecular form of carbon. In most cases graphene nanosheets are hydrophilic and this property can be enhanced by reacting it with allylamine, graphene nanosheets can also be changed into hydrophobic via functionalizing its surface with phenylisocyanate (C₆H₅NCO) through the solvothermal synthesis process.¹⁹



The reaction is

1.5 Methods to Produce Graphene

1.5.1 Micro-mechanical cleavage

Micro-mechanical cleavage is a physical way to produce graphene.²⁰ It can produce one-atom-thick graphene structures by repeated exfoliation of small mass of high oriented pyrolytic graphite.²¹ Figure 1-5 shows that micro-mechanical cleavage produces graphene by breaking the Van der Waals force between the monolayer carbon planes inside the graphite.

1.5.2 Drawing method²²

On 2004, a research group in Manchester University provided graphene by rubbing the pencil against an oxidized silicon wafer, turning the thick graphite flakes of the pencil into monolayer carbon structure graphene.²³

The reason that oxidized silicon wafers were used instead of paper was that oxidized silicon wafers reflected a rainbow of colors, which enhanced the interface contrast between the thin layer of graphene and the wafer.²²

1.5.3 Epitaxial growth on SiC²⁴

Graphitization of silicon carbide (SiC) by Si sublimation during high temperature (>1100°C) vacuum annealing reduces it to graphene. Silicon carbide is a material with

high resistivity and it is already available in the form of large-diameter wafers. Epitaxial growth on SiC is the most common way to produce graphene-based electronics.

However, epitaxial growth on SiC can lead to problems of graphene growth disorder.²⁴

1.5.4 Graphene oxide reduction²⁵

There are four steps to make graphene nanosheets from graphite flakes: 1. Prepare graphite oxide by using Hummer method for starting graphite.²⁶ 2. Exfoliate graphite oxide into hydrophilic graphene oxide by ultrasonic vibration.²⁷ 3. Reduce hydrophobic graphene oxide into hydrophilic graphene by reacting with hydrazine.²⁸

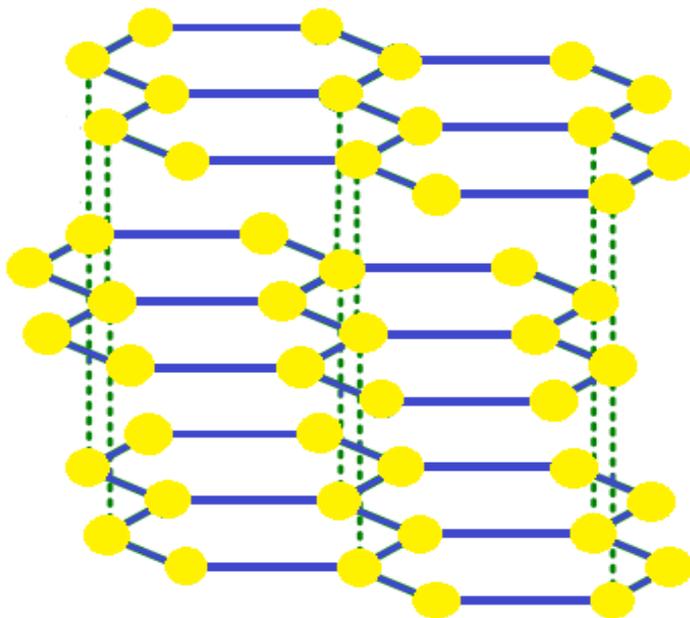


Figure 1-1. Structure of Graphite Oxide

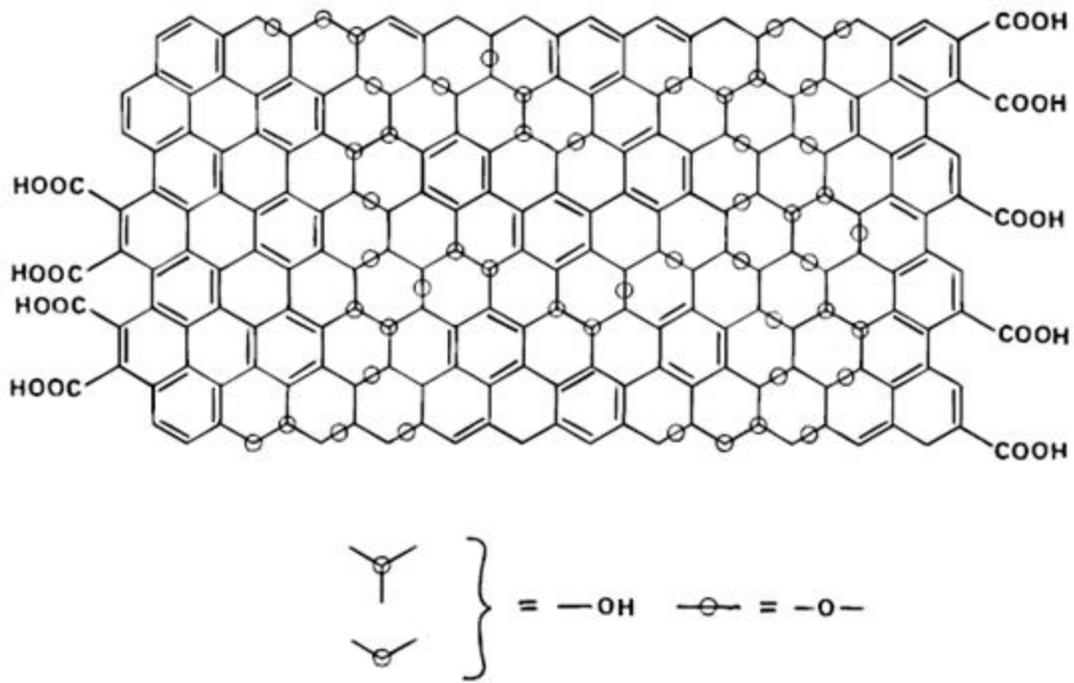


Figure 1-2. Structure of Graphite Oxide.

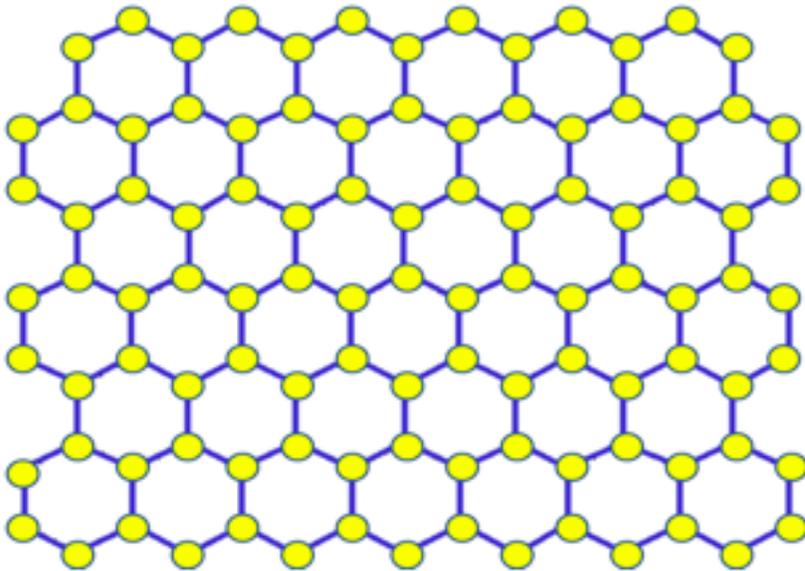


Figure 1-3. Structure of Graphene

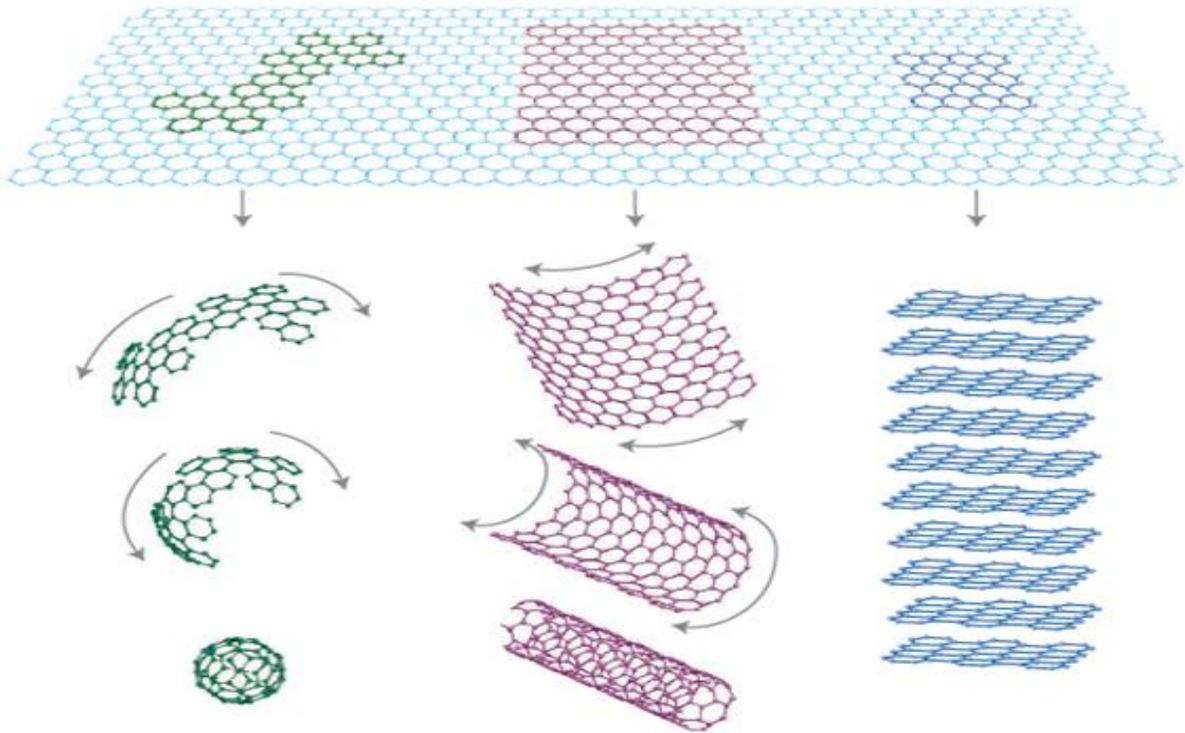


Figure 1-4. Different structure formed by graphene

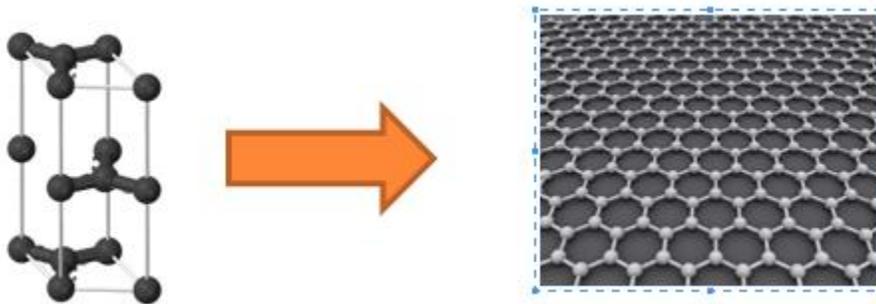


Figure 1-5. Micro-mechanical cleavage produce graphene by break the Van der Waals force between the monolayer carbon plane inside graphite.

CHAPTER 2 SYNTHESIS OF GRAPHENE

2.1 Synthesis of Graphite oxide

The aim of this process is to transform graphite flakes into graphite oxide. We measured 1 g of powdered graphite (Grade 3243, Asbury Graphite Mills Inc, Khtanning, Pa) and left it in a Petri dish. When we took the graphite from its container, we checked and made sure the graphite wasn't decayed and that it was in powder form. Using a graduated cylinder, we measured 3 mL of H_2SO_4 (95% - 98%, Sigma-Aldrich Inc, St. Louis, MO) and put it in a 50 mL beaker, adding 1 g of $\text{K}_2\text{S}_2\text{O}_8$ (99+%, Sigma-Aldrich Inc, St. Louis, MO) and 1 g of P_2O_5 ($\geq 98\%$, Sigma -Aldrich Inc, St. Louis, MO) into the beaker. At the same time we set up a water bath system and heated the water. When the water temperature reached 80 °C, we placed the beaker with all the chemicals into the water bath and stirred all the reactants with a glass stick for 15 minutes. Afterwards, we took the beaker out of the water bath and let it cool down in room temperature for 6 hours. After the beakers temperature equilibrated to room temperature, we took out the black mud-like products from the beaker. This reaction is part of the modified Hummers method, which involves an additional oxidation step prior to the real Hummers method. In order to remove the acid residue from the product, we built a vacuum filter and put the product we got on top of the filter paper. Figure 2-1 shows the equipment setup for this step, the pipe on the left opening side of the Erlenmeyer flask was connected to an air vacuum pump.

By adding water into the product and letting the vacuum to drain the water away through the filter, we ensure that the product gets rinsed thoroughly. When the PH strips we put on the outlet of the filter shows that the PH of the liquid is between 6 and 7, it

indicates that the product doesn't contain acid residue anymore and therefore we can stop adding more water. The next step is to dry out the water from the product. We put the black mud-like product into a 200 mL beaker and then we left it in a lab drying oven (Isotemp vacuum oven, model 281 A) with a medium-high temperature (Level 6, about 85°C) over night. Figure 2-2 shows the graphite inside the beaker was partially oxidized and it formed a uniform fine powder with a dark metallic grey color.

The next morning we picked up the product from the oven and started to run the Hummers method to make graphite oxide. The first thing we did was to build a 0°C ice bath by adding ice cubes into a water bath to offset the heat released from the Hummers reaction. Afterwards we added 26 mL 98% H₂SO₄ with a stir-bar followed by 3 g of KMnO₄ into the beaker really slowly, leaving it stirring under 35°C for 2 hours. Two hours later we added 46 mL of water into the graphite oxide and this gave the product a bright brown color.

Soon another 140 mL of water and 4 mL (the range is 2-5 mL according to the recipe) of H₂O₂ were added into the solution to stop the reaction. By now we finished the Hummers method and the next step is to purify the products. Instead of using DI water, we used 250 mL 1/10 HCl solution (using 25 mL HCl (32% - 38% solution. Fisher Scientific, Fair lawn, NJ) and 225 mL DI water under 50 – 60 °C) to wash the extra ion residue from the graphite oxide. After adding the 1/10 HCl solution, we put the solution in a centrifuge (IEC centra cl2, Thermo Electron Corporation) and kept the bottom aqueous colloids while pouring away the clear solution on the top of the centrifuge tube after every centrifuging. After finishing the first round of centrifuging, we added 15 mL of DI water to each tube and ran the same centrifuge steps another 2

times. At this stage we have successfully synthesized the graphite oxide solution from graphite. Figure 2-5 shows a sample of graphite oxide solution with dark brown color.

We also obtained the weight percentage data by leaving a graphite oxide colloid sample in a Petri dish and letting it dry out overnight in the lab oven.

The formula used to calculate the wt % is

$$\frac{\text{weight of sample after overnight dry out} - \text{weight of petri dish}}{\text{weight of sample before overnight dry out} - \text{weight of petri dish}}$$

We needed to dilute graphite oxide colloids into 30 mL of graphite oxide solution with a concentration of 1 mg/mL with the aim of making graphite oxide paper and graphene paper later. So we prepared the amount of graphite oxide aqueous colloids and the DI water we needed based on the wt% calculated for the aqueous colloid graphite oxide. Shortly afterwards, we mixed them together in a large glass vial and used ultrasonic vibration to make the graphite oxide homogenously dispersed in water.

2.2 Exfoliate Graphite Oxide into Graphene Oxide

We used ultrasonic vibration to exfoliate the multi-layered structure of graphene oxide. The parameters we set for the ultrasonic vibration in the lab was level 9 and we let it run for one hour while protecting the glass vial in a room-temperature water bath. Once the vibration was done, we took out the graphen oxide solution and separated it into two centrifuge tubes. The solution then got centrifuged under 3900 rpm for 30 minutes.²⁹ By that time we had already obtained the uniform graphite oxide solution with a concentration of 1 mg/ mL, the last step involved the extraction of the extra ions generated from the reaction. Therefore we cut a adequate length of ion exchange membrane (Dialysis tubng,#21-152-4, Fisher Scientific) for 30 mL graphite oxide solution and withdrew up the clean solution from the centrifuged solution into the

membrane. After sealing both ends of the membrane with clips, we placed it in a big bowl of water with a stir-bar and let it dialysis in DI water overnight. As shown in Figure 2-5, graphene oxide solution had a similar carbon black color as the graphite oxide colloids. The graphene oxide was well dispersed and there were no graphene oxide flakes that could be seen in the solution.

Before we used the graphene oxide solution, we let the solution go through the ultrasonic vibration again for 5 minutes to make sure there was no aggregated graphene oxide turned into graphite oxide in the solution. To prevent aggregation of graphene oxide from occurring during the following filtration process, we took out 10 mL of the 1 mg/mL graphite oxide solution and diluted it with another 10 mL of DI water. After dilution, the GO solution showed a light yellow color as shown in Figure 2-3. Later on, the same 0.5 mL/ mg graphene oxide solution was used to prepare both graphene actuator and graphene paper.

2.3 Synthesis of Graphene from Graphene Oxide

During this process we reduced the 0.5 mg/mL graphene oxide solution into 0.25 mg/mL graphene solution. 20 mL 0.5 mg/mL graphene oxide solution was used in this process. Before we used it in this process, we let the solution go through the ultrasonic vibration to eliminate the possible aggregation of graphene oxide. Then we took 5 mL from the same solution and put it in a small glass vial. Later we mixed it with another 5 mL of DI water and we got 10 mL of graphene oxide solution with a concentration of 0.25 mg/mL. Since 10 mL solution was only enough for one piece of graphene paper and we wanted two pieces every time, we diluted another 5 mL of 0.5 mg/mL graphene oxide solution in another small glass vial. After the dilution, we brought another clean glass vial and injected 2 mL of NH_4OH into it. Using a 1-200 μL syringe, we added 35

μL of NH_4OH (Fisher Scientific, Fair lawn, NJ) into each graphene oxide solution vial and shook both vials by hand to ensure good mixing. Then we switched to a 1-200 μL syringe to add 5 μL of Hydrazine (35 wt%, solution in water. Sigma-Aldrich Inc, St. Louis, MO). For this step we mixed the hydrazine with the solution by shaking both vials for 5 minutes. We then prepared a 98 °C water bath and let both vials get heated up in the water bath for 1 hour. As shown in Figure 2-6 and 2-7, compared to the graphite oxide solution, graphene solution seemed to be darker. The graphene solution was homogenous and had almost the same density as pure water.

2.4 Results and Discussion

The concentration of graphite oxide colloids was 6.773 g/cm^3 . Figure 2-4 was a picture of a GO colloid sample in a Petri dish. We could tell that GO colloids has a large surface tension. During the graphene oxide reduction process, we found serious aggregation of graphene in the solution after reacting in 98 °C water bath for one hour. We made two assumptions based on that fact: the first was that the 0.5 mg/mL graphene oxide solution we used to manufacture graphene had aggregated or small graphene oxide flakes inside it; the second assumption was that there were extra ions in the graphene oxide solution when we ran the reduction. Figure 2-8 shows the poor dispersion of graphene in aggregated graphene solution.

In order to avoid the aggregation, we sonicated the graphene oxide solution for 20 minutes before we reduction step. In addition, we sonicated the graphite oxide solution every time we used it after a while. However those measures didn't have any effect on the aggregations.

Therefore we started to think about the possibility that the graphene solution was contaminated by some extra ions before or after the reduction step. The first

contaminant source we thought about was water; therefore we ran the whole process again using all DI water. But the aggregation didn't reduce because of that. The second possibility was that the ions were introduced into the solution after reduction, which could be caused by having excess hydrazine or NH_4OH in graphene solution. This reminded us about the fact that there might not be enough graphene oxide to reduce during the reaction. After the centrifuging step for the dialysis of the 1mg/mL graphite solution, we removed all the flakes present that might contain aggregated graphite from the bottom of the centrifuge tube. Although the amount of hydrazine and NH_4OH was designed to reduce the exactly 10 mL of 0.25 mg/mL graphene oxide solution, the concentration was calculated based on data we got from the graphite oxide collides and we hadn't updated the concentration of graphite oxide or graphene oxide solution after that. There were chances that the solute in the solution might decrease; for example, the graphite oxide flakes left in the bottom of the centrifuge tube before we ran dialysis, the solution we lost while transferring it from one container to another.



Figure 2-1. Filtration system for rinsing graphite oxide products.

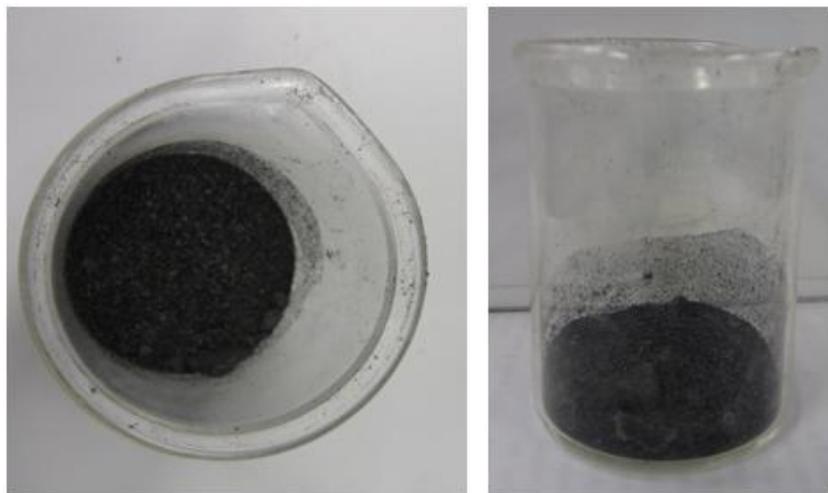


Figure 2-2. Graphite Oxide after one night drying in the oven



Figure 2-3. Graphite oxide solution after diluted

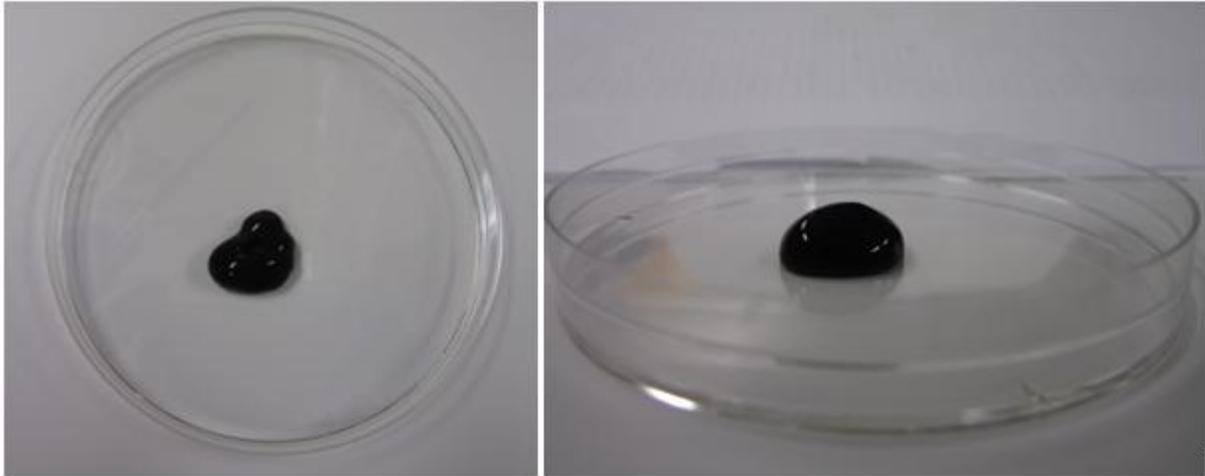


Figure 2-4. Graphite oxide aqueous colloids in a Petri Dish



Figure 2-5. 0.5 mg/mL Graphene oxide solution in a centrifuge tube



Figure 2-6. Graphene solution

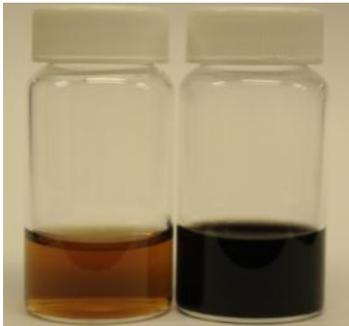


Figure 2-7. Color difference of graphite oxide solution and graphene solution



Figure 2-8. Aggregation in the graphene solution

CHAPTER 3 ASSEMBLY OF GRAPHENE SHEET

3.1 Experimental

During this process we manufactured conductive graphene paper from the homogenous graphene solution we made from the last step. We built a filtration system with a water circulation pump that provided a low pressure difference.³⁰ The same system was also used to manufacture graphene actuators.

Figure 3-1 is the equipment setup for the filtration. The right opening on the Erlenmeyer flask can help attract water down from the solution by providing a pressure difference between the inside of the flask and the solution on top. The pipe connects the open end of the flask with the water-circulation pump installed in the air cabinet. For the filter, we used a anodisc membrane filter (25 mm diameter, 0.2 micrometer porosity. Whatman Inc, Maidstone, England) instead of regular filter paper to gain a more smooth graphene paper surface³¹. After setting up the filtration system, we used a pipette to take 8 mL 0.25mL/ mg graphene solution and dropped it carefully onto the filtration membrane. We observed the status of the filter system and made sure that it was stable. After six hours the graphene solution became a cake slightly attached to the membrane. In order to remove the graphene cake from the filtration system, we took off the clip and used slight air flow to dry the graphene inside the pipe. After that we used a razor to lift up the membrane slightly, and the graphene oxide cake slid from the pipe with the membrane. We used another old membrane to cover the naked side of the graphene cake and put a weight on top of it to reduce the moistness inside the cake. After one night we came back and removed the weight and the graphene cake became a thin, conductive graphite paper with a smooth surface.

3.2 Results and Discussions

The ideal product of graphene paper should be a metallic black thin membrane with mirror smooth surface as shown in Figure 3-2. Compared to GO paper, graphene paper should not have any aggregated carbon structure on the surface. From Figure 3-3 (a), we could see that there were lots of aggregations on the surface of GO paper thus the surface was not smooth. Figure 3-3 (b) is a SEM image of graphene paper we made showed that there was almost no aggregation on the surface(. From the cross-section SEM image Figure 3-4 (a), we could observe that GO paper had multiple layers of carbon structure and they were connected with each other. Figure 3-4(b) shows that the graphene paper we made consisted of a monolayer of carbon structure that is parallel to each other. However we mainly found two kinds of defects in our graphene paper products. The first kind of defect is non-smooth surface. Figure 3-5 was a SEM picture of our graphene paper sample with some tiny particles scattered on the surface. There were two possibilities for the presence of the particles: first possibility was that the particles had dust on them that got into the solution during the previous step, the second possibility was that the black particle was graphene aggregated into graphite during the overnight filtration step. In both cases, it resulted in a reduction of the conductivity of the graphene paper because both dust and graphite particles are nonconductive. The other kind of defect present was cracks or wrinkled surfaces that could be easily seen in Figure 3-6. The crack was usually due to there being less than enough graphene solution added into the filtration system. The cracks on the surface also reduce the conductivity of the graphene paper. The wrinkled surface was because we dried the graphene cake too soon thus resulting in the shrinkage of the graphene paper surface. Based on our measurement, most of the ideal graphene papers

synthesized had a resistance close to 200 Ω , some even reached a excellent conductivity with a resistance close to 100 Ω ; while the non-ideal graphene paper usually had a higher resistance ranged from 210 Ω to 480 Ω . Therefore it was very important to ensure smooth surface for the graphene paper because most of the defects will influence its performance with the graphene actuator.



Figure 3-1. Filtration system for graphene actuator



Figure 3-2. Ideal graphene paper

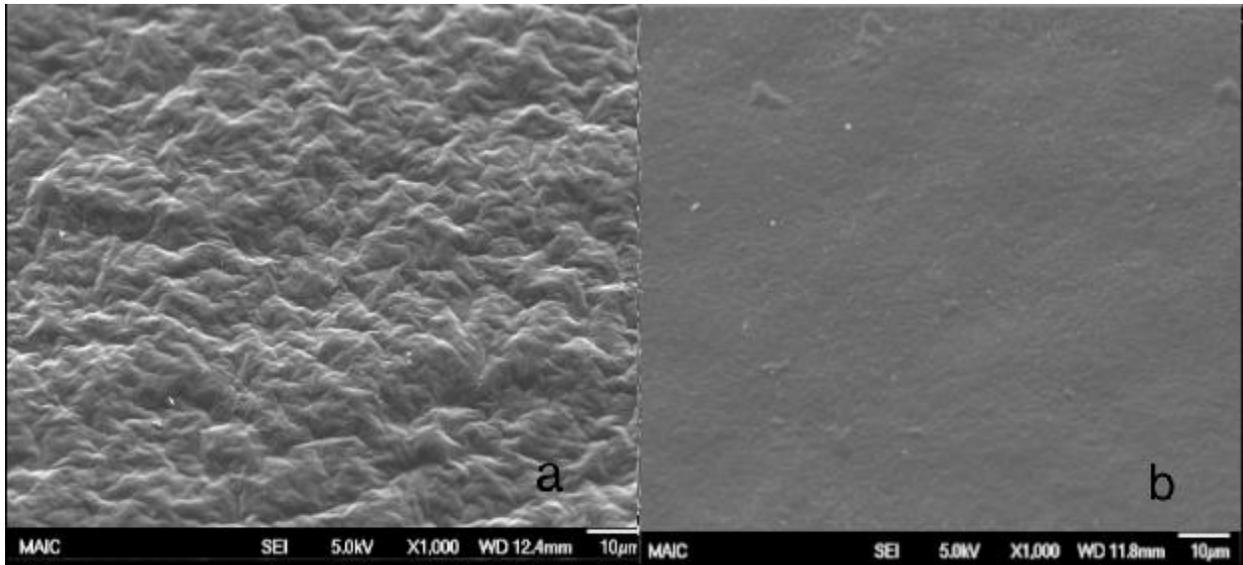


Figure 3-3. SEM picture of the surface of A) GO paper B) Graphene paper

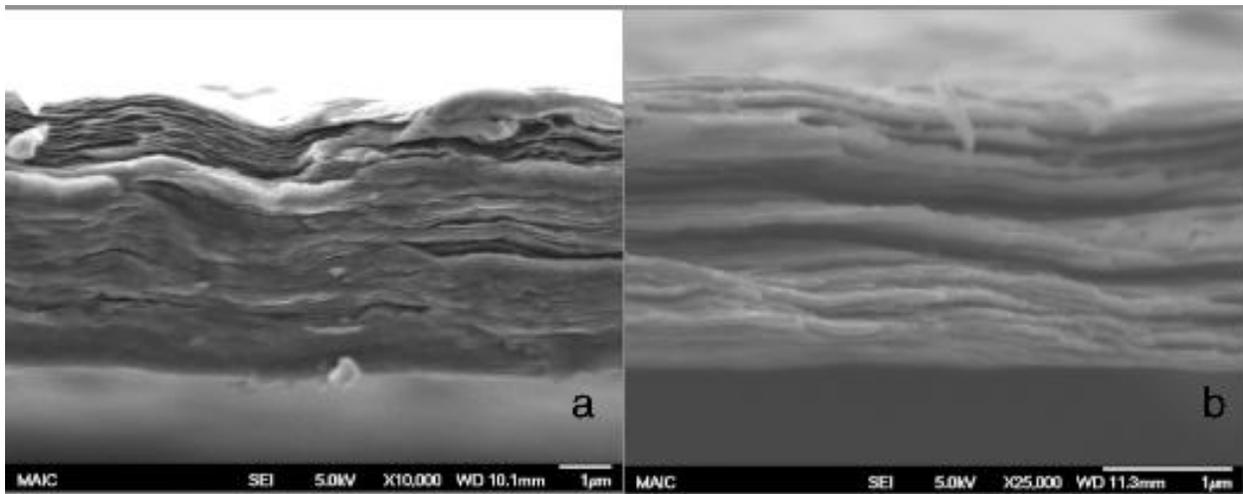


Figure 3-4. SEM picture of cross-section of A) GO paper B) graphene paper.

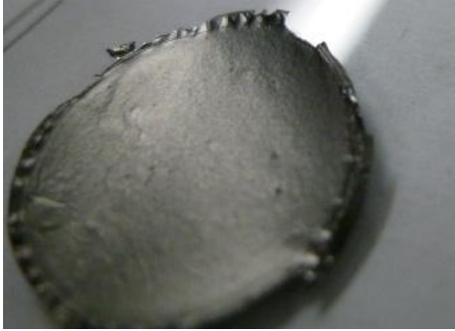


Figure 3-5. Graphene paper with particle on the surface



Figure 3-6. Cracked and wrinkled graphene paper

CHAPTER 4 GRAPHENE ACTUATORS

4.1 Introduction

Actuator is the equipment that could mechanically respond to external change in temperature, light, humidity and current.³² Reversible actuators have various applications in sensors, artificial muscle, switches and memory chips.³³ Graphene actuators focused on developing the electromechanical feature of the material. Graphene has a unique two-dimensional structure with a thickness of one atom. It is zero band gap semi metallic conductor material,³⁴ which exhibits excellent electrical/thermal conductivity,³⁵ high surface area, great mechanical strength and inherent flexibility.³⁶ Compared to carbon nano tube(CNT) material, graphene provides a larger surface area (theoretically $2630 \text{ m}^2 \text{ g}^{-1}$).³⁷ Besides that, single-layer graphene has a steady strength of 130 GPa, Young's modulus of 1TPa, and high electricity conductivity of 6000 S cm^{-1} .³⁸

Because of its natural inversion symmetry, graphene is not intrinsically piezoelectric. In order to induce piezoelectricity for graphene, the inversion symmetry needs to be broken by limiting the adsorption of atoms on the surface of graphene only on one side.³⁹ Research has already been done on graphene-based and CNT-based actuators. A multi-walled CNTs(MWCNT) /GO bilayer actuator was built using solution filtration method. Since the OH and COOH groups on the GO side were sensitive to humidity while the other side(MWCNT) wasn't, the actuator curled in different directions depending on the environment humidity.⁴⁰ However, the high cost of CNTs synthesis as well as the non-linear control of the actuators with humidity, limited the potential application of this process. There was also research done on single-walled CNT

actuator that showed electromechanical material features.^{41,42} The actuation came from chemical-based expansion via the non-faradaic charging/discharging.⁴³

In order to improve the actuation performance and also lower the cost, we assembled the electromechanical graphene actuators. The actuators were made with two paper-thin graphene strips adhered on both side of a dielectric layer. We applied cyclic voltammetry on the actuators and also we treated the actuators with repeated potential steps. Cyclic stability of the graphene-based actuators was also explored.

4.2 Experiment

The actuators were made in sandwich structure with a strip of Scotch® Double Stick Tape as intervening dielectric between two graphene strips. After getting graphene sheet from pervious steps, we cut paper-like graphene discs into 1mm by 15 mm strips. The graphene sheets were cut by a razor blade and usually one piece of graphene sheet can be divided into four graphene strips with the required size. The double-sided tape strips were prepared by cutting the Scotch Double Stick Tape into 1mm wide strips with a length a little over 15 mm. For each actuator we attached two pieces of Au/Cr/glass electrodes pointing opposite direction on the edge of both graphene strips. The electrodes were made by sputter deposition of 20 nm of Cr and 200 nm of Au and each were connected with a clip for applying voltage. Both of the electrodes play an important role in its actuation performance. Figure 4-1 (A) and (B) show detailed imagies of the experiment setting. Figure 4-2 shows that during the experiment there was about 10 mm of the actuators immersed in the rectangular glass tank, which was full of 1 M NaCl solution. First we used potential steps (-2/ 2 V) on actuators and recorded the actuation. Then we used cyclic voltammetry, applying voltage between -2 and 2 volts with a scan rate of 50 mV/s through the electrode. By videotaping the

actuators, we could observe the bending of the actuators in the solution corresponding to the voltage change.

A Kurt J. Lesker CMS-18 Multitarget Sputter was used for the sputtering deposition of Cr and Au. Scanning electron microscopy (SEM) was carried out on a JEOL 6335F FEG-SEM. A thin layer of carbon was sputtered onto the samples prior to imaging. An EG&G Model 273A potentiostat/galvanostat (Princeton Applied Research) was used for potential step and cyclic voltammetry operations.

4.3 Results and Discussions

We immersed 10 mm of graphene actuators in 1 M NaCl solution and then applied repeatedly potential steps between -2 and 2 volts. Before we recorded the actuation performance, we operated several steps to make sure the actuator reaches maximum wetting. We also recorded the whole process and calculated the displacements of actuator's tip based on its position on the grid paper on the back of the water tank. The initial position of the actuator's tip was considered as origin. Figure 4-3(A) showed that the actuator moved to the right when a positive charge was applied and to the left when a negative charge was applied during the eight successive potential steps with a total of four cycles(-2/ 2 V repeatedly). Based on the fact that the actuator always bended to the cathode during the experiment, we believed what happened was anions (Cl^-) and cations (Na^+) in the electrolyte (NaCl) were moved to the anode and cathode. Since chloride ions were larger than sodium ions in size, the dopant intercalations resulted in the bending of actuators. Figure 4-3 (B) showed that under the same operation as (A), the displacement of the actuator's tip was around 1.2 mm.

Then we operated actuators by using the cyclic voltammetry method between -2 and 2 volts in 1 M NaCl solution with a scan rate of 50 mV/s. This time we started

recording the data without waiting for the wetting of the actuator. Figure 4-4 (A) showed the first several cycles of cyclic voltammograms of the graphene actuator and the current in this stage increased with time, which demonstrated that the wetting of the actuator occurred with dopant intercalations at the beginning. After several cycles, the change of the current started to maintain a steady state. From Figure 4-4(B), we could see that the actuation performance was also influenced by the wetting time. We could barely observe displacement of the actuator's tip at the beginning of the experiment. As the cycle number increased, the extent of displacement also increased until it reached a steady value around 1.2 mm, which almost matched the actuation performance under potential steps. After maintaining steady actuation performance for a while, actuators die out after about 140 cycles.

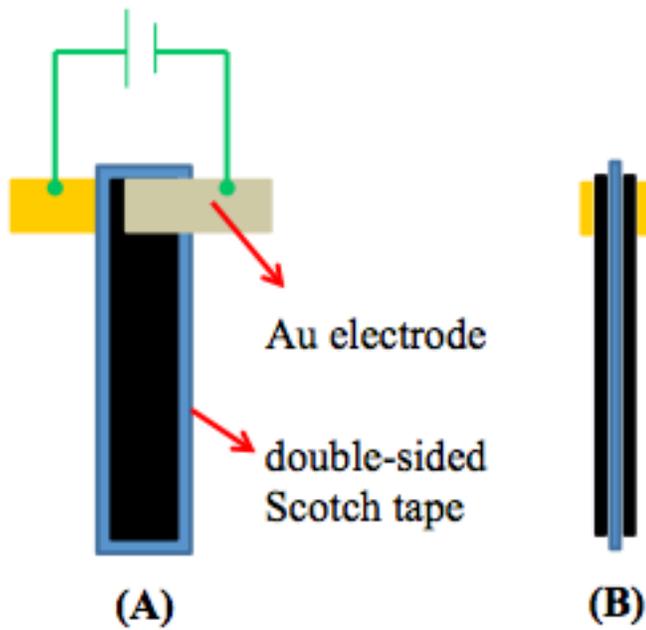


Figure 4-1. Graphene actuator with Au electrodes on both side of the graphene strips. A) front view. B) side view.

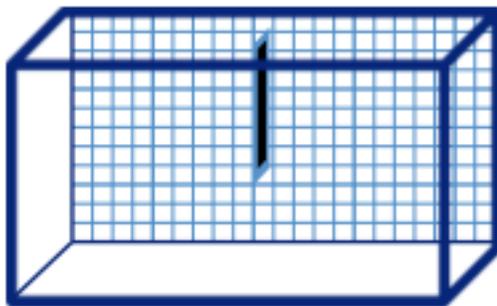
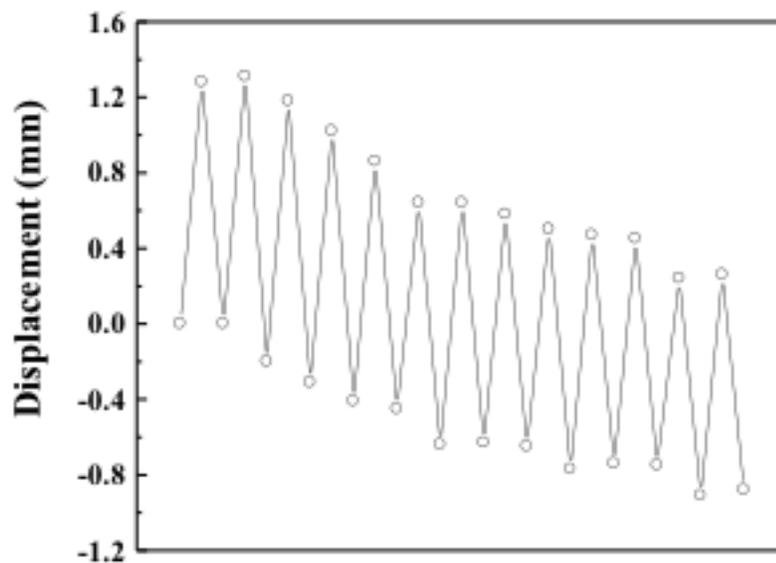


Figure 4-2. Actuator partly immersed in the NaCl solution holding by the rectangular glass tank.

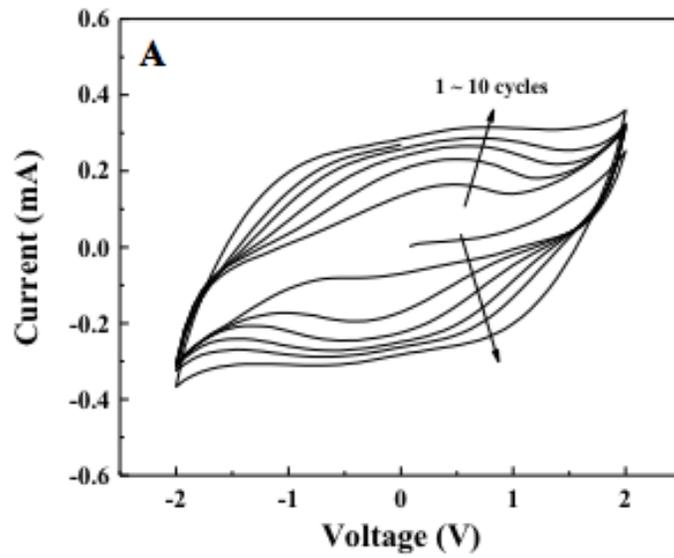


(A)

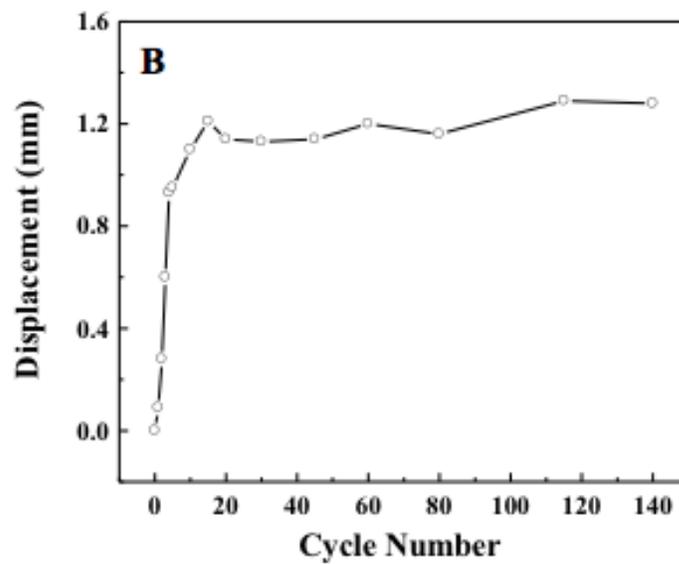


(B)

Figure 4-3. Actuations of a graphene actuator operated by potential step method. A) cross-sectional images of a graphene actuator. B) Displacements of actuator tip.



(A)



(B)

Figure 4-4. Actuations of a graphene actuator operated by cyclic voltammetry method. A) Two-electrode cyclic voltammogram. B) Corresponding displacements of the actuator

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BIOGRAPHICAL SKETCH

Yichen Chen was born in 1988 in Shanghai, China. In 2006 she started her undergraduate in East China University of Science and Technology (ECUST), Shanghai. Three years later, she left the city that she had been living for twenty-one years and went to the United States as an exchange student at Lamar University, Beaumont, Texas. She completed her exchange study one year later then received her Bachelor of Science in chemical engineering from ECUST. On that same year, she was accepted by University of Florida as a graduate student and received a Master with thesis degree in the fall of 2012.