FUNCTIONALIZING GRAPHENE SURFACES WITH PRECISE DYE ABSORBED OXYGEN DEPOSITION

A Thesis

by

KYLE HOGAN KING

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Chair of Committee,	Jonathan R. Felts
Committee Members,	Sarbajit Banerjee
	Debjyoti Banerjee
Head of Department,	Guillermo Aguilar

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ABSTRACT

This thesis studies the properties found in graphene and combines them with the potential of increased responsivity due the addition of dyes which could allow for more efficient and effective optoelectronics. Here, we theorize the bonding between 2,4,6-trichloro-1,3,5-triazine (Cyanuric Chloride) and Graphene Oxide to allow the bonding of 1-amino-2-methylanthraquinone (Disperse Orange 11) to occur. With this bond occurrence, future studies can investigate the local bonding of such organic bonds onto graphene oxide for the use in micro and nanotechnology. The specific design is as follows. Cyanuric Chloride is covalently bonded to the oxygen of the Graphene Oxide sample. Disperse Orange 11 is then added to the mixture allowing for the covalent bonding of the dye. This sample is then tested with a series of spectroscopy instruments including a UV-Vis machine and an XPS machine as well as height testing with an AFM to determine the success of the dye bonding.

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I would first like to thank my advisor, Dr. Jonathan Felts. Whether or not I continue down the field of nanotechnology, or something similar, what I have learned and will continue to learn from Dr. Jonathan Felts will have lasting impact for the rest of my life. It is not necessarily the content of what I am learning, which is of great use in itself, but the methods of research that are of such great use going forward in my career. Engineering can be defined as the action of working artfully to bring something about, and under the aid of Dr. Jonathan Felts, I whole-heartedly believe I am being prepared to bring about great things for the scientific field and ultimately my community as a whole. I cannot thank Dr. Jonathan Felts enough for the opportunity he has provided me professionally, educationally, and personally. I would also like to thank my undergraduate advisor, Dr. Shannon Timpe. Without his push towards academia and furthering my scientific research at the graduate level, I know I would not have pursued this degree, and I would have found myself on a much different professional path.

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All work presented in this thesis study was completed independently by the student. The work conducted in this thesis was made possible with the support of Texas A&M University Engineering Department and the National Science Foundation (QD1MX6N5YTN4).

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SUMMARY

Utilizing organic molecules, novel device architectures can be created with the use of nanomanufacturing tools and nano-engineered materials. Such tools as the Atomic Force Microscope (AFM) are integral in the creation of the mentioned structures. The study of the surface chemistry of graphene will be the focus point of this paper. With the great conductive properties of graphene, it is an ideal structure to be used for optoelectrical devices as it enables the combination of high speeds and sensitivity. The proposed experimental study will focus on strongly absorbed structures being able to efficiently transport charges atop 2D structures. In this case, the graphene will serve as the 2D structure and the deposition of oxygen atoms on the graphene surface will serve as the structures. These structures will be placed with extreme precision using the AFM down to the nanometer. Utilizing the incredible properties found in graphene and combining them with the potential of increased responsivity due to the fluorescence of such dyes could allow for much more efficient and effective optoelectronics in the future. We theorize the bonding between 2,4,6-trichloro-1,3,5-triazine (Cyanuric Chloride) and Graphene Oxide to allow the bonding of 1-amino-2-methylanthraquinone (Disperse Orange 11) to occur. With this bond occurrence, future studies can investigate the local bonding of such organic bonds onto graphene oxide for the use in micro and nanotechnology. The specific design is as follows. Cyanuric Chloride is covalently bonded to the oxygen of the Graphene Oxide sample. The organic dye being Disperse Orange 11 is then added to the mixture allowing for the covalent bonding of Disperse Orange 11. This sample is then rigorously tested with a series of spectroscopy instruments including the Ultraviolet-Visible spectroscopy (UV-Vis) machine and the X-Ray Photoelectron Spectroscopy (XPS) machine as well as height testing with an Atomic

Force Microscope (AFM) in order to determine whether or not the bonding of the dye was successful.

INTRODUCTION

The world is continually pushing towards increasingly smaller devices and understanding of things at micro and nano scales in order to continue scientific advancements. Understanding surface chemistry in the biological and chemical sense can be a large part of this improvement in many fields including optoelectronics [1,2], energy storage [3-5], medicine [6-8], nanofabrication [9,10], and friction and wear modification [11,12].

Optoelectronics, the technology that would integrate the findings from this study, utilize the quantum mechanics of light within electronic systems. This gives these sensors and instruments extremely high speeds. This occurs by relying on the conversion between electromagnetic waves and excited charge carriers. The optical excitation of an electron-hole pair must occur for this conversion. With sufficient charge, the electron and hole will separate, and what follows when they recombine is either light, heat, or both. Photodetectors generally utilize voltage bias to make this occur and photovoltaic cells usually rely on complementary hole transport and electron transport layers [13,14].

The use of 2D films in optoelectronics have great possibilities due to the uncommon electronic band structures, unmatched charge mobility, and their ability to be produced in large quantities [13,15-17]. Photodetectors have also used graphene in their technology, which have shown impressive results. The issue is the lack of bandgap with pristine graphene that causes a poor optically absorbing surface or material. With the use of strongly absorbed materials, such as photosensitive dyes that are discussed in this study, the optical sensitivity can be greatly increased due to the effective charge donation and the production of electron hole pairs.

The current devices often have their covalent bonds break up which reduces the charge mobility. This causes these devices to unfortunately come with large response times generally. The hypothesis is that through chemical modification nanomaterials can be created that strongly absorb photons and transport the charges with high speeds. Today, many aspects of chemical modification have not yet been explored or at least to their fullest potential. The use of chemical doping for electronic transport has been studied more in depth, and this is where the chemical nanostructures that are created on graphene surfaces with the use of tip-based and electron beam fabrication processes can be found. It has been found that in chemically modified graphene sheets, graphene nanoribbons can be written in by locally removing covalent bonds and then restoring the conductivity of the graphene [18,19]. Even with the findings in these studies, there is still a lack of exploration in the optical response of the nanostructures created with the use of chemical modification.

In other studies, it has been found that certain materials such as transition metal dichalcogenides can be doped non-covalently with other metals and organic materials to increase the charge carrying and improve the photoluminescent response. They did not account for local chemical modification and there has been less work showing more stable surface atoms at the 2D scale. There have been more recent studies concerning diazonium salts and their ability to locally modify 2D materials including graphene among other materials. Through these studies it shows the ability to covalently attach high optically active structures to materials such as graphene [20-26].

Graphene

The first exfoliation of graphene occurred in 2004. With this discovery, a large attention has led to many studies of this ever-growingly fascinating material. Graphene, a single carbon atom layer thick material, has unique electrical, mechanical, optical, and sensing properties [27-32]. It was found that for any micromechanically deposited graphene, the electron mobility was measured up to 2,000cm^2/V s at room temperature. With graphene's large lateral extension, it has become an appealing alternative to carbon nanotubes. In suspended and annealed graphene devices the electron mobility has even been found to reach 200,000cm^2/V s. At the time of this study, this was the fastest mobility found in any semiconductor or semimetal [36]. Mechanically, graphene has set records in terms of hardness and Young's Modulus. The stiffness has been found to be in the order of 300-400 N/m while the Young's Modulus has yielded around 0.5-1.0TPa. This being compared to steel's Young's Modulus that is commonly found at 215GPa at the higher end [37]. Graphene has also been found to be quite transparent at the monolayer levels. This optical characteristic combined with the conductance capabilities makes it a promising replacement to Indium Tin Oxide, a higher cost material, as a transparent electrode for solar cells [38]. Each of these properties give graphene the capability to create high quality sensors, which is the end goal of such a study.

With the ability to create monolayer and few-layer flakes of graphene, the development and studies of 2D materials has greatly expanded. The methods of creation of such flakes have not changed much in order to get high quality flakes for study. The use of adhesive tape to extract flakes from graphite and placed on a substrate proves to be a high-quality way to obtain graphene for study. Figure 1 depicts the process of obtaining graphene through a micromechanical process [39]. There have been other methods found since the initial adhesive tape method as well.

Chemical vapor deposition is another common method used for larger scale growth on substrates such as copper, ruthenium, as well as others, but it comes with its downfalls [33-35]. This process can be very time consuming due to the formation of defects and grain boundaries that occur.

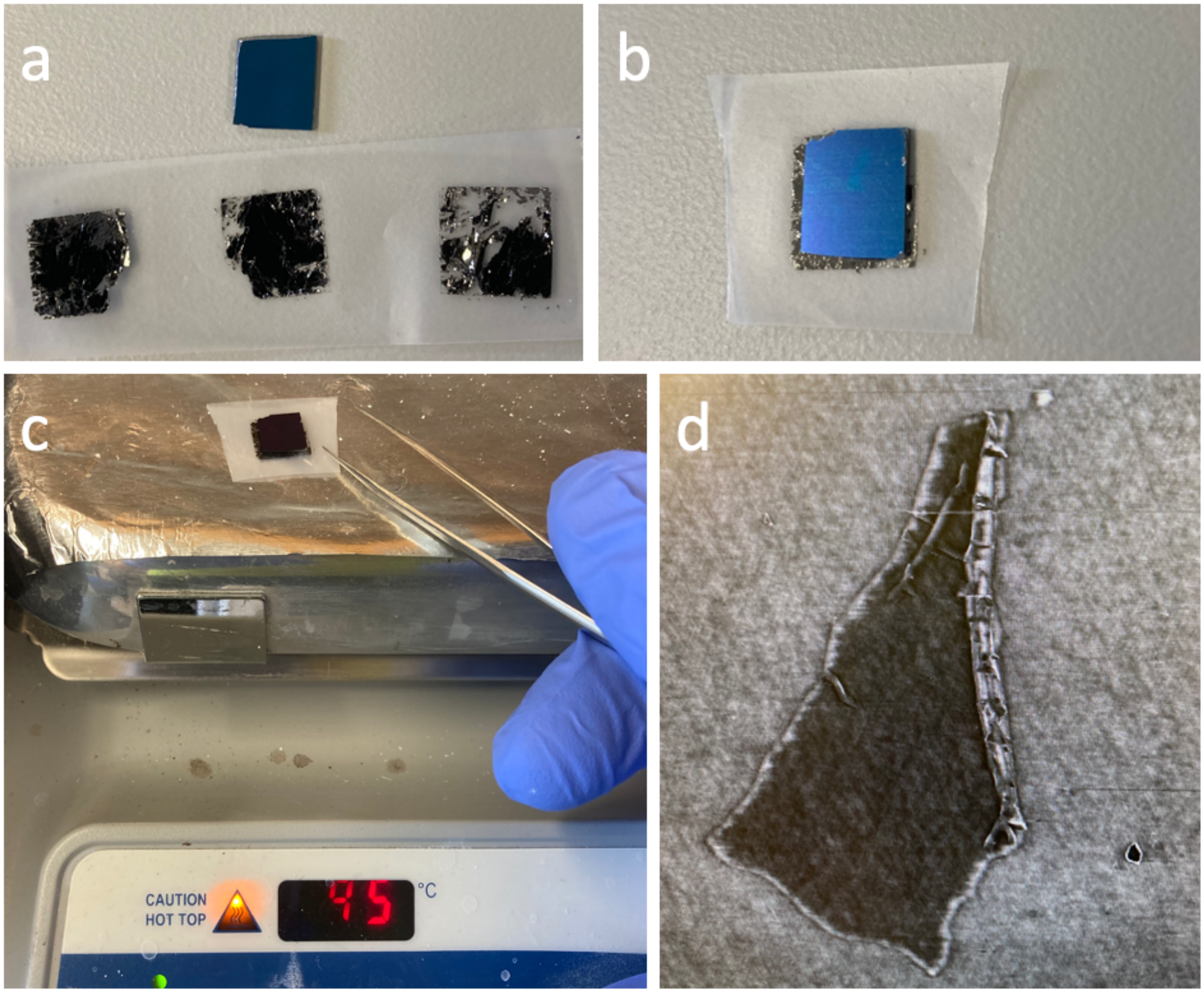

Figure 1: Process of obtaining graphene monolayers from modified exfoliation. (a) Adhesive strips after being applied to graphite material along with a SiO2/Si substrate. (b) Applying the SiO2/Si to the adhesive strip containing the graphite material (c) Heating of the substrate with the adhesive tape applied to the substrate (tape side on hot plate) for 5 seconds at approximately 100°C. (d) AFM image of the graphene flakes on the silicon substrate.

Graphene Oxide

Graphite oxide at the monolayer scale known as graphene oxide (GO) is very similar to a graphene structure with the difference of being heavily covered in oxygen groups. GO can have the oxygen locally reduced creating what is known as rGO. A graphene sheet is comprised of sp^2 carbon atoms and is completely flat as compared to GO that is made up of tetrahedrally bonded sp^3 carbon atoms creating a less than flat surface. Graphite can be oxidized with oxidizing agents then this graphite oxide can be placed in water and sonicated thoroughly in order to create GO.

GO is easily dispersible in water as well as other organic materials due to the oxygen groups, making it an important material for mixing with ceramic and polymer matrixes to improve their electrical and mechanical properties. The use of GO has been studied for possible drug delivery methods, biodevices, and optoelectronics by substituting amines in for the organic covalent functionalization of graphene, which allows for more dispersibility in organic solvents [40].

There have been numerous devices starting to implement GO within their technology. GO has been found to be of use in field effect transistors (FET) where they use rGO as chemical sensors and biosensors. The functionalized rGO is used as a semi-conductor in the biosensors to detect hormonal catecholamine molecules, avidin, and DNA [41-43]. As mentioned with graphene materials, the transparent properties of graphene are apparent in GO as well making them a suitable material for devices such as solar panels where their conductive properties can be of great use. With their high surface area, GO and rGO can be used for electrode materials in fuel cells, batteries, and capacitors as well [44].

The creation of GO samples is a relatively simple task depending on the initial form being used. Throughout this study, the GO used was dispersed in water at the concentration of 4mg/mL. The GO is added dropwise onto a SiO2/Si substrate while the substrate is spun at a rate of 100rpm. A single droplet of the solution is added to the substrate so that the substrate does not get over concentrated. The GO solution can be diluted with deionized water depending on the concentration of GO needed on the substrate. The substrate is then allowed to dry for 24 hours to allow for the water to evaporate leaving the GO monolayers to disperse evenly throughout the substrate. Figure 2 depicts the creation of such a sample.

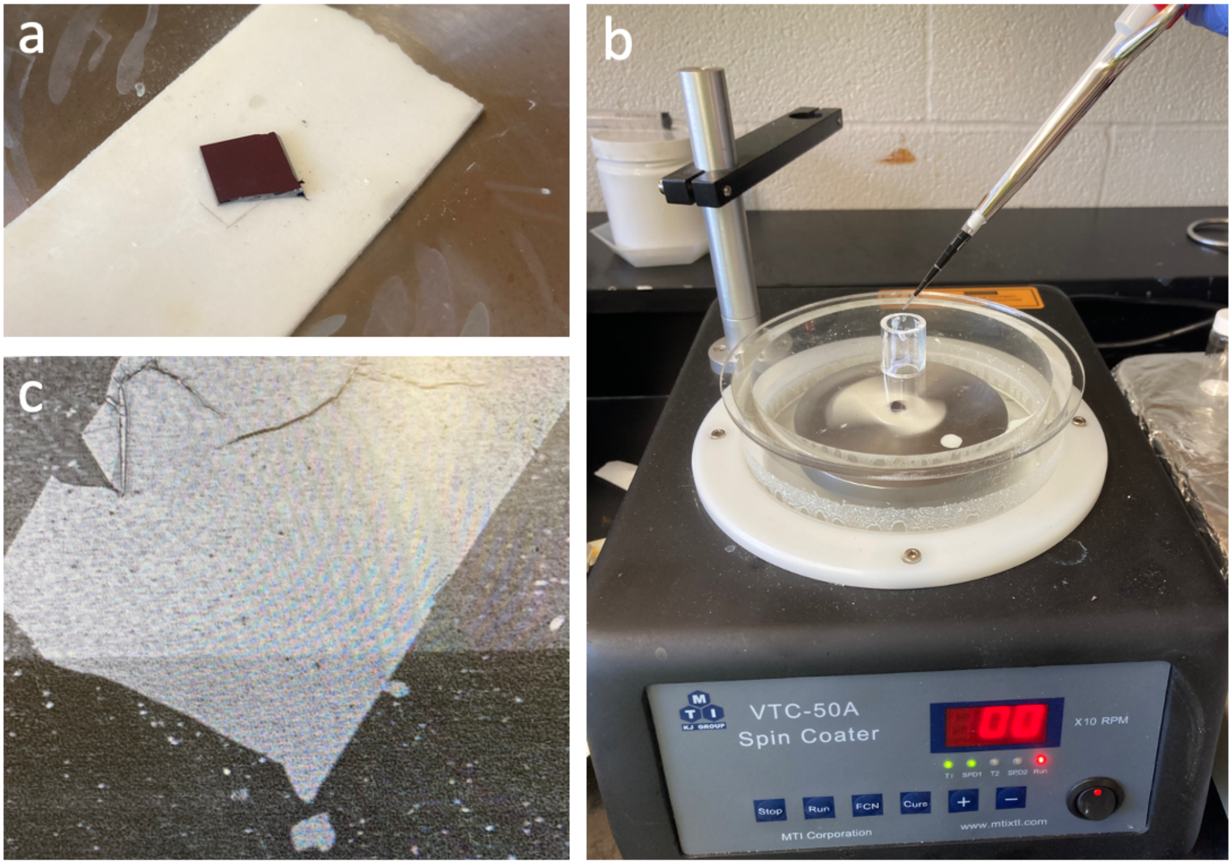

Figure 2: Process of obtaining GO monolayers on a SiO2/Si substrate. (a) Placement of the SiO2/Si substrate on the spin coater. (b) Adding a single drop of the 4mg/mL GO solution to the substrate as it spins at 100rpm. (c) AFM image of a GO monolayer.

Atomic Force Microscopy

With the invention of the Atomic Force Microscopy (AFM), mechanochemistry has had many new scientific discoveries and findings. The AFM is made up of a scanning tip that scans the surface of a material by running this atomically sharp tip directly on the surface. A laser is directed to the tip head and measures the displacement of the tip as it scans an area. As the tip travels over the surface, a depiction of what the tip scans is shown on the monitor allowing for one to study materials at the micro, nano, and even atomic level.

The tip is a cantilever allowing it to flex over the surface of the material being studied. Using a piezo positioner, the tip's z axis location can be adjusted with extreme precision. If the tip were to be introduced to the surface with too much force, damage or complete destruction can occur to the tip as well as the surface being studied. As mentioned, the laser that adjusted to the top side of the tip is what determines how the tip is moved as scans are performed. The laser bounces off the tip to a photodetector with four quadrants. The intensities of the laser in each quadrant will then be used to calculate the height of the surface measured. Figure 3 below depicts the AFM setup. For the measurements conducted in this study, the tip will be in direct contact to the surface. There are other methods of measurement with the AFM such as tapping mode, but it was decided that for best results direct scanning of the surface is what is needed.

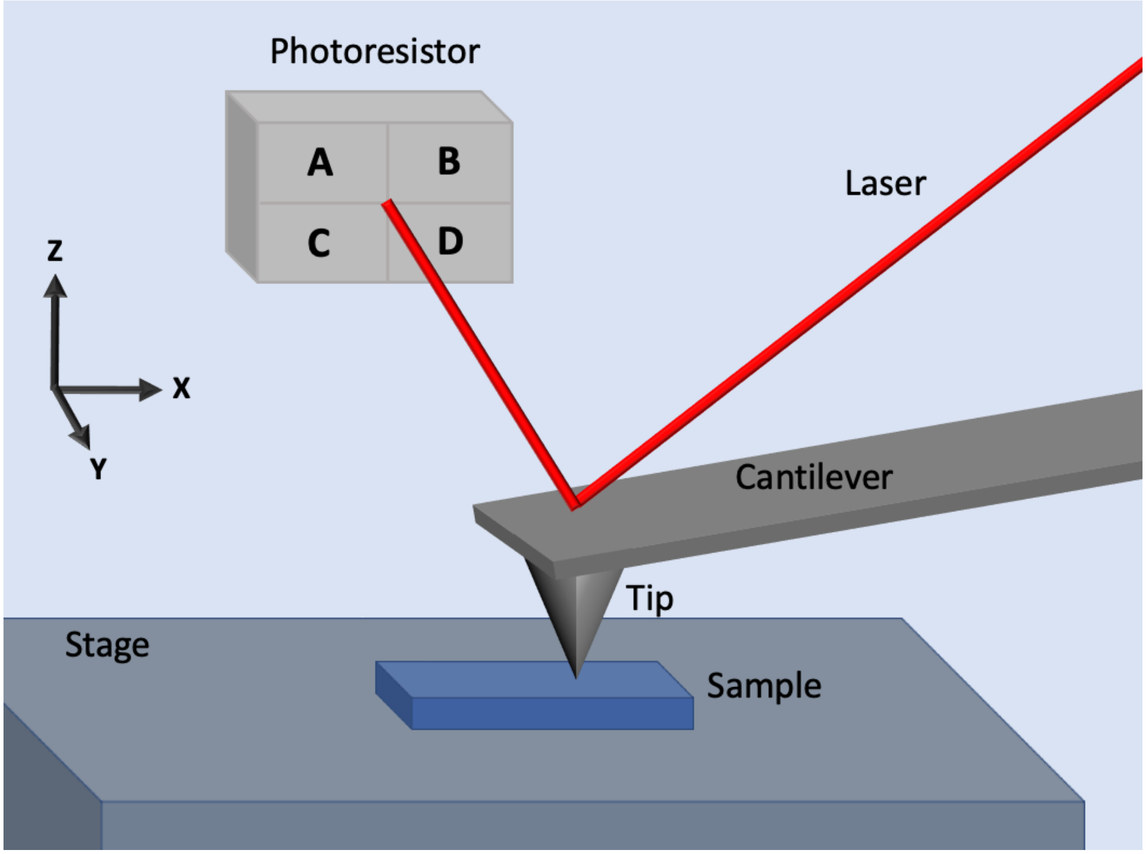

Figure 3: Depiction of Atomic Force Microscopy (AFM) instrument.

The environment of the AFM can be adjusted to different studies as well. Full or partial vacuum seals can be implemented if necessary. The humidity of the sample can also be adjusted as needed. Different tips are used for different experiments depending on what is needed in the study. The spring constant of the tip is crucial to what kind of measurements are being taken as well as the material of the tip itself. A platinum coated silicon tip, for example, gives the user the ability to run a current through the tip into the sample, which has implications that will be discussed in the next section.

Oxygen Deposition and Reduction

A crucial goal in this study is to be able to deposit oxygen on the surface of graphene in localized patterns with high precision. This is conducted by electrochemical oxidation using an AFM tip with an applied current. The graphene is placed on a super flat gold substrate. Using a platinum coated tip, a wire is run to the tip from a function generator and another wire is applied to the gold substrate. This allows for a circuit to be completed from the tip through the graphene into the gold substrate.

The humidity in the air accumulates onto the head of the tip creating a water meniscus between the tip and the surface of the graphene. Once the current is applied with varying voltage, the hydrogen and oxygen atoms from the water begin to split allowing the oxygen groups to covalently bond to the surface of the graphene. This is depicted in Figure 4. It is shown that localized patterns can be created at the precision of 12nm.

Reducing oxygen from GO has similar applications for optoelectronic use. The process to locally reduce oxygen is a similar process, but it is more mechanical than electrical with chemical structure change. A tip has the capability to remove the oxygen groups from the GO to create rGO by applying an increased scanning force to the sample. This can happen in a very precise manner creating nanostructures within the GO. The issue at hand is the increased probability of tearing the GO as a whole with too much force being applied [45-48].

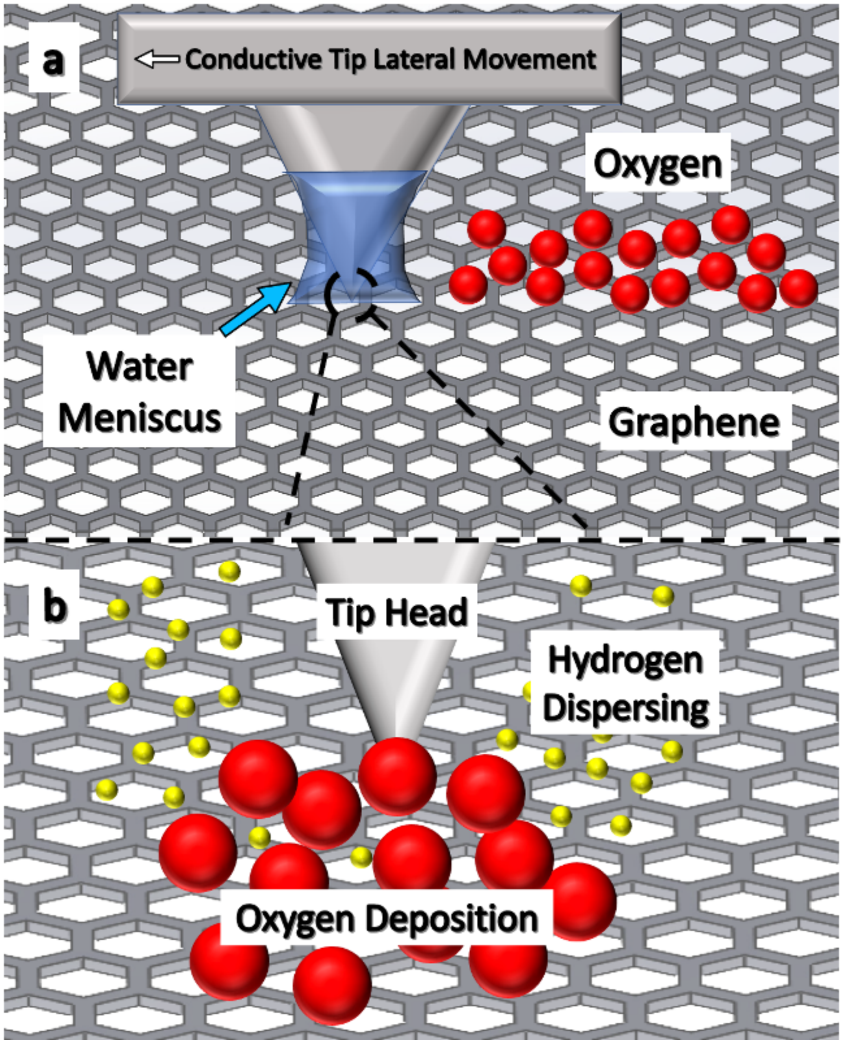

Figure 4: (a) Applying a current through the AFM tip head that causes the splitting of the water molecules leaving oxygen attached to the graphene. (b) A closer depiction of the hydrogen dispersing as the oxygen groups are bonded to the graphene.

Dye Absorption

The next step of this study is to absorb dyes onto the oxygen groups that are on the graphene. The dyes' purpose is to increase the sensitivity and photoluminescent responsivity of the functionalized structures on the graphene. Certain dyes such as Procion Red MX-5B, Disperse Orange 11, and Methylene Blue have shown promising results of covalently bonding to organic materials such as the oxygen groups present. There are a few ways it is theorized this reaction will occur being a chemical reaction between the dye chosen and GO, or there will be a current applied that forces the GO into absorbing the dye. The main process used in the results of this paper is using a chemical reaction. Appendix A refers to the electrochemical process theorized that was not used for the official results.

Optoelectronics

Optoelectronics are a type of device that rely on the conversion between electromagnetic waves and excited charge carriers. The study of optoelectronics utilizing these 2D films (graphene) has been increasing recently due to the characteristics that graphene can offer as mentioned [51-53]. Graphene has a high charge mobility, which is potentially very useful for photodetectors, but the lack of band gap makes it a relatively poor optically absorbing material. Functionalizing the graphene with photosensitive dyes such as Disperse Orange 11 and semiconducting quantum dots has shown to result in an increase in optical responsivity.

Even with the success of chemically defining graphene electronic surfaces, there has been minimal work studying the optical response of nanostructures formed with chemical modification. This is where the contents of this paper further the study of such phenomena in order to create devices with a high charge mobility along with high optical responsivity. As later discussed, the development of the given 2D surfaces will allow for a large photon interaction and high charge mobility.

The intention of this study is to prove that fluorescent dyes are able to be covalently bonded to graphene and, more specifically, GO to achieve the increased responsivity. Disperse Orange 11 was the chosen dye due to the expected bonding of the amine group present in the dye. As given in the name, Disperse Orange 11 (DO11) gives off a bright orange fluorescence, which is the characteristic needed for the increased sensitivity. DO11 is also known to have one of the largest irreversible internal quantum efficiencies (IQE) of organic dyes, which is a factor that quantifies the performance of a photodetector [54]. This implies it is highly photostable, which means it will not be effected by the presence of light and will not degrade over time [55]. Cyanuric Chloride is first bonded to the hydroxyl group of the GO allowing for an open chlorine group to be reacted with the amine group in DO11.

MATERIALS AND METHODS

Theoretical Bonding of Materials

As shown in Figure 5, the cyanuric chloride (CC) is first bonded to the GO. This occurs by one of the chlorine atoms present in CC reacts with the hydroxyl group in GO. We then obtain a triazine molecule modified GO or CCGO for short. Next is the addition of the DO11. This occurs from the reaction between one of the two additional chlorine atoms present in the CC (now CCGO) molecule and the amine group in the DO11 being NH2. The final product is the bonded DO11 to the GO denoted as GODO11.

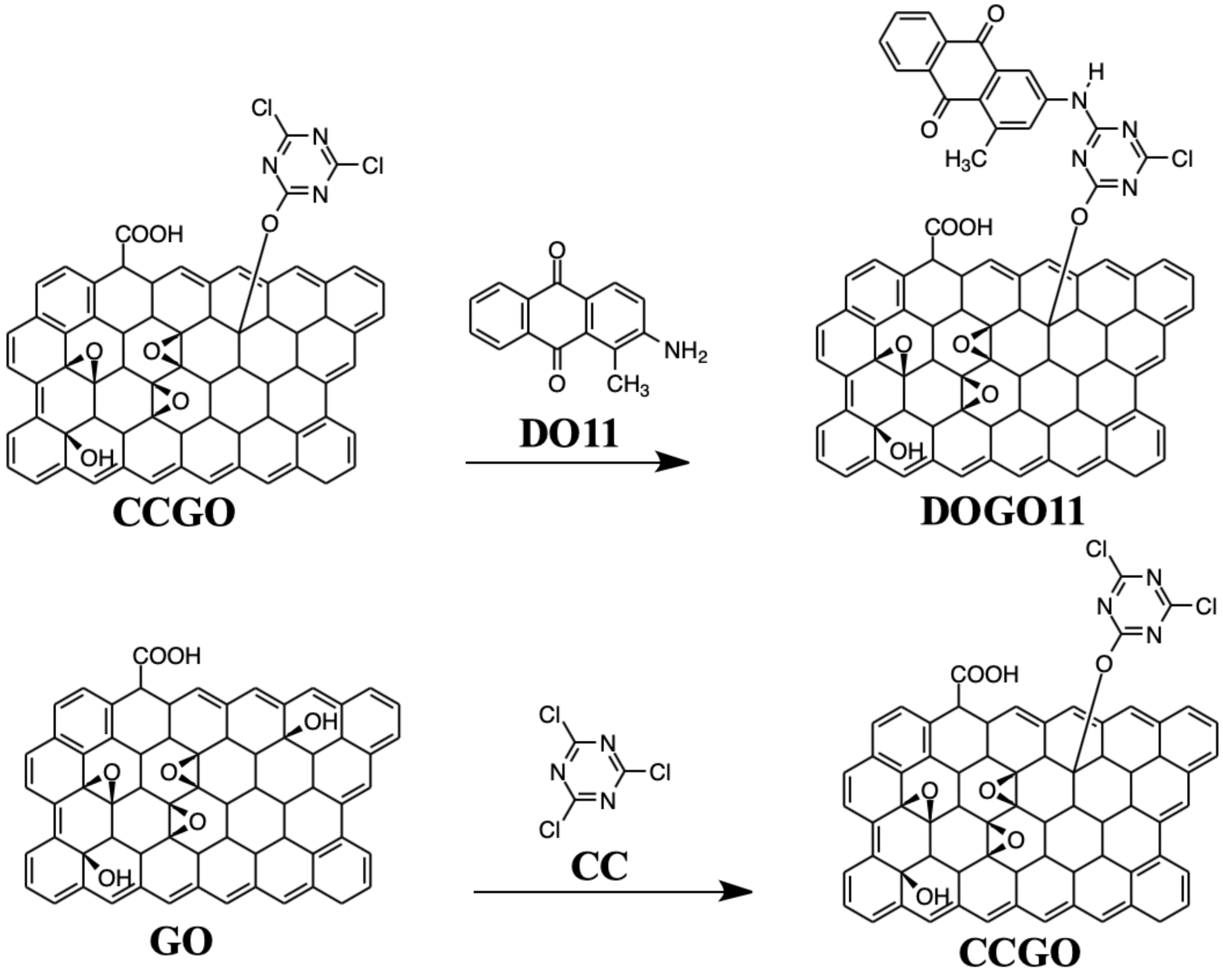

Figure 5: The representation of the hypothesized bonding of first cyanuric chloride onto graphene oxide followed by the bonding of disperse orange 11 onto the cyanuric chloride molecule.

Experimental Setup

All chemicals used in the following experiments were of high analytical grade and were purchased through Sigma Aldrich. There was no further processing of the given chemicals.

The experimental setup is as follows. A 5mL solution of GO, 4 mg/mL dispersion in H_2O, was sonicated in 45mL of Dimethylformamide (DMF). This solution was then placed in a 125mL beaker that was in an ice water bath. Then 0.153g of CC was added to 50mL of DMF into a 50mL burette to be added dropwise to the GO and DMF mixture over one hour. Once the entirety of the CC and DMF mixture is added, the solution is stirred for four hours. This mixture is then heated to 60°C. Then, 0.371g of DO11 is added to the mixture and stirred for six hours [19].

This final mixture contains GO, CC, DMF, and DO11. This mixture is then placed in a centrifuge and spun at intervals of 20 minutes at 4000rpm. This displaces the hypothesized dye on GO from the DMF and excess dye. The DMF and excess dye is removed and fresh DMF at the amount of 20mL is added and centrifuged once again. This is repeated until all excess dye is removed from the mixture. Depending on the following tests of the solution, one of two things would happen. For the liquid measurements, the solution remained in a secured container that is then refrigerated. For all other measurements, the solution was dropped onto a silicon substrate while in a spinner in order for the solution to become dispersed evenly onto the silicon and create monolayers of the hypothesized molecule we will denote as GODO11.

RESULTS AND DISCUSSION

Oxygen Deposition

The first step for the study was to be able to locally functionalize the graphene with oxygen nanostructures. This was accomplished with the separation of water into hydrogen and oxygen atoms where the oxygen groups covalently bond to the surface of the graphene. As previously mentioned, a current was applied through the platinum coated silicon AFM tip with a function generator. The current compliance was set at 1.0mA, and the voltage source began at 2.0V. The voltage was ramped up by 0.2V every 10 seconds until it was shown that the graphene was being oxidized visually on the AFM software. The voltage in which oxidation occurred ranged from 2.0V to 5.0V. This value generally was correlated to the wear and use the tip had been through.

The initial scan sizes were set to be 500nm by 500nm. These were the preliminary structures to confirm that we can create local chemical change to the surface of graphene using this electrochemical method. Figure 6 below shows the initial graphene monolayer with the subsequent oxidation squares. As shown, it appears slight degradation of the oxygen groups occur when they are rescanned but not complete degradation.

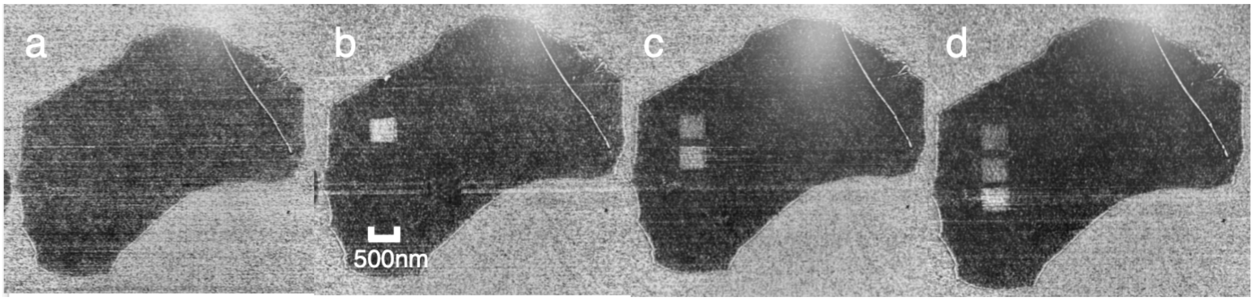

Figure 6: (a) Monolayer of graphene on a gold substrate. (b-d) 3 consecutive 500nm by 500nm oxygen functionalized graphene structures created one at a time.

The next goal was to create the smallest width lines of oxygen groups on monolayer graphene. Figure 7 below depicts the single lines created. It can be shown that this was done on approximately four-layer graphene, which should make minimal difference on the oxygenation. The lines were 500nm in length and roughly 25nm in width.

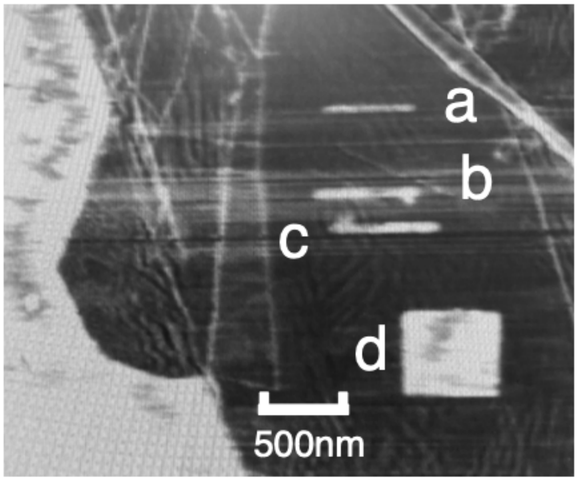

Figure 7: (a-c) Single line 25nm by 500nm oxygen functionalized graphene structures. (d) 500nm by 500nm oxygen functionalized graphene structure for comparison with the lines.

Oxygen Reduction

In a similar fashion of oxygen addition to the graphene, there is the phenomena of reducing the oxygen from GO resulting in a material known as rGO (reduced graphene oxide). This material can be useful in the continuing of this study where dye can be attached to the remaining oxygen groups after the removal process has occurred.

The process of reducing the oxygen from the GO is a relatively simple one, especially compared to the process of oxygen deposition. First, monolayers of GO must be obtained by the process previously mentioned of adding GO dropwise to a silicon substrate as it is on a spinner. Once the monolayers are located using the AFM, the oxygen reduction can begin. An aluminum AFM tip was used in this circumstance due to its higher spring constant as compared to the platinum covered silicon tip used in other experiments. A 500nm square is chosen for the oxygen reduction as shown in Figure 8. The scan begins at a rate of 4.88Hz, and the set point used is slowly increased which is what increases the force being applied by the tip onto the surface. This force is started at 10nN and increased each scan until it is determined that a change is occurring on the surface. It was found that at roughly 30nN of force the oxygen was being reduced on the surface of the material.

In Figure 8 below, there was first a 500nm by 500nm square created with the process explained previously. Next, a same sized square was created above and to the left of the initial square created. After measuring the height difference from the silicon substrate across the rGO and GO, the results were consistent from what would be expected from heights of such material. The difference from the rGO to the silicon was roughly 0.4nm, and the difference from the GO to the silicon was roughly 1.2nm.

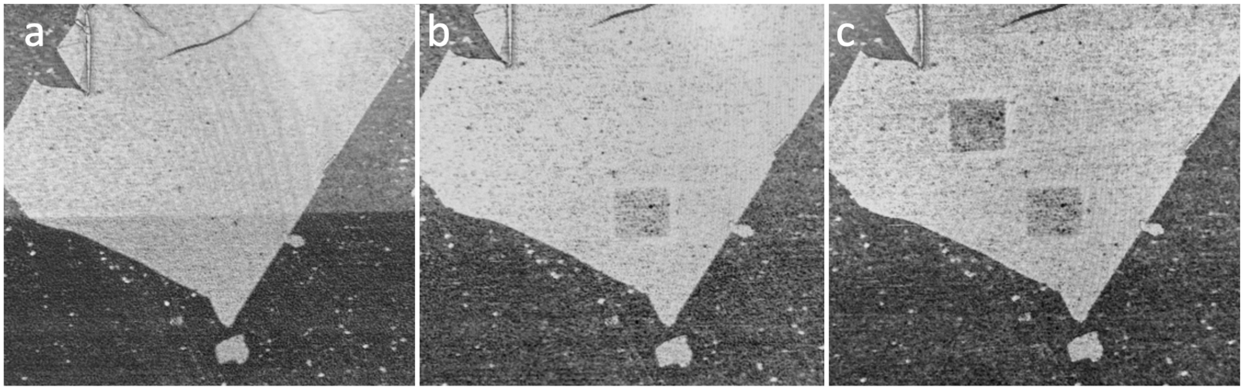

Figure 8: (a) GO monolayer on silicon (b-c) reduction of oxygen to create rGO in the form of 500nm by 500nm squares

Dye Absorption

As discussed previously, the goal was to prove the ability to bond an organic material to GO. Through the following experiments, the bonding of disperse orange 11 is indicated. The first spectroscopy tool used was the Ultraviolet-Visible Spectrometer (UV-Vis). This device measures the light absorbance across the ultraviolet as well as the visible ranges of the electromagnetic spectrum. Both GO and the GODO11 were measured in liquid form in order to determine whether or not the dye molecule was present after the centrifuging and removal of excess dye, which would indicate that the dye was in fact covalently bonded to the GO.

A sample of GO was prepared in DMF at the same molar ratio as the GODO11. After the GODO11 was thoroughly centrifuged, it was transferred to a cuvette along with the GO respectively. The measurements for the absorbance are shown in Figure 9 below. As shown, the GODO11 shows a peak not found in the GO in the 480nm region. This is expected for a dye such as disperse orange 11. The peak found indicates the presence of the dye attached to the GO. The similarities found between the GO and GODO11 are expected following the absorbance that is generally found in GO. Disperse orange 11 is also shown mixed in a deionized water solution (DO) to show the peak that is expected in the DOGO mixture. Finally, a solution labeled as GOb is shown where the disperse orange 11 is mixed in the same fashion as explained previously in GO without the presence of cyanuric chloride to prove that the cyanuric chloride is necessary for the DO11 to bond to the GO.

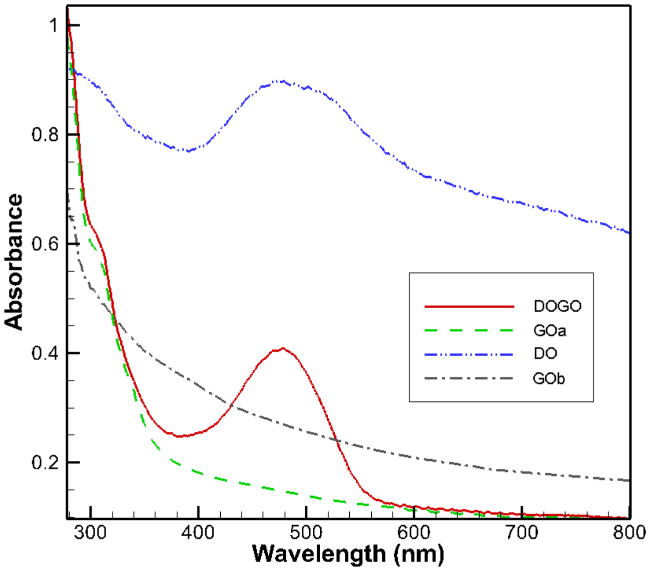

Figure 9: UV-Vis absorbance results comparing graphene oxide (Goa) with the disperse orange 11 graphene oxide (DOGO) where the peak at roughly 480nm indicates the presence of disperse orange 11 bonded to the graphene oxide as expected. Disperse orange 11 (DO) is also shown within a deionized water solution to show the expected peak of roughly 480nm. The GOb is the solution of disperse orange 11 mixed with GO excluding the cyanuric chloride.

The next tool used in order to determine whether or not the dye was still present on the GO was an X-ray photoelectron spectroscopy (XPS) machine. An XPS identifies what atoms and molecules are present by hitting a solid surface with X-ray beams and measuring the kinetic energy that is then reflected back from a 1-10nm range. The liquid created for the GO and GODO11 samples were transferred dropwise onto a spinning silicon substrate to allow for monolayers of the proposed GODO11 as well as GO separately.

Each substrate was individually measured, and the noting factor between the two was the presence of nitrogen with the GODO11 sample. Specifically, the N-H bond would be present within the GODO11 as compared to the GO. As shown in Figure 10 below, the bonding energy indicates the presence of nitrogen solely in GODO11 and not within GO as expected. The peak found in the 401eV range is as expected for the bond believed to have been created with the organic dye and cyanuric chloride.

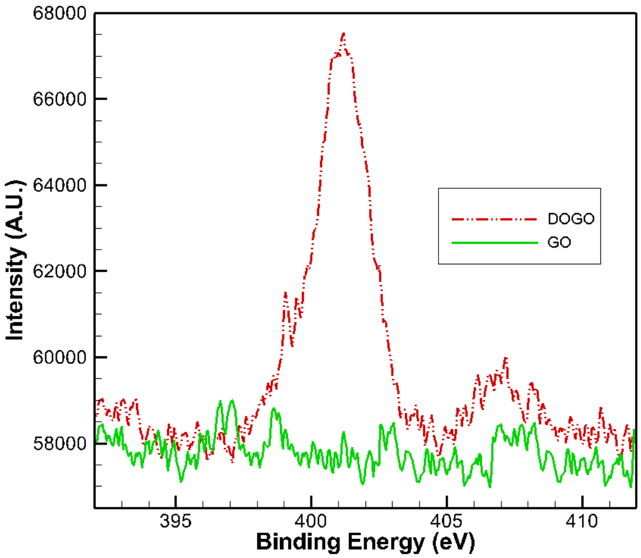

Figure 10: XPS results comparing graphene oxide sample with disperse orange 11 on graphene oxide. The peak in the GODO11 sample is the presence of nitrogen on the sample as expected for the sample unlike the GO sample that should not have nitrogen present.

The final indication that DO11 is present on the GO was the height tests conducted with an AFM. There were four different samples created for comparison. Each of the four samples were created by using a spinner using silicon as the substrate. The silicon substrate was spun, and the solution was added dropwise onto the substrate. This creates the needed monolayers for measuring the height. The first solution was the proposed GODO11. The next was the original 4mg/mL GO denoted as GOa in Figure 11. The third solution was the GO mixed with the dye and was heated at 60°C without the presence of the cyanuric chloride. This solution was also centrifuged repeatedly to allow for excess dye to be removed. This was to test whether or not the dye would be present without the proposed attachment of the cyanuric chloride molecule, and it is denoted as GOb in Figure 11. The fourth and final solution was GO with the added cyanuric chloride added through the process mentioned in the experimental setup. There was no DO11 added to this mixture.

As shown in Figure 11, it is found that the GODO11 has the greatest height of the four samples with an average height of 2.47nm. As expected between GOa and GOb, they were found to have very similar heights with an average of 1.07nm and 1.04nm respectively. This is as expected because all the excess dye should have been washed away leaving only GO on the sample indicating the need for the cyanuric chloride molecule presence in order for the DO11 to bond properly. The CCGO has a slightly higher average height than the GO at 1.53nm. This would also be expected as it is hypothesized that the cyanuric chloride is now attached to the GO.

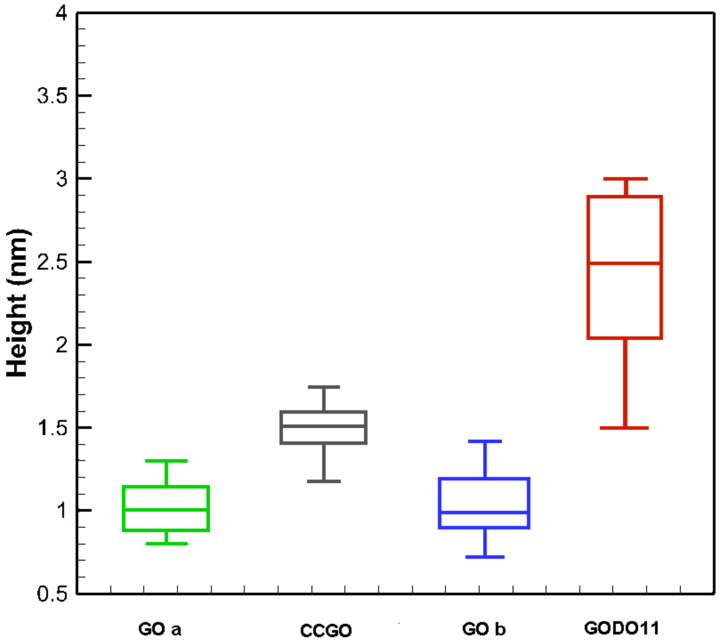

Figure 11: Height comparison of GODO11, GO (GOa), GO mixed with DO11 and centrifuged excess DO11 out (GOb), and CCGO.

CONCLUSION

In summary, we have demonstrated that the bonding of an organic dye to the wonder material graphene is possible. A straightforward and effective method was used to covalently attach first cyanuric chloride to the graphene oxide and then disperse orange 11 to the chlorine atoms available. The presence of the dye was shown within the liquid solution via UV-Vis results. An increased absorbance in the 480nm range pointed towards the presence of DO11. Next, the nitrogen found in the XPS measurements alluded to the presence of DO11 from its amine group in the dye. With the AFM height results, it was shown that the increase in height was due to the bonding of the dye to the graphene oxide. The increase in height was comparable with what was expected from the given size of the molecules being used. The DO11 will have increased the fluorescence and in turn the sensitivity of the GO allowing for the potential of more efficient and effective optoelectronics at the nano scale. To our knowledge, this is the first attempt to attach an organic material to graphene for the purposes of increased sensitivity. From this work, we can continue work to increase the optical absorption of graphene to allow for more effective optoelectronics.

FUTURE STUDIES

The world continues to move toward smaller, faster, and more efficient computing which is where superior optoelectronic nanostructures can come into play. Extremely sensitive optical and chemical sensors will be a huge benefit to military competitiveness, national security, and material development characterization.

With the success of bonding an organic dye to GO, we can now look forward to accomplishing such in a localized manner. Through localized oxygen deposition, we would be able to make precise structures where the dye can then by covalently attached to the oxygen groups made. Optoelectronics are a type of device that utilize the conversion of electromagnetic waves and excited charge carriers. This study has indicated that the creation of 2D structures at the nano scale is possible that have a large photon interaction and high charge mobility.

Though this study has shown that oxygen can be deposited in a precise, local manner as well as the addition of a fluorescent dye to the GO molecule, it has yet to be determined whether these dyes can be attached to the oxygen groups that have been deposited on the graphene. The continuation of these studies would include discovering if such phenomena is possible. The next steps would be creating the localized oxygen structures on monolayers of graphene, followed by the bonding of a fluorescent dye to these oxygen groups. The dye would have to bond to solely the oxygen groups and not the carbon groups surrounding the oxygen. This study used GO as discussed, which is covered completely in oxygen groups.

Disperse Orange 11 has shown promising results and would be a good first step, but there are many other organic fluorescent dyes that can be of equal success. Possibly these other dyes, such as Disperse Orange 3 that are smaller in nature, could be more effective at attaching to the locally deposited oxygen. It is proposed that instead of creating a solution in which the dye is attached to the GO in liquid form, a sample of graphene has a local deposition of oxygen groups and then is taken through a similar process of attaching the dye to the oxygen groups. This sample will need to be thoroughly washed to remove excess dye with the hope that the local oxygen groups remain, and the dye still attached.

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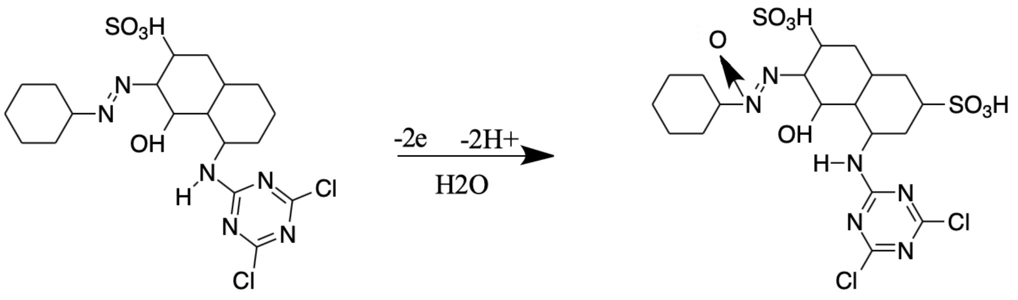
APPENDIX A

The following discussion goes over the practice of Cyclic Voltammetry where it was attempted to bond an organic dye, Procion Red MX 5B, to the oxygen groups present in GO. The attempts were unsuccessful, but helped this study move in the right direction of attaching an organic material to GO. Below is the explanation of how that theoretically would occur as well as an additional spectroscopy tool that was not used specifically for the bonding of DO11 to GO.

Cyclic Voltammetry (CV) can be used to enable for this reaction to occur. It is an electrochemical technique that cycles through a potential sweep that measures the current of an active solution. There is a reference solution along with the electrochemical cell that is in the solution being studied. A function generator then acts as a potentiostat to run the potential sweeps. Figure 5 below shows the oxidation that occurs during the voltammogram of Procion Red MX-5B [49].



Procion Red MX 5B **Azozy Derivative of Procion Red MX 5B**

Figure A1: Representation of the oxidation of Procion Red MX-5B through voltammetry.

Fourier Transform-Infrared Spectroscopy (FTIR) is another instrument that can be used to identify whether or not the absorption is occurring of the dye onto the oxygen groups. The spectrum of graphite and GO can be measured using the FTIR, and once the addition of the dye solution has been added and then washed-out using centrifugation of the heavier GO, it can be determined if the dye has absorbed to the GO [50].