ND*nano* Undergraduate Research Fellowship (NURF)
2013 Project Summary

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2) Faculty Mentor: Dr. Prashant Kamat

3) Manipulation of Graphene Morphology Compounds via Metal Nanoparticle Mediated Hydroxyl Radical Attack

4) During my research, I was trained in the use of UV-visible Spectrophotometry, Fourier Transform Infrared Spectroscopy, and in using a Gas Chromatography/Mass Spectrometry apparatus.

5) Graphene has great potential for use in electrical devices due to its electrical properties which are derived from its unique structure. This project sought to manipulate the structure of Reduced Graphene Oxide in hopes of improving or tuning its properties and thus create a material suitable for specific applications.

Research Summary

As our society becomes more dependent on energy, there is a growing interest in implementing new materials with more favorable properties to make better electronic devices. Graphene is at the forefront of this research due to its excellent electrical properties, including a high intrinsic electron mobility and high surface area, resulting from its unique structure. From previous research[1], it is known that gold nanoparticles in the presence of hydrogen peroxide and ultraviolet radiation mediate the oxidation of reduced graphene oxide (RGO) via a hydroxyl radical attack. The goal of this project was to investigate whether other types of nanoparticles resulted in a similar effect. Then the investigation turned to whether the structure of the RGO could be manipulated with good precision by varying the type of nanoparticle, intensity of irradiation, and duration of the irradiation with the ultimate goal being to tune or improve graphene's properties beyond what has thus far been achieved.

The first step of the project was to synthesize gold, copper, and platinum nanoparticles. All were done by first creating an aqueous solution of the respective ions, adding sodium citrate which acts as a capping agent, and then reducing the ions using sodium borohydride. In order to get a suitable suspension of the nanoparticles it was necessary to ensure that the ion concentration was not too high else the particles would aggregate and crash out of solution. It was also found that the copper nanoparticles were not stable for longer than a few hours, however, this was long enough for the purpose of our experiments. Next, each was separately added to a solution of RGO with some hydrogen peroxide. A 300 W Xe lamp with a quartz water filter were used to generate white light to irradiate the samples for 1-2 hours. A Varian UV-Visible Spectrophotometer was used to monitor the absorbance of the sample over the course of

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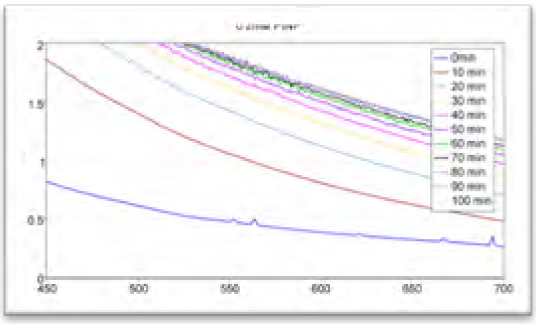
[1] Radich, J.G.; Kamat, P.V., Making Graphene Holey. Gold-Nanoparticle-Mediated Hydroxyl Radical Attack on Reduced Graphene Oxide. *ACS Nano* **2013** 7 (6), 5546-5557.

the irradiation. A decrease in absorbance was characteristic of an oxidation of the RGO. It was found that platinum did not catalyze the oxidation, but both the gold and copper nanoparticles did. Figure 1 shows the absorbance spectra for the various nanoparticles over the course of their irradiation.

a)



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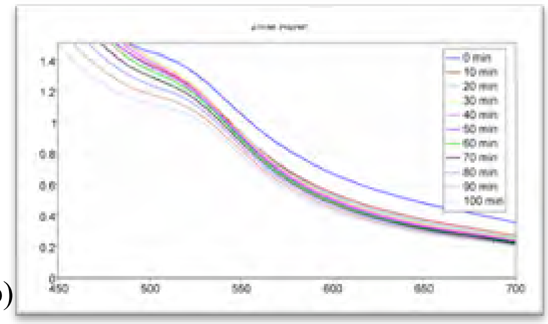

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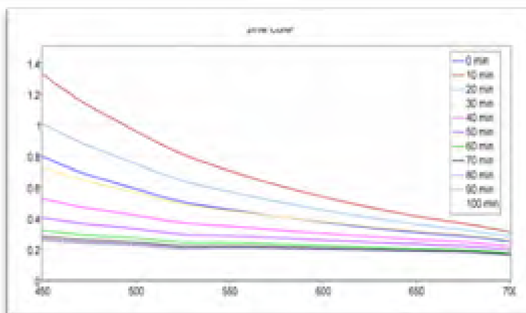

Figure 1. Absorbance Spectra of RGO Post-Irradiation with H_2O_2 and a) Platinum Nanoparticles, b) Gold Nanoparticles, and c) Copper Nanoparticles

As is evidenced by the spectra, copper nanoparticles result in an increased rate of oxidation beyond what the gold particles exhibit. In fact, by allowing the reaction to progress for extended amounts of time, it was possible to oxidize the RGO to the point where the solution had lost most of its color. At this point, the products of this extended oxidation were investigated. Using Gas Chromatography-Mass Spectrometry, it was possible to deduce the presence of diethyl phthalate in an extract from one of the copper nanoparticle samples which underwent an extended amount of irradiation. TEM images of the gold and copper RGO samples post-irradiation were obtained. These are shown in Figures 2 and 3.

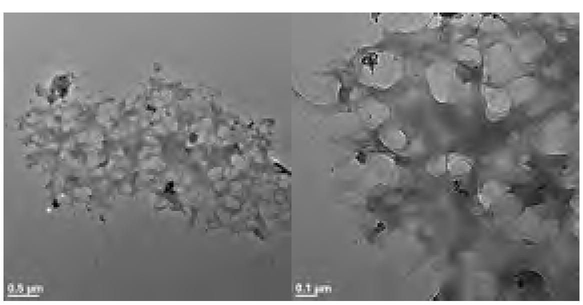

Figure 2. TEM of RGO/Gold Nanoparticles After 20 min Irradiation

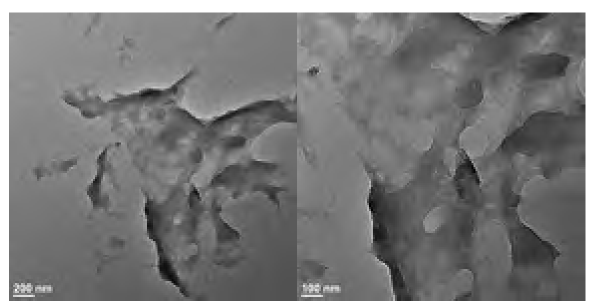

Figure 3. TEM of RGO/Copper Nanoparticles After 5 min Irradiation

The images show that the copper nanoparticles cause a similar deterioration of the RGO surface as the gold nanoparticles do, but copper achieves this with a lower amount of irradiation time. There are also some minor characteristic differences noticeable in the holes produced in the RGO surface. The copper nanoparticles appear to result in a much smoother and deeper hole, while the gold nanoparticles result in a shallower hole which is much rougher and less uniform. This is promising because it means we can obtain different results given different particles. Investigations as to the effect of irradiation intensity and duration as well as actual impact on electrical properties of RGO are areas for future research.

One final aspect of the experiment was to examine what was happening to the RGO after an irradiation for an extended period of time. The reaction was done using the copper nanoparticles. Following the irradiation, the RGO solution had been oxidized to the point of losing almost all color. A liquid-liquid extraction was done on the aqueous RGO solution using a 1:1 volume ratio of methylene chloride and acetone to extract any organic products. Gas Chromatography/Mass Spectrometry was then done to analyze the solution. Figure 4 shows these spectra, which indicate the presence of diethyl phthalate, whose structure is shown in Figure 5.

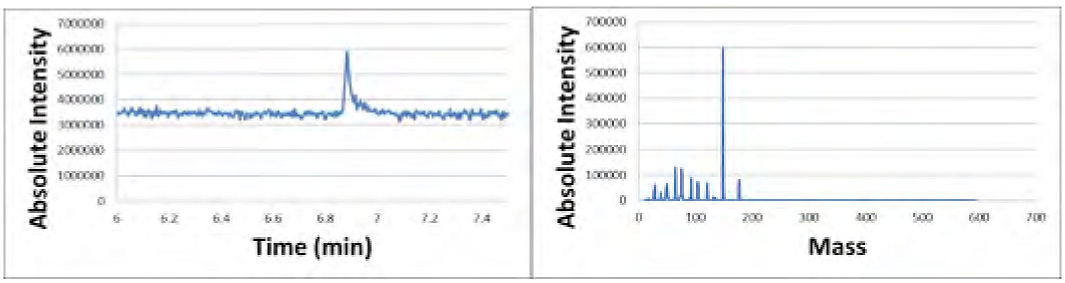

Figure 4. GC-MS for Extended Irradiation with RGO/Copper Nanoparticles

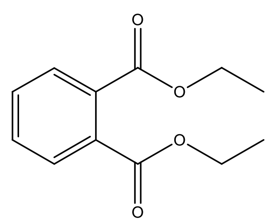

Figure 5. Structure of Diethyl Phthalate

I had the opportunity to participate in a poster presentation of this research at the 2013 Undergraduate Research Symposium at the University of Notre Dame. For a small copy of my poster please see the next page.

Manipulation of Graphene Morphology Compounds via Metal Nanoparticle Mediated Hydroxyl Radical Attack

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Introduction

This project sought to modulate the morphology of 2-dimensional Reduced Graphene Oxide (RGO) sheets through a controlled oxidation via hydroxyl radical attack catalyzed by various metal nanoparticles.

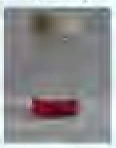
Background

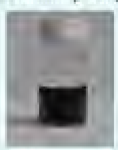
Graphene is emerging as a material with great potential for electronic applications due to its incredibly unique properties, including a high intrinsic electron mobility and large surface area. Since these properties are derived from its structure, being able to control the morphology of graphene would allow us to tune these properties to specific needs or even increase them beyond what has been achieved so far. It is also important to understand how graphene reacts in the presence of metal nanoparticles, which are being frequently tested in similar electronic applications.

Methods

- Nanoparticles tested:

Gold (AuNP) Copper (CuNP) Platinum (PtNP)





- The RGO-nanoparticle solutions were subjected to white light irradiation in the presence of H_2O_2 by a 300 W Xe lamp with a quartz water filter for various amounts of time
- Oxidation was monitored using a Varian UV-Visible Spectrophotometer
- Characterization of results were done using the following:
  - -Thermo Scientific ISQ Series GC-MS
  - -Shimadzu IR Prestige-21 FTIR
  - -FEI Titan 80-300 300 kV Transmission Electron Microscope

Results

Comparing Nanoparticle Species

It was observed that PtNP did not catalyze the oxidative degradation of the RGO. The absorbance spectrum indicates an increase in absorbance indicative of the further reduction of the RGO.

Both CuNP and AuNP appear to catalyze the hydroxyl radical attack. The rate of reaction appears faster with the CuNP given the larger decreases in the absorption spectrum given the same irradiation time.

Impact on RGO Structure

TEM images of the RGO surface after irradiation with AuNP and CuNP also show the increased rate with CuNP, since the holes in the structure with AuNP and 20 minutes of irradiation is comparable to the CuNP after only 5 minutes of irradiation.

Environmental Implications

If the reaction with CuNP is allowed to progress for long enough, the solution of RGO loses almost all color. The presence of other compounds created by the reaction was investigated.

The FTIR spectrum shows signals for O-H bonds and carbon double bonds.

The GC-MS is consistent with this as it shows a small peak indicating the presence of Diethyl Phthalate.

Conclusions

The data shows the increased rate of oxidation using copper nanoparticles. However, we have yet to examine other factors such as light intensity and concentration variations. The environmental applications of graphene must be scrutinized, since the experiment shows its use can lead to the production of contaminants.

References

Radich, J.G.; Kamat, P.V., Making Graphene Holey. Gold-Nanoparticle-Mediated Hydroxyl Radical Attack on Reduced Graphene Oxide. *ACS Nano* 2013 7 (6), 5546-5557.

Acknowledgements

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