Scalable Synthesis of Graphene Quantum Dots from Coal

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Purpose

This experiment intends to synthesize graphene quantum dots using coal as a starting material. Specifically, graphene sheets under 10 nm in diameter will be separated from bulk coal by an oxidative delamination process. These sheets will be characterized for quantum dot-like optical properties. Additionally, the resulting optical data will be analyzed in the hopes of finding correlation between the type of coal used and the optical properties of the yielded structures.

Background

Quantum dots (QD) are commonly touted as one of the most promising nanotechnological innovations. Their possible applications reach through various industries, including use as quantum computing gates, photonic sensors for monitoring of biological processes, and the improvement of photovoltaic energy conversion efficiency. Though many of these devices can be created in a laboratory environment, quantum dot technology has yet to be realized commercially due to issues of scalability. Costs of both raw materials and the execution of highly controlled synthesis procedures limit the feasibility of bringing quantum dot-based devices to the consumer.

A process developed at Rice University aims to synthesize quantum dots using basic materials and coal \(^1\). It was shown that graphene sheets ranging from roughly 2 nm to 8 nm in diameter naturally exist in coal. Once separated from coal by an oxidative cutting reaction, these pieces of graphene exhibit quantum dot-like photonic properties. The photoluminescent emission peaks of these graphene structures was shown to correlate to the diameter of the graphene sheet, suggesting that the emission is due to localization of electronic states across the plane of the graphene. Optimization of this process could drastically decrease the cost of quantum dot devices, as the materials and techniques needed to separate graphene quantum dots (GQD) from coal is far cheaper than standard QD synthesis methods currently used.
Literature from Rice has shown that quantum dot synthesis can be done cheaply via a simple fabrication process. However, they have not shown that the photoluminescent properties of the GQDs can be reliably predicted or controlled. Their study shows that three unique samples of coal yielded three unique photoluminescence spectra. If GQDs are to have any effect on the QD device market, there must be demonstrated control of photonic properties to ensure consistency of device behavior.

We predict that the photonic properties of GQDs from coal are dependent on the type of coal used. There are various types of coal that occur naturally in our earth’s crust, primarily differentiated by the percentage of their weight that is constituted by carbon. The Rice University study managed to show that three different types of coal (anthracite, coke, and bituminous) have unique photonic properties. Our study aims to show that various samples of the same type of coal will yield GQDs with identical photonic properties. Specifically, we chose bituminous coal for our study. Bituminous coal makes up about 40% of the coal mined in the United States, and though it is slightly less common that subbituminous coal, it has a higher carbon content by weight [3]. As we are hoping to synthesize carbon structures, the higher carbon content likely
increases the chance of a successful synthesis. As a control to confirm that any correlation of results between GQDs from two bituminous samples is, in fact, due to them being the same type and not due to our synthesis process, GQDs will be synthesized from a sample of lignite coal as well.

Two chemical processes are utilized in the synthesis – oxidative cleaving of graphene sheets from bulk carbon, and neutralization of acidic solution by addition of a base. Graphitic structures have been shown to form carbonyl and epoxy groups at the edges between graphene sheets as a result of oxidation. These groups prefer to align, then “unzip” by breaking the C-C
bonds between graphene sheets. [2] This phenomenon will be used to separate graphene quantum dots from bulk carbon.

The neutralization step involves the addition of sodium hydroxide to a mixture of sulfuric and nitric acid.

\[ HSO_4^- + NaOH \rightarrow NaHSO_4 + H_2O \]
\[ NO_3^- + NaOH \rightarrow NaNO_3 + H_2O \]

These reactions are carried out in an acidic environment, allowing the hydroxide group from the base to form water. The resulting sodium and nitride salts are ideally removed in the filtration after neutralization has occurred.

Methods

**Oxidative Separation of Graphene from Coal**

300 mg of coal is ground into a fine powder. This powder is mixed into an 80 mL 3:1 solution consisting of 60 mL concentrated sulfuric acid and 20 mL nitric acid. The acidic coal solution is sonicated for 2 hours to ensure maximum exposure of all surfaces of the amorphous coal powder to acid. Finally, the solution is heated to 100°C for 24 hours, allowing the oxidative separation reaction to run to completion.

The resulting solution is extremely acidic, and must be neutralized. Sodium hydroxide is added to the solution until the pH is roughly 7.

**Filtration**
The oxidative separation step yields a solution of graphene oxide, amorphous carbon, and salt crystals from the neutralization step. The solution is filtered sequentially through Teflon membranes with pore sizes of 650 nm, 450 nm, and 220 nm via vacuum filtration. Next, the solution is dialyzed through 1 kDa cellulose dialysis tubing in an aqueous solution for 5 days. The aqueous solution is changed daily to maintain a concentration gradient across the membrane. The aqueous solution is stored each time it is changed, as it holds the GQDs.

After dialysis is complete, there is a large volume of aqueous GQD solution. This solution must have the solvent removed, leaving solid graphene residue. Initially, the solution is heated to about 80°C, evaporating most of the water from the solution. The last few mL of solvent are removed from solution via rotary evaporation, to avoid thermal damage to the sample once all solvent is removed.

**Characterization**

UV-visible photonic absorbance spectra of the GQD solutions are taken at various dilutions at two points of the synthesis process. Specifically, the absorbance spectra are taken before dialysis and after the full filtration process is complete. Each sample is imaged at four dilutions at a time, with each dilution being 50% the concentration of the previous (1, 1:2, 1:4, and 1:8 solvent ratios). These spectra are analyzed for peaks and shoulders, which would signify absorbance from the GQDs.

Next, fluorescence spectra of the GQD solutions are taken. These measurements are taken after the dialysis process is complete. The excitation wavelength is controlled to 390 nm., to ensure a photonic response from the carbon structures in solution. Similar to the UV-vis absorbance data, these spectra are analyzed for peaks and shoulders, which would signify
fluorescence from the GQDs. Additionally, qualitative fluorescence analysis is done by noting the visible response of GQD solution to a ultraviolet light source.

Finally, the GQD solutions are analyzed under Raman spectroscopy. This is done after all filtration and solvent removal is complete. Solid GQD residue is returned to an aqueous solution, then drop casted onto a silicon substrate. The water is allowed to evaporate, leaving a solid sample on silicon to be tested. These spectra will be analyzed for peaks at 1350 cm$^{-1}$ and 1582 cm$^{-1}$, as these are the characteristic signals of graphene oxide and graphene, respectively.

**Results**

Three coal samples were picked for this experiment. Two bituminous coal samples (BC and BZ) were selected, as well as one lignite coal sample (POC). This was done such that any similarity in the results between BC and BZ would likely be a result of the coal type used, and not the location the coal is mined from.

Figure 5 displays the UV-visible spectrum absorbance of the three coal samples after dialysis. At this point, the GQD solution is in an aqueous solution. The large peaks between 200-250 nm are likely due to instrumental error, and are ignored in all analysis of the GQD absorbance. A clear similarity can be seen in the absorbance spectra of BC and BZ, which both exhibit mild peaking/shoudering at 300 nm. POC barely shows any absorbance response, with possible shouldering in the 250-300 nm range.
Figure 6 shows both quantitative and qualitative fluorescence response of the GQD solutions after dialysis. The quantitative fluorescence spectra were measured with an excitation wavelength of 390 nm. As can be seen in both data sets, there are marked similarities between BZ and BC, while POC is somewhat of an outlier. Both bituminous samples exhibit large peaks at roughly the same

Figure 7: Raman spectra of the three coal samples. The peaks of interest are labeled on the BC graph. Significant peaking was not seen at the sites for graphene or graphene oxide. Large peaks at 995 and 1061 cm⁻¹ can be seen in the bituminous samples, while minor peaking at 1061 cm⁻¹ can be seen in the lignite sample.
wavelength (440 nm and 443 nm), as well as a minor peak at 600 nm. The lignite sample, however, shows little to no peaking at 462 nm, and has no sign of minor peaking at 600 nm. The visible fluorescence of the BC and BZ coals are virtually identical in both their green-white color and intensity, while the POC has little to visible fluorescence.

Raman spectroscopy of the three coal samples revealed nearly no presence of graphene or graphene oxide in our product. There were, however, large peaks at 995 cm\(^{-1}\) and 1061 cm\(^{-1}\) in both bituminous samples, again showing strong similarity between results from the same coal type. The lignite coal had much lower signal strength than the bituminous coal, with minor peaking at 1061 cm\(^{-1}\). The peak at 500 cm\(^{-1}\) seen in each sample is from the silicon substrate holding the samples, and is not used in the analysis.

Discussion

All data showed almost identical results between the bituminous coals and starkly different results for the lignite. For this reason, discussion will be done in two sections – one for the lignite sample, and one for the bituminous samples.

Lignite (POC)

All three quantitative tests showed rather mediocre results for the lignite coal sample. The lignite absorbance spectrum showed essentially no shoudering or peaking, suggesting that there are no particles with marked absorbance present in the solution. Graphene sheets in aqueous solution are expected to have absorbance around 300-400 nm \(^{[4]}\), which is clearly not seen in this data.
Fluorescence data is also underwhelming for the lignite sample. The lignite fluorescence data technically has a peak near the expected range \(^5\) at 462 nm, but the magnitude of this peaking is so low that convincing conclusions cannot be drawn.

As expected from the first two tests, Raman spectroscopic data further affirmed the lack of graphene in the lignite sample. Graphene and graphene oxide display peaks at 1350 cm\(^{-1}\) and 1582 cm\(^{-1}\), respectively. Neither of these signals is seen in the lignite Raman spectrum.

Overall, data strongly suggests that no graphene structures were yielded from oxidative treatment of lignite coal. Various types of data taken at various points in the synthesis procedure proved a significant discrepancy between expected and found results. This may be explained by the fact that lignite has the lowest carbon content and highest moisture concentration of any coal type \(^6\). This is largely due to lignite being the youngest coal, with little time to excrete impurities and increase in carbon content through coalification. The oxidative synthesis of graphene sheets relies on small graphene sheets naturally existing in the coal samples. It may be that a combination of the low carbon content and lack of time spent under high pressure before mining limits the ability for graphene to naturally form in lignite. Additionally, the presence of water in the lignite may also inhibit graphene formation.

*Bituminous (BZ and BC)*

The two bituminous coal samples showed nearly identical properties under all tests performed, and will be discussed simultaneously.

UV-vis spectra of the bituminous coals showed absorption in the 300 nm range. This is exactly the region in which absorbance is to be expected for graphene in an aqueous solution. The absorbance is not very great in magnitude, which would suggest the concentration of graphene sheets in our solution is not very high. Absorbance data was taken prior to the evaporation of solvent, which may imply that graphene was present in solution before that step.
The bituminous coals showed fluorescence in the 440 nm range. Fluorescence peaking is expected around 400 nm for graphene oxide [5]. This makes the bituminous fluorescence a telling sign of having graphene or graphene oxide in the solution. The fluorescence data was also taken prior to the evaporation step, and is consistent with the assumption of graphene or graphene oxide being present in solution at this point.

The positive correlation between expected and actual results ends with the Raman spectra of the bituminous samples. Expected peaks at 1350 cm\(^{-1}\) and 1582 cm\(^{-1}\) are not present in the recorded Raman data. However, strong peaks are shown at 995 cm\(^{-1}\) and 1061 cm\(^{-1}\), which correspond to thiophene-like compounds [7] and amorphous carbon, respectively. Raman data was recorded after the evaporation step, in which the graphene solutions were subjected to heat in an aqueous solution. If residual sulfur salts from the neutralization step were still present in solution at the time of heating for evaporation, graphene oxide may have been reduced to thiophene [8]. This would explain both the positive absorbance and fluorescence results and the strange Raman results. The amorphous carbon may be small amorphous regions that made it through all the filtration steps, or may have been formed by coagulation of graphene into bulk carbon structures during the evaporation step.

Though the end product did not contain graphene structures, there is the possibility that graphene was successfully synthesized from the bituminous samples prior to the evaporation step. Even if this is not the case, strong similarity has been shown between two bituminous coals despite a difference in mine location. As graphene sheets were extracted from bituminous coal successfully in the Rice University study, our data suggests that the properties of GQDs could be predicted by coal type, and that GQDs yielded from bituminous coal would likely share the same properties.

**Conclusion**
Coal samples of the same type exhibit nearly identical properties, despite being from geographically different areas of origin. This suggests that the properties of graphene quantum dots synthesized by oxidative separation can be predicted by the type of coal being used. Supplemented with the extremely low cost of materials and synthesis steps, our study shows promise for the use of coal-based quantum dots as a cheap source for scalable quantum dot device fabrication.

Further studies could go in two directions – optimizing the synthesis procedure, and further analysis of lignite as a source of graphene quantum dots. The evaporation step was a problem area for the synthesis, and must be replaced with a less volatile procedure in order to preserve graphene structures in solution. Lignite did not show any sign of producing graphene, but more trials would be needed to fully rule out lignite as a possible GQD source.

Citations


