An Experimental study of Graphene Quantum Dots as a Potential Fluorescent, Anti-Bacterial Additive for Water Based Paint

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Project Objective and Goals

Based on a 2020 report, an estimated 100,000 people die every year in the US due to poor sanitation standards in hospitals [4]. This statistic shows an underlying issue with hospital room sanitation, and new methods to reduce the spread of diseases are needed to save lives. One common way that bacteria spreads in hospitals are on surfaces that doctors, family members, and visitors commonly touch. This includes tables, doorknobs, TV remotes, etc. With an antibacterial paint containing GQDs, surfaces like these can be thoroughly cleaned with just the addition of UV light.

The GQD-paint solution must follow specific design specifications for it to be effective in a hospital room setting. The solution must first and foremost be safe to touch and to be around for extended periods of time. Ease of manufacturing is another important design specification as this aims to be an addition to preexisting sanitation standards. In conjunction with manufacturing, the design must be a cost-effective solution to the problem for it to see implementation.

Background

GQDs have attracted widespread attention for their controllable photoluminescence properties and relatively simple fabrication. Researchers have been able to apply the photoluminescence property of GQDs in the application of biosensors, light emitting diodes, and bioimaging. There are two main methods of synthesizing GQDs in a laboratory setting: top down and bottom up [2]. The former involves taking larger carbon sources like graphene oxide and breaking them down either chemically or hydrothermally. For example, Ku et al. synthesized red, blue, green, and yellow GQDs through hydroxyl-radical-induced decomposition of graphene oxide. Color was simply determined by how long the solutions were heated. On the other hand, a bottom-up approach to GQD synthesis involves using small carbon precursors under usually harsh reaction conditions. Fortunately, Wu et al. have found a method for synthesis using only a common amino acid, L-Glutamic Acid, and heating as pyrolysis. The synthesized GQDs were found to have hydrogen peroxide based catalytic activity with high emissivity. Producing GQDs with only common amino acid and heat is extremely exciting as a synthesis as simple as this has the potential to be industrialized. Aside from its photoluminescent properties, graphene quantum dots also have intrinsic antibacterial properties [1]. Previous research from Sun et al. proved that a combination of hydrogen peroxide and GQDs can kill both E. coli and S. Aureus. This was tested by doping the band-aids at different concentrations of the solution and applying it to mice wounds; their data can be seen in figure 2 [1]. Figure 1a quantitatively shows how the presence of hydrogen peroxide and GQDs resulted in less bacteria growth over time compared to only water treatment. The figure also shows how a stronger concentrated solution decreased the percentage survival of bacteria. Figure 2b shows qualitatively how the presence of GQDs, H2O2, and a combination of both accelerated healing by reducing infectious bacteria growth.

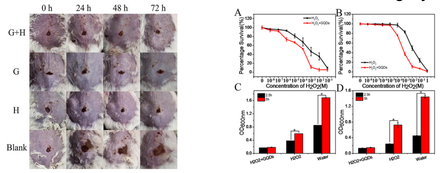


Figure 1: Bacteria rates on mouse wounds treated with either water, hydrogen peroxide, or hydrogen peroxide and GQDs. Quantitative data is shown on the left (1a), and qualitative images of the mouse wounds are shown on the right (1b) [1].

GQD Fabrication

As explained in the background, the process of forming GQDs from L-Glutamine loosely follows *Wu et al's.* experimental procedure of pyrolyzing the amino acid at 210 degrees C in a heating mantle [3]. With a melting and decomposition point of 185 degrees, the process aims at breaking down the sp2 network by the sp3-bonded C atoms to form the GQDs. In my experiments, a hot plate was used rather than a heating mantle due to availability. Issues arose with this as a heating mantle would have allowed for better dispersion of heat on the bottle. Thus, higher temperatures were tested to gather similar results to *Wu et al.*

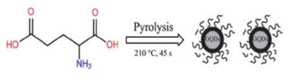


Figure 2: Schematic diagram of the formation of GQDs through the pyrolysis of L-glutamic acid

SEM and Spectroscopy Data

Both SEM and Spectroscopy analysis was conducted to characterize the GQDs. Figure 3 shows the UV/Vis absorption data based on percentage, with peak absorbance at around 300 nm. Raman data in figure 4 confirms D and G group formations which prove the existence of GQDs on the sample and is based on data collected from *Wu et al.* SEM imagining is also given in figure 5 which shows uniform body on the sample surface

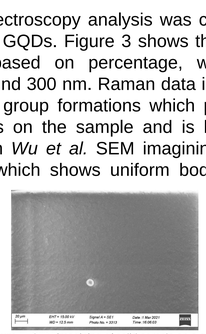


Figure 5: SEM imagining of solid sample on a glass slide. The white region is an impurity on the sample.

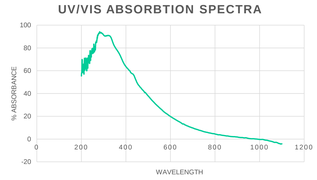
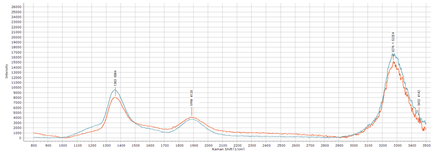


Figure 3 (**left):** UV/Vis absorption data of solid GQDs on a glass slide.

Figure 4 (Below): Raman spectroscopy data using a 765 nm laser. Peaks at 1363 and 1888 1/cm show the formation of D and G groups, respectively [1].



Florescence and Anti-Bacterial Testing

Florescence testing of the GQD solutions was mainly qualitative and was determined by the intensity of blue florescence under longwave radiation. Original fabrication of the GQDs used a hot plate at temperatures ranging from 210 – 255 degrees C, with stronger florescence at the latter temperature (figure 6). An industrial oven was also used at varying temperatures and can be seen in figure 7. Figure 7 also shows testing done on doubling the concentration of L-Glutamine to water with no change, if not a decrease, in florescence.

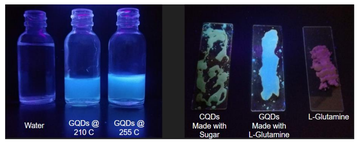


Figure 6: Various mediums under longwave UV light. GQD solutions on the left were formed following *Sun et al.* experimental procedure while the CQDs and GQDs on the right were pyrolyzed directly onto glass slides.

Figure 7: GQD solutions using an industrial kiln as the heating source with the left solution being 2g Glutamine to 10 mL of water and the middle solution being 4g Glutamine to 10mL water. Water is shown on the right for reference

Antibacterial testing was conducted using E.coli grown on agar covered petri dishes. Previous research has shown that GQDs have innate antibacterial properties to an extent. An experiment was set up to determine if the L-Glutamine based GQDs would have any of these properties where varying concentrations of solution were tested on the dishes. It was found that the GQDs do not have any intrinsic antibacterial properties, at least at the tested concentrations.

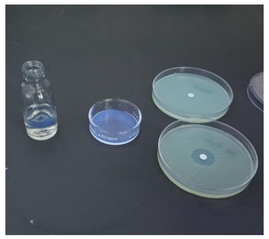
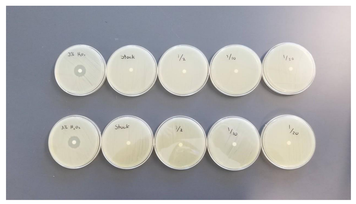


Figure 8 (Left): GQD stock solution and solid sample are shown on the left half of the image, respectively. E.coli testing is shown on the right half with the peroxide control on the bottom showing a clear ring of inhibition. Stock solution is shown on the top dish with no ring of inhibition. The entire scene is under longwave UV light.

Figure 9 (Right): Antibacterial testing using E.coli grown on agar covered petri dishes. Hydrogen Peroxide is used as a control on the left with GQD solutions ranging from stock concentration to 1/20th the concentration. No ring of inhibition is seen from the GQD samples.



Paint Testing

The water based GQD solution was applied to two different types of paint, mixed, and applied to glass slides to test florescence. Latex and Acrylic based paints were used with the latex-based paint clumping significantly to the point of not being usable. The acrylic based paint mixed much better with the solution at all concentrations. Regardless, no paint solution showed florescent properties as shown in figure 10. Even with a 50/50 ratio of GQD solution to paint, there was zero florescence. Whether or not this was due to some reaction between the solution and the paint or just low florescence of the GQDs themselves could be tested in the future.

Centrifuging the GQD solution to increase intensity was also tested to poor results. At the highest RPM and 30 minutes of spin time, no supernatant was collected concluding that the GQDs were so small they could not be removed from the water molecules.

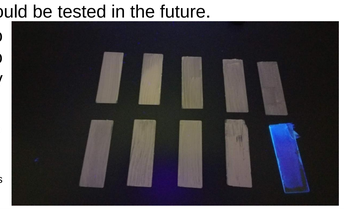


Figure 10: Acrylic paints of two separate tests, separated by row under the same variables with GQD concentration increasing from left to right. The bottom right slide is a pure GQD solid solution as a control.

Conclusions

During Fabrication and Florescence Testing:

- Strongest florescence was seen using the industrial oven at 210 degrees C with a 2g to 10mL ratio of L-Glutamine to water
- Similar results were collected using the hot plate at 255 degrees but more consistent using the oven
- SEM and Spectroscopy data prove the formation of GQDs based on the D and G functional groups and a uniform surface.

From Antibacterial Testing:

- The 2g/10 mL concentration was not enough to show any innate antibacterial properties against E.coli
- Lower concentrations tested did not show any rings of inhibition despite being similar in concentration to previous research

From Paint Testing:

- The addition of GQD solution to acrylic based paint did not yield any florescence at any concentration.
- A lack of florescence could be attributed to:
  - A reaction between the paint and solution resulting in loss of florescence
  - Low florescent concentration such that when applied to paint, the florescence is negligible

Since both the paint and antibacterial tests were a failure to the starting goal, it can be determined that this method of producing GQDs is not an optimal application for the hospital paint. Other methods of producing GQDs such as from a top-down method described in the background may prove advantageous.

Future Work

As touched upon by the conclusion, future work on the project would revolve around why the paint and antibacterial testing saw negligible results. A reaction analysis between the paint and GQD solution could be run to determine a cause for the loss of florescence. Other methods of GQD synthesis could also be tested in hopes of producing stronger florescence as well as particles that could be centrifuged.

Antibacterial tests could be redone with a combination of Hydrogen Peroxide and GQD solution. Previous research shows a combination of the two producing greater results than on their own, and the solution could once again be applied to paint for an antibacterial surface. If antibacterial testing were successful, the GQD-Paint solution could be tested again to ensure these properties are still intact.

Acknowledgements

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References

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