Erbium-Doped Graphene Quantum Dot's Dream to be Part of Bioimaging

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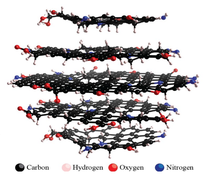
Abstract

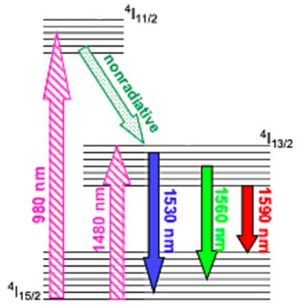
To track drug delivery within the body, the vehicle must be biocompatible, soluble, and transparent in the human body. Being transparent in the human body means the vehicle exhibits fluorescence in the near-infrared (NIR) III biological transparency window (1500 – 1800 nm). These traits will respectively not oppose health defects in the subjects, will be stable within the blood and cells of the body, and be able to be found within the body through the means of infrared detectors. This is where graphene quantum dots (GQDs) come into the picture. GQDs prepared by a one-step hydrothermal method from glucosamine and ascorbic acid precursors are biocompatible and soluble in water. On their own, they do not demonstrate fluorescence in the NIR-III. To add this capability, we dope GQDs with erbium ions (Er-GQDs) as they demonstrate a fluorescence peak at 1550nm followed by excitation at 980nm laser. Fluorescence light coming from erbium ions at 1550 nm covers the NIR-III biological window, which is the last specification needed to have an eligible vehicle. In our work, we synthesized Er-GQDs at 200°C for 8 h and 17 h in deuterium oxide. The fluorescence of erbium ions is known to be quenched by OH functional groups. The average size of Er-GQDs is growing from 3 to 5 nm after 8 h and 17 h treatment times, respectively, and exhibit fluorescence with 1550 nm emission peak in deuterium oxide. All aforementioned results make Er-GQDs a potential imaging agent for bioimaging.

Graphene Quantum Dots (GQDs)

- 0D structures;
- Size < 10nm;
- Have functional groups;
- Soluble in water;
- Biocompatible;
- Can be synthesized from different precursors;
- Exhibit fluorescence in visible;
- Have capability to attach Erbium ions.



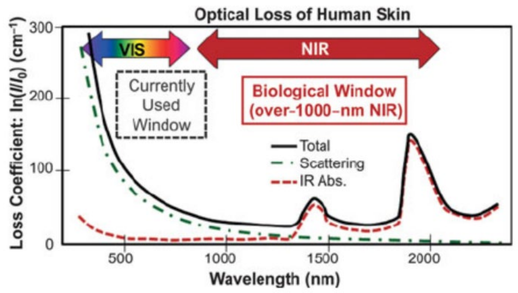
Fluorescence



Er fluorescence is **quenched** by –OH functional groups (**water** molecules)

Motivation

- **Bioimaging:** utilizing near-infrared light (NIR) is more beneficial



- less tissue scattering and absorbance in the third biological windows (1500-1800 nm)
- **Goal:** develop a fluorophore based on Erbium (Er) that exhibits fluorescence with peak ~1550 nm.

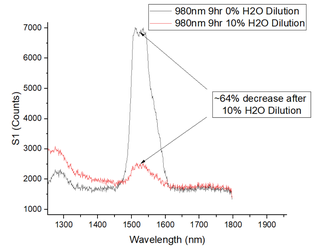
Reinhard, E. et al. Nanoscale. [2013]

Hypothesis 2

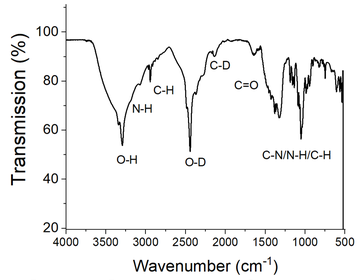
- **GQDs doped with Er ions and synthesized from ascorbic acid in deuterium oxide (D_2O) will exhibit near-infrared fluorescence in solution. Because Ascorbic Acid is known to be a more negatively charged species than glucosamine, it was predicted that Ascorbic Acid GQDs would try to bond more strongly to the Erbium ions.**

9hr synthesis of Erbium-Doped Ascorbic Acid with 0% H2O Dilution vs with 10% H2O Dilution

- A 64% decrease in fluorescence within the IR Spectrum is seen after a 10% H2O Dilution



FTIR spectrum of Er-GQDs



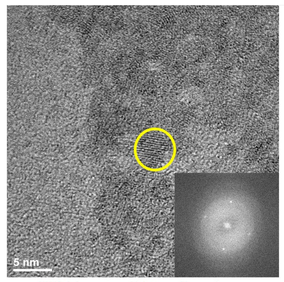
Confirm the replacement of –OH groups on the surface of Er-GQDs with -OD

Hypothesis 1

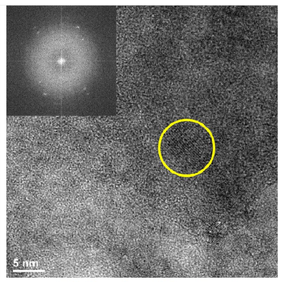
- **GQDs doped with Er ions and synthesized from glucosamine in deuterium oxide (D_2O) will exhibit near-infrared fluorescence in solution. Bigger structure will trap Er ions and protect them from water molecules.**

TEM images of GQDs:

- A longer synthesis time within the autoclave has been proven in imaging to increase the size of the GQD's according to TEM pictures

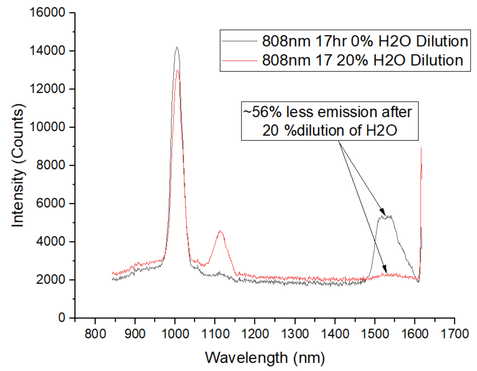


TEM Imaging Erbium-Doped Glucosamine Cooked for 8hr



TEM Imaging Erbium-Doped Glucosamine Cooked for 17hr

17hr synthesis of Erbium-Doped Glucosamine with 0% H2O Dilution vs with 20% H2O Dilution



- A 56% decrease in fluorescence within the IR Spectrum is seen after only a 20% H2O Dilution

Conclusion

- Increasing the size of the GQDs to create less water-Erbium interactions proved not to avoid the quenching in the IR spectrum when a dilution of H2O appeared.
- Using a more negatively-charged precursor (ascorbic acid) to create a more strongly bonded GQD proved to still quench when water was added to the system.
- With the current results of the experiment, Erbium-Doped GQDs will not make an effective drug tracker within the body due to the quenching of IR fluorescence in H2O.

Future studies

- Continue synthesis of GQDs from ascorbic acid for a longer time.
- Utilize different precursors.
- Develop alternate methods of synthesis of larger structure GQDs (>10 nm) (e.g. microwave-assisted method)
- Utilize Erbium coordination complexes.