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Synthesis and Applications of Carbon Materials

by

Andrew Brien Metzger

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APPROVED, THESIS COMMITTEE

James M. Tour, Chair
T. T. and W. F. Chao Professor of
Chemistry, Professor of Computer
Science, Professor of Materials Science
and NanoEngineering

Angel Marti
Associate Professor of Chemistry,
Bioengineering, and Materials Science and
NanoEngineering

Rouzbeh Shasavari
Assistant Professor, Department of Civil
and Environmental Engineering,
Department of Materials Science and
NanoEngineering

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The synthesis and applications of carbon-containing materials is discussed. Carbon materials discussed range from conductive polymer-coated minerals to polymer-functionalized graphene nanoribbons to graphene quantum dots. Applications range from wellbore reinforcement to conductive drilling fluids to lanthanide sensitization. In the first chapter, the preparation and use of polyaniline-coated barite as a weighting agent in conductive drilling fluids is discussed. In the second chapter, microwave-assisted curing of thermosets accelerated by functionalized graphene nanoribbon is discussed. In the third chapter, the synthesis of graphene quantum dots via nitric acid oxidation of coal is discussed. In the fourth chapter, the sensitization of lanthanides by graphene quantum dots is discussed.
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Nomenclature

LWD  Logging while drilling
GQD  Graphene quantum dots
bGQD blue-shifted GQD
rGQD red-shifted GQD
GNR  Graphene nanoribbons
SWNT Single-wall carbon nanotube
PPO  Polypropylene oxide
PI   Polyisoprene
PANI Polyaniline
HSPAN Highly sulfonated polyaniline
B-5  Barite particles ~5 µm in size
B-55 Barite particles ~55 µm in size
OBM  Oil-based mud/drilling fluid
WBM  Water-based mud/drilling fluid
XPS  X-ray photoelectron spectroscopy
TEM  Transmission electron microscopy
EDS (EDX) Energy dispersive x-ray spectroscopy
SEM  Scanning electron microscopy
NIR  Near infrared
PL   Photoluminescence
QY   Quantum yield
Chapter 1

Introduction

Carbon comes in many forms, from the organic materials that compose life to the graphite that composes pencil “lead” to the carbon black filler in car tires, to the sparkling diamonds in jewelry. Rice University has a rich history of (nano)carbon research. The discovery of $C_{60}$ by Richard Smalley in 1985 marks the birth of nanocarbon technology, if not nanotechnology. This discovery also led to the 1986 Nobel Prize in Chemistry being awarded to Smalley, Curl, and Kroto. These zero-dimensional fullerenes found their niche in the area of photovoltaics. The next great development was the synthesis of single-wall carbon nanotubes using an iron catalyst in high-pressure carbon monoxide (HiPCO SWCNTS), before which conductive polymers were the prominent organic conductor. Due to political and environmental stigma, carbon nanotubes have unfortunately not found commercial use, though the opening of multi-wall nanotubes into graphene nanoribbons (GNRs) is promising. The discovery of graphene turned a new page in nanocarbon research.
Atomically thin films were previously only known for gold and other noble metals; such films composed of carbon were thought to be thermodynamically impossible. The difficulty in preparing large amounts of graphene through chemical vapor deposition has directed nanocarbon research to pursue alternative graphitic materials such as graphene oxide, graphene nanoribbons, and even zero-dimensional graphene quantum dots. This document will discuss the synthesis and applications of materials containing conductive polyaniline, functionalized graphene nanoribbons, and graphene quantum dots.
Chapter 2

Polyaniline Coated Barite for Conductive Oil-Based Drilling Fluids

Dr. Paul Cherukuri acquired optical microscope images for this chapter.
Everything else was performed by me.

2.1. Introduction

Resistivity logging is the of imaging technique used by the oil and gas industry to map a wellbore based on the resistivity of its composing geological formations, as the brine saturated formations are much less resistive than hydrocarbons. Typical induction logging tools use two coils – a transmitter and a receiver. An alternating current is driven through the transmitter coil to induce a magnetic field around this coil and through the drilling medium. This magnetic field then produces an alternating voltage in the receiving coil proportional to formation
Logging while drilling (LWD) is imaging and mapping a wellbore while simultaneously drilling through it. Much geological information can be obtained through LWD, including fracture, fault, texture, and saturation data.\textsuperscript{3,4} LWD in oil-based drilling muds (OBMs) poses less risk of corrosion of materials of construction than with water-based muds (WBMs).\textsuperscript{5,6} However, LWD in OBMs is difficult because the drilling fluid acts as a contrast medium, and OBMs are inherently nonconductive due to being composed of oil with a dispersed aqueous phase.\textsuperscript{3} In this case OBM refers to an oil-based drilling fluid with over 5\% water whereas the industry defines an oil-based mud as containing only up to 5\%.\textsuperscript{7}

### 2.2. OBM conductivity

The minimum conductivity for a useful logging fluid is not widely available in the scientific literature because formation conductivities vary from well to well, and as a result the necessary minimum fluid conductivity varies from well to well. Similarly, the frequency of the logging tool varies from well to well. These deficiencies and ambiguities in reporting can be bypassed by examining the conductivities of rocks and soils reported in geological surveys. The more common shales and sandstones have conductivities ranging from $10^{-3}$ to $10^{-1}$ S/m, and the frequency range of such measurements is from 1 kHz to 100 kHz.\textsuperscript{8} See Chart 1 for general conductivities of rocks and soils. It has been reported that a drilling fluid with a conductivity of $8 \times 10^{-4}$ S/m is sufficient to resolve rocks with conductivities up to 0.5 S/m at 120 °C.\textsuperscript{6} Thus, a logical goal would be to develop an additive or modified drilling fluid component that would increase fluid conductivity to $10^{-3}$ S/m.
at ambient conditions. A further reaching goal would be to increase conductivity to $10^{-2}$ S/m. These values are not necessarily conductive in other areas of science but are considered excellent because of oil’s significantly lower conductivity. Due to instrumental restrictions, we are unable to separate conductivity and susceptibility ($\text{susceptibility}^2 + \text{conductivity}^2 = \text{admittivity}^2$) and are only able to report the admittance of fluids. Another primary component of drilling muds is the weighting agent, which imparts density to the fluid and pushes wellbore cuttings away from the drill bit. The most common weighting agent is barite (barium sulfate), an inexpensive, abundant mineral with a density $\sim 4.1$ g/cm$^3$. Weighting agents compose up to 50 wt% of the mud and can potentially adsorb any conductivity additives, hindering percolation. We reasoned that if the conductive additive were already present on the weighting agent as a coating, the fluid would be more conductive.  

2.3. Results and Discussion

Polyaniline (PANI) is an inexpensive polymer, prepared from the oxidative polymerization of aniline in dilute acid. Coating materials with PANI via in-situ polymerization of aniline is not new. The coating of silica,\textsuperscript{9} carbon nanotubes,\textsuperscript{10} polymer latexes\textsuperscript{11}, and cellulose\textsuperscript{12} with PANI have been reported for various applications. Conveniently coating barium sulfate nanoparticles with PANI is also known, though not for conductive weighting agents.\textsuperscript{13}
Figure 2.1 shows a summary of OBM admittivities with different coated weighting agents. PANI coatings increase the admittivity of the OBM. Highly sulfonated polyaniline (HSPAN) coatings yield higher OBM admittivities. Self-doped coatings yield more admittive OBMs. B-5 OBMs are more admittive than B-55 OBMs; that is, smaller particles yield more admittive OBMs. This could be due to lower percolation thresholds for smaller diameter particles.\textsuperscript{14}

Figure 2.2 shows the admittivity behavior of PANI/barite OBMs with varying pH. With increasing pH, PANI/barite OBM admittivity decreases. PANI is doped by acids and rendered nonconductive by bases. The aqueous phase of OBM is typically basic (around pH 9). PANI is known to become nonconductive above pH 4.\textsuperscript{15}

Unfortunately, acidic drilling fluids are inherently corrosive to wellbore formations and thus counterproductive to the industry. Because of this, a pH-insensitive coating needed to be prepared. The only known example of pH-independent PANI is highly sulfonated polyaniline pioneered by Epstein et al.\textsuperscript{16}

Figure 3 shows the admittivity of HSPAN/barite OBMs with varying pH. Self-doping via sulfonation allows polyaniline to retain its conductivity in basic environments.\textsuperscript{15} OBMs with HSPAN-coated barite are as admittive as OBMs with PANI-coated barite (not self-doped). Figure 2.4 shows the admittivity of PANI/B-5 OBMs with varying pH. Polyaniline is doped by acid and de-doped by base. Thus the PANI/B-5 OBMs with more acidic dispersed phases are more admittive.

Figure 2.5 shows the TGA weight loss curves for PANI/B-5 and PANI/B-55 in argon. At 350 °C, there is a small weight loss corresponding to the loss of sulfate
dopant. After 700 °C, there is a sharp weight loss corresponding to the decomposition of polyaniline. The composites each have approximately 12 wt% conductive polymer. Control experiments were carried out to determine the importance of conductive coating instead of simply a conductive additive. Figure 2.6 shows percolation studies of PANI and PANI-coated particles in OBM. Though percolation thresholds are similar, admittivity is higher for the fluids with PANI coated particles rather than just added polymer. Coated weighting agents produce higher admittivity OBMs than added conductive polymer, probably due to better dispersion caused by the barite particles occupying space that PANI alone would occupy.\(^\text{17}\)

In conclusion, we developed a conductive weighting agent to improve oil-based fluid admittivity. Admittivity is higher in OBMs with a conductive polymer coated weighting agent than in OBMs with conductive polymer as an additive not coating the weighting agent. PANI coatings are sensitive to the pH of drilling mud, but fluid admittivity can be increased by three orders of magnitude with self-doped conductive polymer coated barite. In the future, we plan to investigate the effects of coated weighting agents on OBM rheology, lubricity, and HTHP performance.

2.4. Experimental

2.4.1. PANI/B-55

Anilinium sulfate (1.00 g, 3.43 mmol) was dissolved in a dispersion of B-55 (10.00 g) in 1 M \(\text{H}_2\text{SO}_4\) (50 mL) at 0 °C. Ammonium persulfate (1.00 g, 4.38 mmol) in
1 M H$_2$SO$_4$ was then added dropwise at 0 °C, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was filtered under vacuum, washed with 20 mL portions of water and methanol, and dried under vacuum at 60 °C.

2.4.2. HSPAN/B-55

PANI/B-55 (10.00 g) was stirred in neat phenylhydrazine for 1 h, filtered under vacuum, and washed with diethyl ether. The resulting reduced polyaniline on B-55 was added to ice-cold fuming sulfuric acid (20% SO$_3$, 50 mL) and allowed to react for 1 h. The reaction mixture was gently quenched with 150 mL of ice water, filtered under vacuum, and washed with 100 mL of cold water. The resulting powder was dried under vacuum at 60 °C.

2.4.3. PANI/B-5

Synthesized in the same manner as PANI/B-55, with B-55 being replaced with 1012 UF.

2.4.4. HSPAN/B-5

Synthesized in the same manner as HSPAN@B-55, with B-55 being replaced with 1012 UF.

2.4.5. Drilling fluid formulation

The drilling fluid recipe used in all measurements was supplied by M-I SWACO, a Schlumberger company. Escaid™ 110, a product of ExxonMobil, is a low
aromatic hydrocarbon oil. B-55, an M-I SWACO product, is a mined and purified barite with a particle size distribution of 5-75 µm with an average of 55 µm. B-5, another M-I product, is a micronized barite with a particle size distribution of 0.5-10 µm with an average size of 5 µm. VG Plus, a product of M-I SWACO, is an organophilic clay modified with quaternary amines. MulXT is a long carbon chain carboxylic acid used as a surfactant for water in oil emulsions. Lime (calcium carbonate) was used to modify the pH of the fluid. The aqueous/dispersed phase was 25% CaCl₂ brine. To rapidly mixing Escaid™ (160 g), was added VG Plus (5.0 g), lime (3.0 g), MulXT (6.0 g), and 100 g of 25% CaCl₂ brine. The suspension was mixed for 5 min after the addition of each component. To prepare a conductivity sample, an equal weight of drilling fluid (without weighting agent) was mixed with an equal weight of weighting agent. The two were mixed at 1200 rpm for 60 s.

2.4.6. Instrumentation

An IKA Turrax 25 mechanical mixer was used to ensure homogenization of the drilling fluids. Admittivity measurements are performed with a copper parallel plate dip-probe connected to a Hewlett-Packard 3577a Network Analyzer from 1 kHz to 100 kHz at a potential of 100 mV. Calibrations are performed using methanol standards and a short-circuit liquid metal standard (zero resistance). An optical microscope was used to study particle size of B-55 and B-5.
2.5. Particle Size and Coating Thickness

In order to estimate coating thickness, the micronized barite samples (both coated and uncoated) were characterized by optical microscopy. Particle size distributions were obtained from the images. See Figure 3.2.6 for optical images. By number-weighted distribution, average particle sizes for B-55, PANI/B-55, B-5, PANI/B-5 were 5.8 µm, 6.3 µm, 3.4 µm, and 3.9 µm, respectively. By volume distribution, particle sizes for B-55, PANI/B-55, B-5, PANI/B-5 were 71 µm, 78 µm, 10 µm, and 11 µm, respectively (see Figure 3.2.7 for volume distribution histograms). Though the volume-weighted average particle size increases by approximately 10% upon coating with polyaniline, the wide dispersity of particle sizes prevents an accurate determination of coating thickness.

Attempts were made to measure coating thickness with transmission electron microscopy. A coating can be seen with PANI-coated B-5: approximately 100 nm for a 1.5 µm particle, or 12% of the total diameter. In theory, polyaniline at 12 wt% will take up 30% of the total volume of a coated barite particle, assuming commercial PANI has a density of 1.3 g/cm³, commercial barite has a density of 4.1 g/cm³, and a homogeneous coating is produced. Assuming spherical particles and homogeneous coating, this coating will account for approximately 11% of the diameter of the coated particle, which is reasonably close to the measurement by TEM of PANI/B-5. It should be noted that this ratio of coating thickness and particle diameter should remain constant for all particle sizes as long as the density of coating and the amount of polymer remains constant. Additionally, due to the wide
distribution of particles, the coating does not significantly increase the size
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Figure 2.1 – Admittivity of oil and OBM s containing PANI and HSPAN coated B-
5 and B-55
Figure 2.2 – Admittivity of PANI/B-55 containing OBM at pH 1, 4, and 9.
Figure 2.3 - Admittivity of OBM's with HSPAN/B-5 materials as weighting agents with varying pH of internal aqueous phase.
Figure 2.4 – Admittivity of OBM with PANI/B-5 materials as weighting agents with varying pH of internal aqueous phase.
Figure 2.5 – TGA curves of three polyaniline-coated barite samples in argon. Polyaniline content is 11-12 wt% in each sample.

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Figure 2.8 – (left) TEM image of PANI/B-5 particle
Figure 2.9 – Volume-weighted particle size distribution of (a) B-55, (b) PANI/B-55, (c) B-5, and (d) PANI/B-5.

Weighting Agent   Volume Weighted Diameter  Coating thickness
PANI/B-5           10 µm                      ~ 1 µm
PANI/B-55          78 µm                      ~ 8 µm

Table 2.1 – Volume-weighted average size and estimated coating thickness of coated weighting agents from volume-weighted average size.
Chapter 3

Microwave Heating of Functionalized Graphene Nanoribbons in Thermoset Polymers for Wellbore Reinforcement

Adapted from Metzger A., et al. ACS Appl. Mater. Interfaces 2016, 8, 12985–12991. I performed the microwave heating experiments, the infiltration and initial reinforcement experiments, Nam Dong Kim performed the final reinforcement experiments, and Vahid Hejazi performed the mechanical tests.

3.1. Introduction

Wellbore reinforcement in oil and gas recovery has received considerable attention over the last two decades since wellbore instability can lead to substantially higher drilling costs.18,19 Microfractures present in the rock formation are a common cause of severe wellbore instability because drilling fluid seeps into
these fractures thereby inhibiting the stabilizing effect of the drilling fluid overbalance and also reducing borehole pressure integrity by forcing fractures even further apart.\textsuperscript{20-22} Therefore, there has been a great deal of effort to stabilize wellbores and prevent fluid loss by using additives such as mica, calcium carbonate, gilsonite and asphalt to seal microfractures.\textsuperscript{23} However, these attempts have not been widely implemented since the size of conventional additives do not match that of the porous formation and they are far too slow in sealing microfractures. It is therefore recommended that deformable additives be developed with a broad size distribution capable of quickly sealing a wide-range of microfracture openings at an effective concentration that does not adversely affect the functional properties of the drilling fluid.\textsuperscript{23}

Carbon nanomaterials have been used as additives for mechanical reinforcement of polymers and have recently shown that they penetrate through porous media.\textsuperscript{24,25} Specifically, carbon nanotubes (CNTs) have been explored as polymeric reinforcements due to their small size, high Young’s modulus, high tensile strength, and low percolation threshold.\textsuperscript{26-32} Another remarkable property of CNTs is that they are highly efficient microwave absorbers.\textsuperscript{32-38} Although the precise mechanism of CNT microwave interaction is poorly understood, nanotubes generate intense heat that could be used in a thermoset polymer for rapid curing at much lower microwave powers than those currently used in microwave assisted polymer curing (~900 W).\textsuperscript{39-42} However, concerns over their toxicity as well as problems in preparing homogeneous CNT dispersions have plagued their commercial deployment.\textsuperscript{42,43} Alternatively, graphene nanoribbons (GNRs), which are ribbon-like
graphene made from chemically unzipping CNTs\textsuperscript{44} are now being considered for use as polymer reinforcements due to their remarkably low percolation threshold, high load transfer capability, and low toxicity\textsuperscript{45-47}.

This paper shows a proof of concept for wellbore strengthening by microwave heating functionalized GNRs dispersed in an oil based thermoset polymer to rapidly crosslink the matrix and thereby increase its mechanical resilience within sandstone. Polypropylene oxide (PPO) functionalization of the GNRs not only increased their dispersibility in the oil based drilling fluid, but also increased the amount of heat released by the GNRs under microwave irradiation, likely due to their superior dispersion. The temperature of the PPO-GNR polymer suspension dramatically increased above 200 °C within minutes under very low microwave power (30 W). The intense, localized heat from the PPO-GNRs cured the polymer within a short period of time producing both enhanced reinforcement and mechanical integrity of sandstone due to the improved load transfer characteristics from the microwave curing process. This method not only provides a simple and cost effective way to prepare reinforced composites of polymer and carbon nanomaterials, but also may be useful in extreme downhole conditions provided that there is a microwave source tool following the drill head.

3.2. Results and Discussion

Our first goal was to synthesize GNRs that were soluble in an organic phase and aqueous phase, since both types of drilling fluids are used in industry. As
prepared, GNRs have protons at the edges and showed poor dispersibility (Figure 3.1) in both water and Escaid™ 110 (a commercially available mineral oil based drilling fluid). However, GNRs functionalized with PPO emanating from their edges showed good dispersion in both water and Escaid™ 110 (Figure 3.2a, Figure 3.1). Thermogravimetric analysis (TGA) showed gradual weight loss between 200-400 °C due to the decomposition of PPO (Figure 3.2b) thus confirming that 20% (20%-PPO-GNR) and 40% (40%-PPO-GNR) of PPO was functionalized on the GNR surface depending on the synthesis method. The presence of PPO was confirmed by Fourier transform infrared (FT-IR) analysis (Figure 3.2c) with a characteristic peak at 2950 cm⁻¹ indicative of C-H stretches. Raman spectroscopy (Figure 3.2d) showed that the D/G ratios (0.48, 0.61, 0.84 for GNR, 20%-PPO-GNR, and 40%-PPO-GNR, respectively) increased with the amount of PPO functionalization due to the increased C-sp³ content.

Before making a polymeric composite with PPO-GNRs, a suitable thermoset polymer should be selected that is readily available for curing at moderate temperatures. In addition, there are several criteria that must be considered in order to be an adequate thermoset polymer for downhole applications. First, polymerization needs to be done very quickly before fluid loss occurs thus reactive species are required. Second, the polymer should have a relatively high curing temperature to ensure that the high inherent temperature conditions (~70 °C) in the wellbore do not prematurely result in crosslinking. Third, it must be inexpensive. And finally of low toxicity.
Given these selection criteria, we chose 1,2-polybutadiene (1,2-PBD) and ethylene glycol dimethacrylate (EGDMA) as the polymer backbone and crosslinking monomer, respectively (Figure 3.3a and Figure 3.4). A cross linking polymer stock solution (Figure 3.3b) was prepared by mixing 1,2-PBD/EGDMA into Escaid™110 (mineral oil solvent) which could then be heat cured in a 200 °C oven producing a rigid white polymer block. Differential scanning calorimetry (DSC) showed a sharp exothermic characteristic at 150 °C arising from its phase transition during curing (Figure 3.3c).

Figure 3.5a illustrates the microwave waveguide and in situ temperature monitoring system used in our microwave assisted polymer curing experiments. Figure 3.5b shows the heating profile of GNRs alone and PPO-GNRs with increasing amounts of PPO, but a fixed amount of GNRs (0.5 w/v%) in the polymer stock solution. The polymer/GNR suspension slowly heats under microwave exposure and did not increase in temperature to > 120 °C. However, PPO-GNRs show a much faster heating rate with an increase in temperature up to 200 °C within 10 min. 40%-PPO-GNR showed higher heating rates than 20%-PPO-GNR presumably due to the higher dispersibility in the oil-based polymer solution. However, extremely rapid heating and very high temperatures of the polymer may not be good for curing because it may decompose the polymer or induce excessive outgassing from the composite making it a porous structure. Therefore, further experiments were conducted using different amounts of 20%-PPO-GNR to optimize the process. The polymer stock solution itself did not display any significant microwave heating nor did the addition of a small amount of PPO-GNR (0.1 w/v%) significantly affect its
heating rate (Figure 3.5c). But since 1 w/v% of PPO-GNR heated rapidly to very high temperatures that could damage the polymer backbone, 0.5 w/v% of the 20%-PPO-GNR stock solution was selected for further mechanical testing.

Figure 3.6a schematically illustrates the process we used to infiltrate a block of porous sandstone with polymer/PPO-GNRs for microwave curing (SPG-M is designated for sandstone polymer-GNR microwave). Vacuum infiltration was used to drive the polymer/PPO-GNRs into the porous sandstone as a mimic for the pressured infiltration of a wellbore environment. A center cut section of the SPG-M showed numerous white spots that are not naturally present (Figure 3.6b). Scanning electron microscopy (SEM) of SPG-M shows that the polymer and PPO-GNRs form thick film-like structures on the sandstone surface (Figure 3.6c). In the cross-section of the SPG-M, we observed PPO-GNR strands attached onto the sandstone wall which confirms successful infiltration of the stock polymer/PPO-GNR solution (Figure 3.6d). The carbon/oxygen ratio inside the sandstone increased from 0.21 to 0.72, before and after polymer/PPO-GNRs infiltration, respectively (Figure 3.7), indicative of infiltration of noncarbonate carbon. Elemental mapping of the sandstone using energy dispersive X-ray spectroscopy (EDS) shows the polymer and carbon nanomaterials were throughout the sandstone (Figure 3.6e) as further confirmation that the sandstone and polymer composite structure had been successfully prepared.

Figure 3.8 shows the ensemble mechanical properties from the compression experiments on the polymer-infiltrated sandstone. The compression system using
the parallel bottom and top platens to apply uniaxial force develops a rather complex system of stresses due to the end restraints by the platens. However, due to Poisson's effect, the samples all undergo lateral expansion which results in creating cracks and eventually leads to failure of the samples (Figure 3.7). To compare the properties of SPG-M, several control samples were prepared using a convective oven to cure the materials. These control sandstone samples SP-O and SPG-O were cured in an oven without and with PPO-GNRs, respectively (O refers to oven-cured). By comparing these materials, the effect of either the addition of PPO-GNRs or microwave assisted polymer curing on the mechanical performance reinforcement was investigated.

Addition of polymer alone inside the sandstone increased the maximum compressive strength of the sandstone from 5.8 MPa to 8.4 MPa (Figure 3.8a,b). This agrees well with the common intuition about such rock-type materials wherein the lower the porosity, the higher the compressive strength. However, with addition of PPO-GNRs, the maximum compressive strength of the SPG-M sample increased even higher to 11.3 MPa. Assuming equivalent porosities for oven cured sandstones infiltrated by polymer alone (SP-O) or polymer/PPO-GNRs (SPG-O), the ~35% increase in the compressive strength of SPG-O compared to SP-O is likely due to 1) the reinforcing effect of GNRs, which strengthen its surrounding matrix, and 2) the high thermal conductivity of the GNRs, which causes more adequate and rapid curing of the polymer in SPG-O compared to SP-O, resulting in a more efficient high-strength adhesive bonding between polymer and sandstone. More impressive enhancement in reinforcement can be found in SPG-M, where the maximum
compressive strength of SPG-M (13.3 MPa) increased more than 130 % compared to that of pure sandstone, and is even ~18% higher than that of SPG-O, the oven cured equivalent.

Such a strong reinforcement in SPG-M can be understood by comparing microwave assisted heating to convective heating of the polymer in SPG-O. In the oven-heated thermoset polymer, GNRs are just one part of a physical mixture inside the composite. Due to the low thermal diffusion through the sandstone and also through the non-uniformly distributed pores filled by polymer, heat cannot be homogeneously transferred to the GNRs dispersed in the polymer. However, with microwaves, each GNR absorbs microwave energy independently and acts as a nanoscale heat generator with local temperatures that are high enough to thoroughly cure the surrounding polymer. Moreover, since the GNRs generate heat to induce polymerization, it can be assumed that the interface between the GNR and polymer has greater van der Waals interactions and will provide a more effective load transfer for stronger reinforcement than SPG-O. It could also be that the polymer chains added into the planes of the GNRs, but that was not confirmed here.

Furthermore, we know that GNRs toughen related polymers. Here, the total toughness of the SPG-M (28.5 GPa) was ~1.6x higher than that of SPG-O, and also ~6x greater than that of pure sandstone (4.9 GPa) (Figure 3.8c). Toughness is defined as the amount of energy a material absorbs before failure (representing the work-of-fracture), which is different from the classical “fracture toughness” with the unit of $P_a\sqrt{m}$. The work-of-fracture is the area under the stress–strain curve, which
is deeply affected by gradual, “graceful fracture”, whereas the fracture toughness does not incorporate this entire process.\textsuperscript{46}

To investigate the micromechanics of the samples and to study the microstructural reinforcement effects of GNRs, a matrix-based algorithm was developed to conduct hundreds of indentations on the surface of the samples in order to directly obtain the mechanics of individual phases of the samples. The nanoindentation measurements were conducted by indenting 100 spots in a 10x10 matrix form using a Berkovich tip with a size of \(\sim 50\) nm which allowed us to investigate the mechanical properties of the composite structure on both the nanometer and micrometer scales. Figure 3.9a,b shows the surface of the SPG-M sample before indentation. Some imprints (triangles) of the indentation on the sample surface can be seen in Figure 3.9c after unloading.

From the control experiments for the polymer and sandstone, the hardness value (which relates to strength) was found to be 30 MPa for the polymer alone, and over 1000 MPa for the sandstone alone (Figure 3.9d inset). Therefore, to compare the mechanical reinforcement contribution of the polymer, hardness values larger than 1000 MPa were excluded from further analysis as they would correspond to the sandstone alone and not the cured polymer/PPO-GNRs. As GNRs were introduced to the polymer in the SPG-O, the hardness of the polymer was increased up to 180 MPa. However, for SPG-M, hardness values were > 200 MPa with values ranging from 200 to 900 MPa (Figure 3.9d). The variation is due to the localized grid-like indented spots, which may or may not be in the vicinity of the GNRs.
Nevertheless, the average hardness (~600 MPa) of all these spots in SPG-M is significantly higher than the average hardness of SPG-O (~100 MPa). Considering the measurement capabilities of nanoindentation (50 nm tip size and ~10 μm distance between the indentation spots), our results show the enhanced mechanical properties of SPG-M are mainly due to the strong-interaction between GNRs and the polymer, which improves the cross-linking and mechanical integrity of the polymer upon microwave irradiation. The elastic modulus of the samples was also calculated using the load-displacement curves (inset of Figure 3.9e). All P-h curves in this figure showed smooth shapes and no pop-in behavior could be detected. The lower displacement of the SPG-M at the peak force indicates the higher hardness of this sample, compared to SPG-O/SP-O, resulting in lower material deformation. SPG-M also showed a highly enhanced elastic modulus compared to SPG-O owing to the incorporation of stiff GNR fillers into the polymer chains resulting in a stiffer composite material (Figure 3.9e). These results indeed demonstrate that microwave assisted polymer curing in the presence of carbon nanomaterials can be a highly efficient for structural reinforcement.

3.3. Conclusions

In summary, we demonstrated that the use of GNRs as highly efficient fillers in polymers, combined with microwave-assisted localized heating, results in the significantly improved mechanical properties of polymer reinforced sandstone. Systematic investigation of the mechanical properties (e.g. strength, toughness, and stiffness) of the polymer-reinforced sandstone at multiple length scales suggests
that the interaction of carbon nanomaterials with a polymer matrix provides enhanced reinforcement even with a very low amount of carbon filler. Finally, while we showcased the benefits of this approach in the context of enhancing the mechanics of porous sandstones and wellbore reinforcements, the concepts and strategies of this work, especially the use of low power microwave energy, can be easily applicable to a variety of porous materials and extreme conditions such as those found underground or in outer space. Although this study focused on using GNRs, alternative graphitic materials that are microwave responsive can be explored.

Since GNRs are produced commercially from unzipping of MWCNTs, materials synthesis process could be readily applicable and their price will of course be tied to the cost of MWCNTs since that is the source.

Figure 3.1. Comparison of the dispersibility GNRs and PPO-GNRs. (1) GNR in water, (2) GNR in Escaid™110, (3) PPO-GNR in water, and (4) PPO-GNR in
Escaid™110. Vials were shaken and permitted to settle for 1 day before photographing.

Figure 3.2 – (a) Synthesis of PPO-GNRs from MWNTs. Only one tube within the MWNT is represented. Characterization of GNRs and PPO-GNRs by (b) TGA, (c) FT-IR, and (d) Raman.
Figure 3.3 – (a) Chemical structures of the polymer and crosslinker. (b) Image of the thermoset polymer stock solution before and after curing in an oven at 200 °C. (c) DSC characterization of the polymer solution and polymer/PPO-GNRs suspension.
Figure 3.4. Pictures of thermally cured mixture of 1,2-PBD with different (meth)acrylates. We confirmed that di(meth)acrylates could successfully cure 1,2-PBD producing a solidified monolith, while mono(meth)acrylates do not polymerize into solid products.
Figure 3.5 – Microwave-assisted curing of polymer/PPO-GNR suspensions. (a) Illustration of the microwave-assisted polymer curing system using a waveguide and an \textit{in situ} temperature monitor with a photograph of the polymer/PPO-GNRs suspension before and after microwave curing. (b) Microwave heating profile of GNR, 20%-PPO-GNR, and 40%-PPO-GNR suspensions. (c) Microwave heating profile of the polymer/PPO-GNR suspension containing different amounts of 20%-PPO-GNR.
Figure 3.6 – (a) Experimental scheme for preparation of microwave-cured polymer/PPO-GNR infiltrated sandstone (SPG-M). (b) Photograph of the cross-section of SPG-M. The black squares, 1 and 2, correspond to SEM images (c) and (d), respectively. (e) SEM image of the inside of SPG-M and corresponding EDS elemental mapping of Si, O, and C.

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Table 3.1. EDS analysis results for starting sandstone, and polymer/PPO-GNRs infiltrated sandstone. Atomic % of each element was summarized in the table. Carbon background signal for starting sandstone could be found as ~13%. The signal for carbon inside the sandstone, after polymer/PPO-GNRs infiltration, increased to ~36%.

![Image of sample before and after compression mechanical testing.](image)

**Figure 3.7** – SPG-M sample before and after compression mechanical testing.

![Image of stress vs strain plot, maximum compressive strength, and toughness.](image)

**Figure 3.8** – Compression mechanical tests of sandstone alone and polymer/PPO-GNRs infiltrated sandstones cured either by convective oven or microwaves. (a) Stress vs strain plot, (b) maximum compressive strength, and (c) toughness. Note: SP = sandstone infiltrated with polymer alone, SPG = sandstone infiltrated with polymer/PPO-GNRs, O = oven cured, and M = microwave cured.
Figure 3.9 – Nanoindentation test for the effect of microwave-assisted cured polymer on mechanical enhancement. (a) Optical image of the SPG-M sample before indentation experiments. Enlarged images (b) before and (c) after indentation. A part of the 10x10 matrix of indentation imprints (triangles) can be seen in (c). (d) Hardness values from nanoindentation experiments for polymer alone, SPG-O, and SPG-M. Inset shows difference of hardness between polymer and sandstone. (e) Elastic modulus value from the nanoindentation experiments for polymer, SPG-O, and SPG-M.
Figure 3.10 – Schematic illustration of microwave curing system equipped with a waveguide and *insitu* temperature monitor. ① Microwave power generator with transmitted and reflected power meters. ② Coaxial cable antenna (E-field directed horizontally to eliminate thermocouple heating), ③ Waveguide (intensity of microwave is highest in the middle of the waveguide), ④ Thermocouple with PTFE insulator (shielded and ungrounded), ⑤ Cuvette with polymer/PPO-GNR suspension, ⑥ Glass vessel filled with water to absorb transmitted microwaves (minimize reflection at the end of the waveguide), ⑦ Microwave oven chassis functions as a shield (enclosed power supply is disabled).
Figure 3.11 – Representative trapezoidal loading and force versus time plot of the nanoindentation experiment.
Figure 3.12 – Microwave heating of multiwalled carbon nanotubes (MWCNT), PPO-GNRs, thermally expanded graphite, carbon black, and activated carbon in Escaid™ 110 under 30 W at 1 w/v%
4.1. Introduction

Graphene quantum dots (GQDs) are nanocrystalline sp\(^2\) carbon sheets that exhibit size-dependent photoluminescence in the visible region.\(^{51-52}\) Though GQDs are being considered for a variety of applications, including phosphors,\(^{53-54}\) photovoltaics,\(^{55-56}\) and biologically compatible fluorescent probes,\(^{57-58}\) most synthetic methods are both laborious and costly. Bottom-up methods of producing GQDs usually involve carbonizing a precursor, which can be as complex as hexa-peri-hexabenzocoronene\(^{59}\) or as simple as glycerol\(^{60}\) or citric acid.\(^{61}\) With more
complex precursors, narrow particle size distributions can be obtained at the cost of the multistep synthesis required to prepare the precursor, while simpler precursors are more commercially available but produce GQDs with broader size range.\textsuperscript{59,60} Top-down syntheses of GQDs include the cutting of graphitic materials via expensive electron beam lithography\textsuperscript{62} or chemical oxidation. GQDs have been prepared from the mixed acid oxidation of carbon fiber,\textsuperscript{52} graphene oxide,\textsuperscript{63} carbon nanotubes,\textsuperscript{64} and the electrochemical exfoliation of graphite.\textsuperscript{65} These reactions typically result in low mass yields and low quantum yields. Our group recently developed a cost-effective method that utilized coal as the graphitic starting material for GQD synthesis.\textsuperscript{66} However, even though coal is quite inexpensive, at $60/ton,\textsuperscript{67}$ the scalability of using the mixed nitric-sulfuric acid method has been limited due to the possibility of polynitrated arenes, and the required large volume neutralization of concentrated mixed acids.\textsuperscript{68,69} We report here a rapid, scalable method for the synthesis of GQDs by eliminating the need for sulfuric acid and using nitric acid alone. This minimizes the production of polynitrated arenes, and it also permits removal of the acid after the reaction by simple rotary evaporation. Moreover, following hydrothermal treatment, the GQDs attain a quantum yield (QY) of 10%. Other groups have reported syntheses of GQDs using dilute nitric acid, but have not removed small molecules, taken advantage of nitric acid’s volatility and/or have not produced a high quantum yield material.\textsuperscript{60,71} Additionally, GQDs can be synthesized from biochar, a renewable coal substitute.
4.2. Results and Discussion

Scheme 1 illustrates the simplified, high-yield process for synthesizing GQDs using nitric acid. In the context of mixed acid reactions, the purpose of sulfuric acid is to increase the oxidizing power and nitrating ability of the reaction. Removal of sulfuric acid is complicated by its high boiling point (337 °C). Because nitric acid can be evaporated (boiling point 121 °C for 70%), it can be recycled instead of being quenched, making desalting much faster due to the much lower concentration of salts formed upon evaporation. Additionally, the mass yield of GQDs is 50% higher than our previously reported method. The mixed acid method produces GQDs in 20% mass yield and treated GQDs in 10% mass yield. This nitric acid method produces GQDs in 30% mass yield and treated GQDs in 13% mass yield.

Figure 4.1 shows transmission electron microscope (TEM) images of GQDs derived from either anthracite coal or biochar and their size after treatment with NaOH and NaBH₄. Figure 4.2 shows that nitric acid oxidation of anthracite coal yielded GQDs with a size distribution between 2 to 30 nm. Figure 4.1a shows that the 1-3 kDa fraction of this mixture is from 2 to 15 nm. Figure 4.1b-c shows that treatment of anthracite coal derived GQDs with NaOH and borohydride showed no significant change in their size distribution. Similarly, as shown in Figure 4.1d-f, biochar derived GQDs were equivalent in size distribution to anthracite derived GQDs and the size distribution was not affected by NaOH or borohydride treatment.

However, we found that hydrothermal NaOH treatment increased the photoluminescence quantum yield (PLQY) of anthracite derived GQDs from 0.2% to
10% and blue shifted their emission, as shown in Figure 4.3a-b. Figure 4.3b-c shows that treatment with NaBH₄ narrows the GQD emission from blue-green to blue, despite not increasing the PLQY. Figure 4.3d-f shows that the photoluminescence (PL) shifts of biochar GQDs with post treatments are similar to those of anthracite. A noticeable difference is the lower PLQY of the biochar GQDs (0.5%, 2% and 5% for as-produced, NaOH-treated, and NaBH₄-treated, respectively). The origin of this lower QY is unknown.

In our previous report,⁷⁰ we improved the QY of GQDs to 10% with hydrothermal NaOH treatment, without characterization. Figure 3 shows the high-resolution carbon XPS spectra of both anthracite and biochar GQDs, containing many oxygen functionalities. Figure 4.4a-b demonstrates that after NaOH-treatment, anthracite GQDs show a decrease in carboxylic acid content. Figures 4.4b-c show a reduction of carbonyl content, which is expected from treatment with NaBH₄. Figures 4.4d-e show that biochar GQDs also show a decrease in carboxyl content, and Figures 4.4e-f showing a decrease in carbonyl content. Raman spectra of size-selected GQDs show G and D bands similar in size (see Figure 4.5). Upon NaOH and NaBH₄ treatment, the G/D ratio increases, indicative of healing the defects in the basal plane of the GQD. The changes in the Raman spectra of biochar GQDs are similar to those of the Raman spectra of anthracite GQDs.
4.3. Conclusions

In summary, the oxidative synthesis of GQDs from carbon materials has been improved by eliminating sulfuric acid. The lack of sulfuric acid allows the evaporation of nitric acid and avoids quenching concentrated acids. Size separation and post-treatments yield GQDs with PLQYs up to 10%. The method has also been extended to biochar as a starting material, yielding GQDs with PLQYs up to 5%. We plan to apply this new process to other inexpensive carbon materials to obtain higher PLQYs.

4.4. Experimental Details:

4.4.1. Synthesis of GQDs.

Anthracite coal (5 g) was added to a round-bottom flask equipped with a stir bar and mixed with 90 mL of 70% HNO$_3$. The reaction mixture was heated to reflux (120 °C) while stirring for 17 h and then allowed to cool to room temperature. The mixture was filtered through a fine glass frit and the HNO$_3$ was removed via rotary evaporation. Aqueous dialysis was performed against a 1 kDa membrane for 1 day. Evaporation of the retained solution resulted in 1.5 g of brown-red powder (30% yield). Size-selection by crossflow filtration was conducted as described previously. Hydrothermal NaOH treatment was performed by adding 400 mg of the prepared GQDs to a stainless steel autoclave with 20 mL of 0.5 M NaOH. The solution was
heated at 200 °C for 24 h and allowed to cool to room temperature. The GQDs were then further reduced by adding 1.2 g of NaBH₄ to the GQDs in the NaOH solution and allowing the reaction to occur under ambient conditions for 2 h. The solution was filtered to remove precipitated solids before being neutralized with 0.1 M HCl, then diluted with deionized water, and finally dialyzed using crossflow filtration. After rotary evaporation, a brown powder was obtained (650 mg).

4.4.2. Characterization of GQDs.

Transmission electron micrographs (TEM) were collected using a JEOL JEM 2100F. Elemental analysis was performed with a Phi Quantera X-ray photoelectron spectrometer. Photoluminescence spectra were collected with a Jobin-Yvon Horiba Nanolog spectrometer. QY were obtained relative to quinine sulfate in 0.5 M H₂SO₄ (350 nm excitation). Raman spectra were obtained with a Renishaw microscope with 514 nm excitation.
Figure 4.1 - TEM images of GQDs derived from anthracite (top row) and biochar (bottom row). (a) Untreated anthracite derived GQDs, (b) NaOH-treated anthracite GQDs, (c) NaBH₄-treated anthracite GQDs, (d) biochar derived GQDs, (e) NaOH-treated biochar GQDs, (f) NaBH₄-treated biochar GQDs. Scale bars 20 nm.
Figure 4.2 – TEM images of GQDs; a) as-produced anthracite, b) as-produced biochar before size-separation.

Figure 4.3 – Excitation-emission matrix of GQDs. (a) untreated anthracite, (b) NaOH-treated anthracite, (c) NaBH₄-treated anthracite, (d) untreated biochar, (e) NaOH-treated biochar, (f) NaBH₄-treated biochar.
Figure 4.4 - XPS of GQDs. (a) untreated anthracite; (b) NaOH-treated anthracite; (c) NaBH₄-treated anthracite; (d) untreated biochar; (e) NaOH-treated biochar; (f) NaBH₄-treated biochar.

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Table 4.1. Percent composition of anthracite derived GQDs functional groups based on XPS analyses.
Binding Energies

GQDs: 284.80 eV (C-C/C=C), 286.01 eV (C-OH), 288.13 eV (C=O), 289.87 eV (-COOH)

NaOH-treated GQDs: 284.80 eV (C-C/C=C), 286.12 eV (C-OH), 288.24 eV (C=O), 289.27 eV (-COOH)

NaOH- and NaBH₄-treated GQDs: 284.80 eV (C-C/C=C), 286.22 eV (C-OH), 288.21 eV (C=O), 288.75 (-COOH)

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Table 4.2: Percent composition of biochar derived GQDs based on XPS analyses.

Binding Energies

GQDs: 284.80 eV (C-C/C=C), 286.15 eV (C-OH), 287.42 eV (C=O), 288.96 eV (-COOH)

NaOH-treated GQDs: 284.80 eV (C-C/C=C), 286.01 eV (C-OH), 287.70 eV (C=O), 288.73 eV (-COOH)

NaOH- and NaBH₄-treated GQDs: 284.80 eV (C-C/C=C), 286.06 eV (C-OH), 287.62 eV (C=O), 288.69 (-COOH)
Figure 4.5 – Raman spectra of GQDs; a) untreated anthracite; b) NaOH-treated anthracite; c) NaBH₄-treated anthracite; d) untreated biochar; e) NaOH-treated biochar; f) NaBH₄-treated biochar.
Chapter 5

Singular Wavelength Dependence on the Sensitization of Lanthanides by Graphene Quantum Dots: an Exception to the Kasha-Vavilov Rule?

Special thanks to Meredith McDowell from Dr. Angel Marti’s research group, who contributed significantly to this work, including lifetime measurements, time-resolved spectra, and ligand studies. I prepared the two GQD samples and performed the initial data acquisition for the steady state PL spectra of GQD, Tb$^{3+}$, and Tb@GQD.

5.1. Introduction

Graphene quantum dots (GQDs) are nanoparticles which are structurally similar to small graphene nanoflakes. Similar to inorganic quantum dots, GQDs exhibit bright fluorescence upon light irradiation where their emission wavelength
shows an hypsochromic shift with decreasing particle size. Our group has previously reported a synthesis of GQD from coal, making this material water soluble and affordable for mass production. These GQDs do not show a shift in emission with change in excitation, which is common in many carbon dot preparations containing a wide variety of different particles sizes. The top down synthesis leads to some heterogeneity within each sample and therefore wide absorption and emission bands are obtained. Sorting of GQD by size show different emission wavelengths that are characteristic of their size. This property makes GQDs suitable candidates for antennae in solar cells, bioimaging and sensing applications.

5.2. Results and Discussion

Rare earth elements are reveled for their distinct photophysical properties. Spin forbidden f-f* excitations have low extinction coefficient and long phosphorescence lifetimes. Because the f orbitals are shielded and interact very little with ligands, their spectral bands are very sharp (10 nm wide). These traits lead to their use in solid state lasers and as imaging agents. Terbium(III) (Tb\(^{3+}\)), frequently doped into the YAG crystal, has an \(^5\)D\(_4\) excited state which decays down to the \(^7\)F ground state with strongest emissions at ca. 489 nm, 544 nm, 584 nm, and 621 nm. Tb\(^{3+}\) salts have low extinction coefficients and require ligands with accessible triplet states to sensitize their emission, although singlet sensitization has been claimed in certain cases.
In this chapter, the sensitization of the rare earth Tb\(^{3+}\) cation by GQDs will be explored. There have been reports of indium oxide quantum dots sensitizing europium(III)\(^{82}\); however, to our knowledge this is the first report of GQDs being used to sensitize rare earth cations. Blue-GQDs (bGQDs) were obtained from liberating coal nanodomains naturally present in coal using chemical oxidation, and they can contain a variety of functional group on their surface such as carboxylic acids, sulfates, nitrates, and hydroxyl groups, which can potentially bind lanthanide cations. We expect GQDs to have a dual function: (1) act as polydentate ligands binding the lanthanide cations and (2) transfer energy to the lanthanide excited states resulting in long-lived lanthanide PL. The excitation and emission photoluminescence spectrum of bGQDs is presented in Figure 5.1a. As is typical for bGQDs, the emission spectrum shows a broad peak with a maximum of ~435 nm. Addition of different concentrations of TbCl\(_3\) to bGQDs led to the appearance of new peaks in the photoluminescence spectrum that are consistent with the \(5\,D \rightarrow 7\,F\) emission bands of Tb\(^{3+}\) at ca. 489, 544, 584 and 621 nm (Figure 5.1b). These conjugates of bGQDs and Tb\(^{3+}\) were called Tb@bGQDs. The initial excitation wavelength was chosen at 330 nm, which is far from the weak absorption peak of Tb\(^{3+}\) in the ultraviolet (Figure 5.2). Still, while the Tb\(^{3+}\) cation shows a shoulder from 230-300 nm (Figure 5.2) it only shows low intensity emission unless coordinated to a photosensitizer ligand. Plotting the area corresponding to Tb\(^{3+}\) PL as a function of Tb\(^{3+}\) concentration shows that maximum PL is obtained at ~3 \(\mu\)M Tb\(^{3+}\), (although concentrations from 1 to 10 \(\mu\)M still yield quite acceptable PL) with a decrease in PL with increasing Tb\(^{3+}\) concentration (Figure 5.1c). A similar behavior has been
observed for Tb\(^{3+}\) incorporated in poly(vinyl pyrrolidone) and have been attributed to microscopic Tb\(^{3+}\) aggregates where efficient intermolecular energy transfer occurs leading to quenching.\(^{83}\) Control experiments with the same concentrations of Tb\(^{3+}\) in water as in Figure 1b lead to no noticeable photoluminescence (Figure 5.1d), which confirms that bGQDs are photosensitizing Tb\(^{3+}\) \(5\)D excited state. To probe whether this photosensitization is due to an intra or intermolecular energy transfer process, we added ethylenediaminetetraacetic acid (EDTA) to Tb@bGQDs (Figure 5.3). EDTA is a strong chelating agent and is expected to bind more strongly to Tb\(^{3+}\) than bGQDs, stripping the lanthanide cation from the surface of the bGQDs. Addition of EDTA to Tb@bGQDs causes an immediate disappearance of the Tb\(^{3+}\) PL, and the complete recovery of the bGQDs PL (Figure 5.3), which proves that binding of Tb\(^{3+}\) to bGQDs is a requirement for photosensitization to take place, and thus the sensitization reaction is intramolecular. Moreover, we observed that the PL of the bGQDs decreases with increasing Tb\(^{3+}\) concentration (Figure 5.1b). This is likely related to quenching of bGQDs by the heavy paramagnetic Tb\(^{3+}\) cation, probably by promoting intersystem crossing to the triplet state. A similar behavior is observed when bGQDs are titrated with Gd\(^{3+}\) (Figure 5.4), which is a paramagnetic rare earth with a similar size to Tb\(^{3+}\), but that does not have low-lying energy levels (below 32,000 cm\(^{-1}\)) that can be sensitized by bGQDs.\(^{84}\)

Sensitization of Tb\(^{3+}\), commonly occurs from the population of a triplet state of the photosensitizer, following by energy transfer to the \(5\)D\(_{4}\) excited state level of Tb\(^{3+}\) (at 20,400 cm\(^{-1}\)). Nonetheless, other reports have stated that, in certain cases, the singlet excited state of the sensitizer has a big role in the population of Tb\(^{3+}\).
excited states. To assess this, we performed steady-state PL experiments in air and with samples purged with nitrogen. Samples of Tb@bGQDs purged with nitrogen present almost twice the PL from Tb$^{3+}$ than samples in air (Figure 5.5). This enhanced Tb$^{3+}$ emission when oxygen (a triplet state quencher) is excluded from the system strongly indicates that triplet states from bGQDs are central to the photosensitization of Tb$^{3+}$.

The excited state lifetime of bGQDs is presented in Table 5.1. The PL lifetime of bGQDs purged with nitrogen at 435 nm is 3.3 ns, which is consistent with the decay lifetime from a short-lived singlet-state. Experiments in a frozen matrix of ethanol/methanol (77K) did not show new peaks or shifts, nor the appearance of a longer lifetime component. Nonetheless, the phosphorescence of triplet excited states is generally difficult to see even at 77 K, since the long-lived lifetime competes with non-radiative deactivation pathways. Furthermore, these triplet state could be dark states and invisible to fluorescence techniques. To evaluate the existence of triplet states in bGQDs, NIR photoluminescence experiments were performed to test for the presence of singlet oxygen. Triplet molecular oxygen can be converted into singlet molecular oxygen by energy transfer from a triplet photosensitizer. The phosphorescence spectrum for singlet oxygen was clearly observed at 1273 nm for bGQD and the known $^1$O$_2$ photosensitizer phenanelone, indicating that triplet states must be generated by the photoexcitation of bGQDs (Figure 5.6a and b). Notice that no emission at 1273 nm is observed in the sample purged with N$_2$ (Figure 5.6c). While triplet states are present in bGQD and contributing to Tb$^{3+}$ photosensitization,
this does not rule out that singlet states have some contribution to the
photosensitization of PL of Tb@bGQDs.

Time-resolved emission spectroscopy was used to obtain information about
the different components in Tb@bGQDs. As stated before, bGQDs have a short PL
lifetime of 3.3 ns (\(\lambda_{em} = 435\) nm) in aqueous solution and of 2.0 ns in Tb@bGQDs,
while Tb\(^{3+}\) (\(\lambda_{em} = 545\) nm) in Tb@bGQDs has a long PL lifetime of 533 \(\mu s\). These
differences in lifetimes are evident when the time resolved emission spectra (TRES)
are obtained for Tb@bGQDs (Figure 5.7). When the TRES spectra are obtained after
0.15 ms, all the background fluorescence from the bGQDs disappears displaying only
the features of Tb\(^{3+}\) phosphorescence. Additionally, the number of water molecules
can be calculated from the lifetimes of Tb@bGQDs in water and in deuterium oxide
following equation 5.1.\(^{86}\)

\[
q = A[\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}]
\]

Eq. 5.1 – Calculation of number of coordinated water molecules

The number of water molecules bound to Tb\(^{3+}\) in Tb@bGQDs is 5.5, which is
consistent with chelated coordination of the Tb\(^{3+}\) cation by bGQDs (Figure 5.8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\Phi_{\text{Tb}})</th>
<th>(\Phi_{\text{GQD}})</th>
<th>(\tau_{435\ nm})</th>
<th>(\tau_{545\ nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>bGQDs</td>
<td>-</td>
<td>0.09 ± 0.01</td>
<td>0.54 ± 0.01 ns</td>
<td>2.26 ± 0.03 ns</td>
</tr>
<tr>
<td></td>
<td>± 0.01</td>
<td>(20.48 %)</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
Table 5.1 Photophysical parameters for bGQD and Tb@bGQD. a) $\lambda_{\text{Ex}}$: 250 nm, $\lambda_{\text{Em}}$: 375 – 700 nm b) $\lambda_{\text{Ex}}$: 250 nm, $\lambda_{\text{Em}}$: 375 – 700 nm c) $\lambda_{\text{Ex}}$: 371 nm d) $\lambda_{\text{Ex}}$: 330 nm

The effect of excitation wavelength on the PL of Tb@bGQDs was also analyzed. A 3D plot showing the dependence of the photoluminescence as a function of the excitation wavelength for bGQDs, Tb@bGQDs and Tb$^{3+}$ in water are shown in Figure 5.9. All the spectra in the three panels were obtained and plotted with exactly the same parameters. It is immediately noticeable that the PL of bGQDs is quenched by the binding of Tb$^{3+}$. In addition, no appreciable photoluminescence is observed for the free Tb$^{3+}$ cation under the tested experimental conditions. The most remarkable observation is that the emission from Tb$^{3+}$ in the Tb@GQDs sample increases at shorter excitation wavelengths. Since we corrected spectra, knowing the emission quantum yields with excitation at 250 nm from Table 5.1, and correcting for the inefficiency of the lamp at different wavelengths, it is possible to calculate the quantum yields as a function of excitation (Figure 5.10). The quantum yield seems to be independent of wavelength for bGQDs (Figure 5.10a). This is
consistent with the Kasha-Vavilov rule: the PL quantum yield is independent of excitation wavelength.\textsuperscript{87} For Tb@GQDs, two emissions can be studied: the residual PL from bGQDs and the PL from Tb\textsuperscript{3+}. The quantum yield from the PL of bGQDs is lower due to the presence of Tb\textsuperscript{3+}, however it only shows slight variations with wavelength (Figure 5.10b), and in general it just looks similar to Figure 5.10a but with lower quantum yield. On the other hand, the PL from Tb\textsuperscript{3+} shows a strong wavelength dependence, showing a marked increase at shorter excitation wavelengths (Figure 5.10c). This increase is approximately an order of magnitude larger with excitation at 250 nm when compared with the PL exciting at 350 nm. Although the reason for this deviation from the Kasha-Vavilov rule is unclear, we propose that it is due to small aromatic fragments on the periphery of the GQD core (Figure 5.11) that could be directly participating in the photosensitization of Tb\textsuperscript{3+}. The GQDs studied here were prepared from a top-down approach by separating graphitic nanodomains present in coal using a chemically oxidative process; however, workup ensures that small aromatic moieties are not physiosorbed carboxylate carbonaceous fragments.\textsuperscript{88} These GQDs are soluble in water due to a variety of functional groups (e.g. hydroxyl, carboxyl, etc.) induced by the oxidation in \( \text{H}_2\text{SO}_4/\text{HNO}_3 \) used to liberate the GQDs from coal. Carefully controlling the reaction conditions and filtration through 1 and 3 kD membranes (see methods in Supporting information) lead to control in the size of the nanodomains, which then influence the color of the GQDs.\textsuperscript{70} It is expected that chemical oxidation creates defects that isolate small aromatic moieties that can then act as individual triplet sensitizers (see Figure 5.11). For example, small aromatic molecules such as 1,2,4,5-
benzenetetracarboxylic acid,\textsuperscript{89} 4-phenylenediacetate,\textsuperscript{90} p-aminobenzoic acid,\textsuperscript{91} 2,3-dihydroxynaphthalene,\textsuperscript{92} and 2,6-naphthalenedicarboxylic acid\textsuperscript{93} have been shown to photosensitize Tb\textsuperscript{3+} PL. Thus, it is possible that GQDs derived from coal are composed by a graphene core surrounded by a corona of small aromatic molecules (covalently attached to the GQD) capable of photosensitizing the PL of lanthanide ions such as Tb\textsuperscript{3+}. The presence of small aromatic groups derived from a large graphitic core has been observed previously in the synthesis of water-soluble ultra-short single-walled carbon nanotubes by strong oxidation process.\textsuperscript{88} These molecules are spectroscopically invisible either because they are weakly fluorescent, or because their fluorescence is quenched by the bGQD core by π stacking or some other mechanism. The absorption of these simple aromatic molecules increases in the blue part of the spectrum, which is consistent with the increased quantum yield of Tb\textsuperscript{3+} at shorter wavelengths. Binding of Tb\textsuperscript{3+} would promote intersystem crossing into the triplet state of many of these moieties, which are capable of photosensitizing Tb\textsuperscript{3+}.

To further explore the sensitization of Tb\textsuperscript{3+} by GQDs we used red-shifted GQDs (rGQDs), which have an emission maximum of 520 nm (Figure 5.12), and present a bathochromic shift of 85 nm from bGQDs. Interestingly, rGQDs show also sensitization of Tb\textsuperscript{3+} (Figure S7b) with maximum sensitization at 3 μM (5 μg/mL rGQDs concentration) (Figure 5.12c). Tb@rGQDs shows a short-lived rGQDs lifetime corresponding to rGQD as well as long lived lifetimes of 553 μs at 545 nm (Table 5.2). Similar to Tb@bGQDs, the quantum yield of emission for Tb\textsuperscript{3+} seems to
increase at shorter wavelengths, which can be easily observed in the 3D spectrum in Figure 5.13.

In conclusion, binding of Tb$^{3+}$ to GQDs displays a unique emission pattern consisting of the superimposition of the sharp Tb$^{3+}$ bands over the broad GQD emission. Binding occurs by the coordination of Tb$^{3+}$ to functional groups on the surface of GQDs such as carboxylic acids, which decorate the surface of the GQDs in solution granting them aqueous solubility. Excitation of the GQDs leads to the population of the singlet excited state, which decays to the ground state displaying fluorescence. Nonetheless, part of this singlet state undergoes intersystem crossing to the triplet state, which can sensitize Tb$^{3+}$ excited state. The emissive decay of Tb$^{3+}$ is spin-forbidden and thus long lived. The two emission signals can be separated in the TRES using time-resolve spectroscopy due to their very different lifetimes. Quantum yield experiments as a function of wavelength indicate that bGQDs does not follow the Kasha-Vavilov rule, with higher quantum yields at blue excitation wavelengths. We think the higher quantum yields at more energetic wavelengths come from small semi-discrete organic moieties surrounding the graphitic domain of GQDs, which are a byproduct of their top-down synthesis. To the best of our knowledge, this represents the first example of rare earth photosensitization using GQDs. This can have important implications in the design of photoluminescent sensors, labeling, and as unique anti-counterfeit dyes and inks.
5.3. Methods

Materials were purchased and used without further purification. Anthracite coal was purchased from Fisher-Scientific. Sulfuric Acid (98%) and nitric acid (70%) were purchased from Sigma Aldrich. Terbium chloride hexahydrate, 2,2'-bipyridal, sodium hydroxide, and sodium borohydride were purchased from Sigma Aldrich. A Krosflo MidiKros was used for all membrane filtrations. Spectral samples were purged with nitrogen for 20 min unless otherwise noted. UV-Vis spectra were taken on a Shimadzu UV-2450 spectrophotometer. Steady state excitation and emission spectra were taken on a Horiba JobinYvon NanoLog spectrophotometer. All time resolved emission spectra and decays were taken on an Edinburgh Instruments OB 920 using either a 920H microsecond flash lamp or a EPL375 picosecond pulsed diode laser.

5.3.1. Blue shifted GQD

Graphene quantum dots were synthesized similarly to the method previously published.\textsuperscript{46} Anthracite coal (2.0 g) was dispersed in concentrated sulfuric acid (60 mL). Nitric acid (70%, 20 mL) was slowly added to the dispersion. The mixture was heated to 100 °C and allowed to react for 24 h. After cooling to room temperature, the reaction mixture was quenched with NaOH. After filtration through a 0.2 uM mPES membrane, the resulting solution was subjected through cross-flow filtration through 1 and 3 kDa membranes, collecting the fraction retained by the 1 kDa membrane and that passes through 3 kDa. GQDs were isolated via rotary evaporation of the solvent. A 1 mg/mL solution of GQDs (20 mL) in 0.5 M NaOH was
added to a Teflon-lined stainless steel autoclave and was heated to 200 °C for 24 h. After cooling to room temperature, sodium borohydride was added, and the solution was stirred for 8 h at room temperature. Following dialysis (1 kDa membrane), blue-shifted GQDs were obtained after rotary evaporation.

5.3.2. Red shifted GQD

Graphene quantum dots were synthesized similar to the method previously published. Anthacite coal (2.0 g) was dispersed in concentrated sulfuric acid (60 mL). Nitric acid (70%, 20 mL) was slowly added to the dispersion. The mixture was heated to 100 °C and allowed to react for 24 h. After cooling to room temperature, the reaction mixture was quenched with NaOH. After filtration through a 0.2 μM mPES membrane, the resulting solution was subjected through cross-flow filtration against a 70 kDa membrane. The fraction retained greater than filtration using a 70 kDa membrane. The redder-emitting GQDs were isolated via rotary evaporation.

5.3.3. Spectroscopic characterization

To measure the sensitization of Tb³⁺, nine solutions of bGQDs (5 μg/mL) in water were made with increasing amounts of TbCl₃ (0-50 μM). Solutions were purged with nitrogen, then emission spectra measured using the same instrument parameters. The spectra were processed using OriginPro 8.5. The broad emission from the GQD was marked as a baseline and the Tb³⁺ peak centered at 545 nm was
integrated. This peak was used because it was visible at all concentrations other than 0 μM Tb\(^{3+}\). The peak area was then plotted versus concentration of TbCl\(_3\).

The average lifetime was calculated from the multiexponential decay using the following equations given a tri-exponential fit.

\[
y = y_0 + A_1e^{(-x/\tau_1)} + A_2e^{(-x/\tau_2)} + A_3e^{(-x/\tau_3)}
\]

**Eq. 5.2 – Fitting Equation for tri-exponential decay**

\[
P_n = \tau_n \times \left( \frac{\tau_n A_n}{\tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3} \right)
\]

\[
\tau_{avg} = \tau_1 P_1 \times \tau_2 P_2 \times \tau_3 P_3
\]

**Eq. 5.3 – Calculation of average lifetime**

The quantum yield (QY) of bGQD was measured using [Re(bpy)(py)(CO)\(_3\)]\(^+\) as a reference, given that the QY of [Re(bpy)(py)(CO)\(_3\)]\(^+\) is 0.015, bGQD was found to have a quantum yield of 0.094 following equation.

\[
\Phi = \Phi_R \frac{I_{nt}}{I_{nt_R}} \left( \frac{\eta^2}{\eta_R^2} \right)
\]

**Eq. 5.4 – Calculation of photoluminescence quantum yield**

This was also used to measure the quantum yield of Tb@bGQD, rGQD, and Tb@rGQD. For Tb@bGQD and Tb@rGQD, emission spectra were processed with
OriginPro 8.5. The total area was integrated, then the broad GQD emission was marked as a baseline and the area of the four Tb\(^{3+}\) peaks were integrated and used for \(\Phi_{\text{Tb}}\). The area of Tb\(^{3+}\) was then subtracted from the total area and the result was used to determine \(\Phi_{\text{GQD}}\). Once the quantum yield was determined at 250 nm it could be used to determine the QY over all excitation wavelengths. The ratio of PL area /Abs was of the 3D spectra at 250 nm, then that coefficient was applied to the PL area /Abs ratio at each excitation wavelength.

Singlet oxygen was detected using a fluorometer with near-IR detection. Samples were prepared in D\(_2\)O so that they had an absorption of 0.2 at 365 nm. The phenalenone standard and one bGQD sample were purged with oxygen for 15 min and sealed with parafilm, the other bGQD sample was purged with nitrogen. Samples were excited at 365 nm and spectra were measured 1210 – 1325 nm. The quantum yield of singlet oxygen production was measured using singlet oxygen sensor green (SOSG) as reported by Lin et al.\(^{94}\) Briefly, aqueous solutions of bGQD and a phenalenone standard (\(\Phi_d = 0.98\))\(^{95}\) were irradiated with 350 nm light using a 450 W xenon lamp. The spectra of SOSG was measured (\(\lambda_{\text{ex}} 488 \text{ nm}, \lambda_{\text{em}} 495-700 \text{ nm}\)) and the peak at 530 nm was plotted against time. The initial rate of emission increase was plotted against the absorbance at the irradiation wavelength (350 nm). Then the slope of this plot was compared to the reference using equation 5.5.

\[
\Phi = \Phi_R \left( \frac{k}{k_R} \right)
\]

\textbf{Eq. 5.5 – Calculation of singlet oxygen quantum yield}
Considering that Tb$^{3+}$ cations bind to the surface of GQD we can then calculate the number of coordination sites left exposed on Tb$^{3+}$. To do this, the lifetime of Tb@GQD was measured in water and in deuterium oxide. The number of water molecules coordinated to Tb$^{3+}$ can then be calculated using the following equation\textsuperscript{15}:

$$q = A[\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}]$$

where $q$ is the number of water molecules coordinated and $A$ is a constant found to be 4.2 for Tb$^{3+}$. When bound to bGQDs the Tb$^{3+}$ is also bound to on average 5.5 water molecules whereas when bound to the rGQDs it is also coordinated to 5.3 water molecules.
Figure 5.1 – (a) Absorption (black), excitation (solid blue) and emission (dashed blue) spectra of bGQDs (5 μg/mL) in water excited at 330 nm. (b) Emission spectra of TbCl₃ titration into aqueous solution of bGQDs. (c) Plot of emission intensity recorded at 545 nm from (b) the TbCl₃ titration. (d) Photoluminescence of TbCl₃ at varying concentrations in water excited at 330 nm.

Figure 5.2 – Absorption (black), excitation (blue solid) and emission (blue dashed) spectra of TbCl₃ excited at (a) 280 nm and (b) 330 nm.
Figure 5.3 – Sequestering of Tb$^{3+}$ with two equivalents of EDTA.

Figure 5.4 – Titration of Gd@bGQD. Quenching of emission intensity is seen with increased concentration of GdCl$_3$. 
Figure 5.5 – Photoluminescence bGQD and Tb@bGQD (a) purged with nitrogen and (b) open to air. \([\text{Tb}^{3+}] = 10 \ \mu\text{M} \ \text{and} \ [\text{bGQD}] = 5 \ \mu\text{g/mL.}

Figure 5.6 – Near IR emission spectra showing singlet oxygen generation of (a) phenalenone standard, (b) bGQDs purged with oxygen, and (c) the absence in bGQD purged with nitrogen. Excited at 365 nm with 800 nm filter.
Figure 5.7 – TRES of Tb@bGQD excited at 330 nm.

Figure 5.8 – Lifetime of (a) Tb@bGQD and (b) Tb@rGQD in water and deuterium oxide excited at 330 nm and emitting at 545 nm.
Figure 5.9 – 3D emission spectra of (a) bGQD (10 μg/mL) (b) Tb@bGQD (10 μg/mL and 6 μM) and (c) TbCl$_3$ (6 μM).

Figure 5.10 – Quantum yield at varying excitation wavelengths (a) bGQD, (b) the bGQD peak from Tb@bGQD, and (c) the Tb$^{3+}$ peaks from Tb@bGQD.
Figure 5.11 - Schematic showing sp² carbon core with oxidative defects. Small organic molecule-like moieties on the periphery could partake in binding and sensitizing Tb³⁺.
Figure 5.12 – (a) Absorption (black), excitation (blue solid) and emission (blue dashed) spectra of rGQDs (5 μg/mL) in water excited at 330 nm. (b) Emission spectra of TbCl₃ titration into aqueous solution of rGQDs. (c) Plot of emission intensity recorded at 545 nm from (b) the TbCl₃ titration. (d) Photoluminescence of TbCl₃ at varying concentrations in water excited at 330 nm.

<table>
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<tr>
<th>Sample</th>
<th>φₜb</th>
<th>φₕqD</th>
<th>τ₅20 nm</th>
<th>τ₅45 nm</th>
</tr>
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<tbody>
<tr>
<td>rGQD</td>
<td>-</td>
<td>0.018</td>
<td>0.424 ns</td>
<td>-</td>
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<td></td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
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<td>(32.88%)</td>
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Table 5.2. Photophysical parameters for rGQD and Tb@rGQD.

Figure 5.13 – 3D emission spectra of (a) rGQD (b) Tb@rGQD and (c) TbCl₃.
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