


Heterogeneity in the fluorescence of graphene and graphene oxide quantum dots

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Abstract Heterogeneity is an inherent property of a wealth of real-world nanomaterials and yet rarely in the reporting of new properties is its effect sufficiently addressed. Graphene quantum dots (GQDs) – fluorescent, nanoscale fragments of graphene – are an extreme example of a heterogeneous nanomaterial. Here, top-down approaches – by far the most predominant – produce batches of particles with a distribution of sizes, shapes, extent of oxidation, chemical impurities and more. This makes characterization of these materials using bulk techniques particularly complex and comparisons of properties across different synthetic methods uninformative. In particular, it hinders the understanding of the structural origin of their fluorescence properties. We present a simple synthetic method, which produces graphene quantum dots with very low oxygen content that can be suspended in organic solvents, suggesting a very pristine material. We use this material to illustrate the limitations of interpreting complex data sets generated by heterogeneous materials and we

highlight how misleading this “pristine” interpretation is by comparison with graphene oxide quantum dots synthesized using an established protocol. In addition, we report on the solvatochromic properties of these particles, discuss common characterization techniques and their limitations in attributing properties to heterogeneous materials.

Keywords Graphene quantum dots · Quantum yield · Fluorescence lifetime · Photoluminescence · Characterization · TEM · NMR · Raman spectroscopy

Introduction

Heterogeneity is a major obstacle when investigating real-world materials. Graphene quantum dots (GQDs) – predominantly heterogeneous luminescent nanoscale fragments of graphene – are a promising new material which have gained attention due to their potential applications given their relationship with graphene [1–10]. Like graphene, they can be derived from cheap and abundant precursor materials [11–14]. Their optoelectronic properties have seen their application in energy-related fields as supercapacitors, photocatalysts and in LEDs to name only a few [15–17]. These properties, combined with their proven lack of toxicity, have made them suitable for applications such as cellular and deep tissue imaging and biosensing [18–23]. Currently, the synthetic methods that are employed to produce such particles also cause compositional heterogeneity where particles have varied oxygen content, structural defects and functional groups so they are not directly comparable. Because – for the most part – particles made using oxidative and non-oxidative methods have been presented as if they had similar structural composition, this has made it difficult to narrow

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down a direct relationship between their structure and optoelectronic properties [24–26].

Synthetic routes to GQDs often employ top-down, oxidative methods (e.g. Hummers' method) that yield heterogeneous batches of particles both in terms of the variation between particles and also within a particle [6, 13, 25, 27–30]. For example, a single batch will contain a distribution of particles with regards to size, extent of oxidation, edges, defects and potentially more, all of which may contribute to their optoelectronic properties [25, 31, 32]. In more detail, a key difference is the presence of functional (mostly oxygen) groups on the edges and basal plane of graphene oxide quantum dots (GOQDs). The presence of oxygen functionalities located on the basal plane severely affects GQD properties such as charge mobility, peak emission wavelengths and polarity, the latter determining the solvent that can be used for suspending the GQDs. Several groups developed bottom-up synthesis routes or precise top-down nanotomy methods to produce *truly* pristine GQDs but their complex, multi-step syntheses limit their wide-spread study and use [27, 28, 33]. The high quality of the produced compounds did however allow for some careful probing of their physico-chemical properties, which shows that there remain vast differences between these GQDs and those produced from oxidative top-down syntheses.

Some authors have focussed on a 'best of both worlds' approach, developing top-down syntheses to produce truly pristine particles, but thus far these methods are low-yielding and highly complex requiring the use of specific equipment or expensive catalytic single-crystal ruthenium, surfaces [33, 34].

In the literature for top-down approaches to GQDs there have been numerous reports of simple relationships between fluorescence and GQD structural features [29, 35]. A key example of this is Liu et al. who exfoliated graphite nanoparticles (GNPs) in both acidic, oxidative conditions and in a 1:1 water:ethanol mixture [6]. They reported a significant difference in oxygen content between the two samples, and postulated that the latter method produced pristine particles and therefore blue emission as compared to the green emission of the more oxidised GQDs. However, the pristine GQDs could be suspended in water, which is unexpected of a pristine graphene lattice given its hydrophobic nature and the fact that bottom-up synthesized GQDs – i.e. truly pristine GQDs – suspend in organic solvents [27]. Secondly, bottom up-synthesized GQDs exhibit luminescence in the near-IR region compared with the blue luminescence reported in the study by Liu making it unlikely that these GQDs were pristine. Their results exemplify the dangers of inadequate analysis of complex data sets.

To bridge the gap between the reliable knowledge of bottom-up produced GQDs and the vast discrepancies in reports from top-down syntheses, we created a top-down

approach designed to produce pristine GQDs in terms of their crystallinity, which is largely affected by the amount of oxygen defects. Our aims were two-fold; develop a non-oxidative, simple method to produce pristine quantum dots and thoroughly inspect each of the characterization techniques that are currently employed in the GQD literature, bearing in mind the variability of the sample, in order to narrow down the possible contributions to the luminescence in GQDs. We envision that our findings will assist future work on GQDs, to increase understanding of the many aspects affecting fluorescence in order to establish accurate structure–property relationships.

Experimental

Improved synthesis of “pristine” GQDs

Our new synthesis of “pristine” GQDs is a very simple exfoliation method that differs from common methods in that it does not involve strong acids and oxidising agents but instead an organic solvent that is a very good candidate for solubilising graphitic materials based on its surface tension – chloronaphthalene [36]. We label these particles “pristine” as they prove to have a very low oxygen content indicating few oxygen defects in the structure but further analysis in the characterisation sections shows this is not the case. Like many liquid-phase exfoliation methods, a shearing force is applied by sonication to exfoliate each layer of graphene. Once in solution, a favourable interaction with the solvent by matching the surface tension values of the individual sheets and solvent stabilises the sheets preventing reaggregation [37–39].

In order to keep the size distribution narrow we used graphite nanoparticles (GNPs) as a starting material. The exfoliation occurs through sonication of the GNPs in chloronaphthalene followed by a purification procedure, during which, this toxic solvent may be recovered and reused for subsequent reactions. Although chloronaphthalene is toxic, naphthalenes that have similar but slightly lower surface tension values should also be effective in this synthetic protocol. Using a conventional silica column, the chloronaphthalene was removed with hexane before the GQDs themselves were isolated using chloroform or dichloromethane (DCM). Furthermore, they can also be suspended in DCM and tetrahydrofuran (THF). Post-column, the GQDs must also be precipitated with hexane and centrifuged several times to remove any additional impurities. The advantage this method has over common Hummers'-based methods is that it employs organic solvents rather than acids and aqueous solvents meaning it is less oxidative and resulting particles are less defective. In order to investigate possible fluorescent impurities we performed size-exclusion chromatography. The “pristine” GQDs were compared with GOQDs synthesized using an oxidative exfoliation method,

again with GNPs as precursor [40]. Our results showed that there is a clear difference between the two types of quantum dots in terms of oxygen content, photoluminescence and the solvents they can be suspended in, yet both types of particles are evidently heterogenous and thus neither can correctly be labelled “pristine”.

Synthesis of GQDs

GQDs were synthesized by exfoliation of GNPs (Skyspring Nanomaterials Inc. TC, USA www.ssnano.com) in 1-chloronaphthalene (Sigma-Aldrich, US www.sigmaaldrich.com). Briefly 100 mg of GNPs were added to 50 mL of chloronaphthalene and this was sonicated using a probe sonicator (UP100H, Hielscher, Germany) operated at 100 W, 30 kHz and 100% amplitude for 24 h. After this period, the mixture was purified using silica column chromatography. 10 mL of the mixture was mixed with 10 mL of hexane and this was loaded onto the column. The chloronaphthalene was first eluted with hexane (fraction 1) followed by GQDs with chloroform or dichloromethane (fraction 2). Fraction 2 was concentrated via rotary evaporator and subsequently further washed with hexane and centrifuged 5 times to remove any residual chloronaphthalene.

Synthesis of graphene oxide quantum dots

As a “standard” comparison, GOQDs were synthesized using a published procedure. Briefly, 1 g of GNPs were oxidized in concentrated H_2SO_4 (60 mL) and HNO_3 (20 mL) for 3 h under mild ultrasonication (100 W). The solution was refluxed for 12 h at 100 °C. The resulting mixture was diluted with deionized water and centrifuged at 34,000 rcf for 20 min after which the pellet was dispersed in a minimum volume of water and purified by dialysis.

Characterization

The size and crystallinity of the particles were characterized using a JEOL 2100F 200 kV field emission gun transmission electron microscope (JEOL, Japan). The extent of exfoliation was assessed using a Bruker Nanoscope atomic force microscope (Bruker, MA, US). Steady-state photoluminescence measurements were recorded using an Edinburgh Instruments FLS980 fluorescence spectrometer with a Xe lamp as light source (Edinburgh Instruments, Edinburgh, Scotland). Lifetime measurements were performed using TCSPC with a 320 or 380 nm pulsed LED-laser. Lifetimes were recorded in a 500 ns time range using 8192 channels. The measurement was stopped when the number of counts in the first channel had reached 5000. XPS measurements were undertaken using monochromatized Al $K\alpha$ X-rays (1486.7 eV) at a power of

225 W on a Kratos Axis-Ultra spectrometer (160 eV analyzer pass energy for survey scans, 20 eV for high-resolution scans). The analysis spot size was $\sim 300 \times 700 \mu\text{m}$. Core electron binding energies are given relative to an adventitious hydrocarbon C 1s binding energy of 284.7 eV. All XPS spectra were processed with CasaXPS (ver. 2.3.16 PR 1.6) data processing software using a Shirley background correction. The purity of particles was assessed by NMR using a Bruker 500 MHz NMR spectrometer. Particles themselves give very few signals [27]. Size exclusion chromatography was performed using Biorad Biobeads S- \times 1 Support (Bio-Rad Laboratories, US, www.bio-rad.com) with THF as solvent.

Results and discussion

Structure and composition of GOQDs/GQDs

The average particle size for GQDs and GOQDs were very similar ($2.91 \pm 0.8 \text{ nm}$ and $3.28 \pm 0.4 \text{ nm}$ respectively) indicating that particle size is determined by the precursor graphite nanoparticles which are $\sim 3 \text{ nm}$ size (Fig. S1 and S2). The GOQD sample had a larger distribution of sizes. High resolution images of single particles show lattice fringes similar to the lattice parameter reported for graphene (0.24 nm; see Fig. 1). We estimate the heights to be between 1 and 6 layers with the majority being between 1 and 4 (Fig. S3) [41, 42].

The composition of the GQDs and GOQDs was assessed by x-ray photoelectron spectroscopy. The spectra show a significant difference in the composition of the two types of particles. Namely a much higher proportion of carbon relative to oxygen for GQDs compared with GOQDs (Fig. S4). Consistent with the graphene oxide literature, the O/C ratio is in the range of chemically reduced graphene oxide at 0.24 for GQDs but is much higher at 0.75 for GOQDs [43, 44]. The GQDs contain a weak signal for a chlorine impurity and the GOQDs contain a sodium and nitrogen impurity from the acids used in the synthesis and the bases used in the neutralization step. The high resolution C1s and O1s spectra are shown in Fig. 2. The GQD spectrum has fewer oxygen environments and a smaller proportion of oxygen relative to the C = C/C-C peak. The peaks are assigned: 284.9 eV C = C/C-C, 286.9 eV C-OH, C = O and 289.0 eV O = C-OH. For GOQDs the peaks are assigned: 284.7 eV C = C/C-C, 285.9 eV C-O-C, C-OH, 287.7 eV C = O, 288.6 eV O = C-OH and 289.5 eV π - π^* shake-up. Peak positions and weights are given in Table S1.

Although we confirmed a very low oxygen content for GQDs, further evidence of a regularly repeating carbon lattice was still required before confirming these particles are pristine. We therefore performed Raman spectroscopy of both the GQDs and GOQDs. Employing a 633 nm laser (Fig. S5),

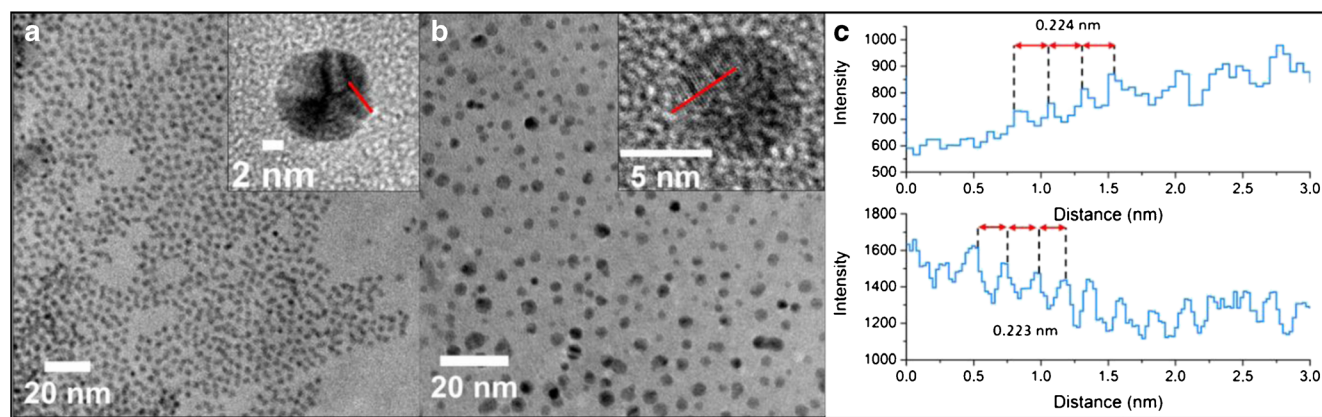


Fig. 1 TEM of GQDs (a) and GOQDs (b) with HRTEM insets showing lattice fringes. Line profiles of indicated regions of HRTEM images showing distances between fringes (c). Note the different scale bars

produced too much fluorescence to see Raman signal beneath. Switching to a shorter wavelength of 568 nm we still found that it was impossible to reliably resolve the D and G bands within the fluorescence background using standard techniques despite similar reports already being published [13, 45, 46]. It is worth noting for comparison that the Raman spectrum of Nile Blue A excited at 633 nm – with a quantum yield of 4% in water – cannot be resolved over its fluorescence using standard techniques [47]. With the very broad emission of GOQDs/GQDs, it is possible that there is a very wide window over which Raman signals are overwhelmed by fluorescence.

Optical properties of GOQDs/GQDs

Steady-state and time-resolved photoluminescence

Steady state PL revealed that GQDs have broader excitation and emission spectra than GOQDs (Fig. 3a and c). Peak excitation is centred at 460 nm while peak emission is centred at 550 nm. For GOQDs the excitation spectra shows an additional feature at 350 nm and narrower excitation and emission. Peak excitation is at 475 and peak emission is at 540 nm.

Time-resolved photoluminescence measurements were recorded for both GQDs and GOQDs excited with a 380 nm

Fig. 2 High resolution C1s (a) and O1s (b) XPS spectra of purified GQDs showing relatively few oxygen functional groups. Equivalent C1s (c) and O1s (d) spectra of GOQDs show more oxygen functionalities and in higher proportions

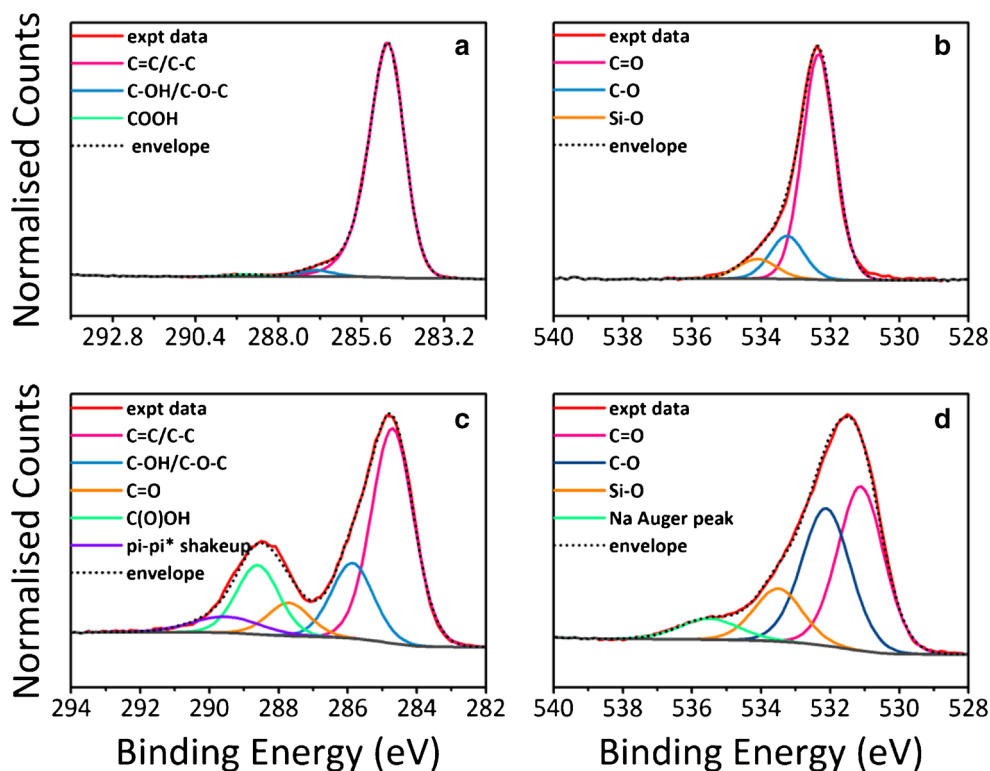
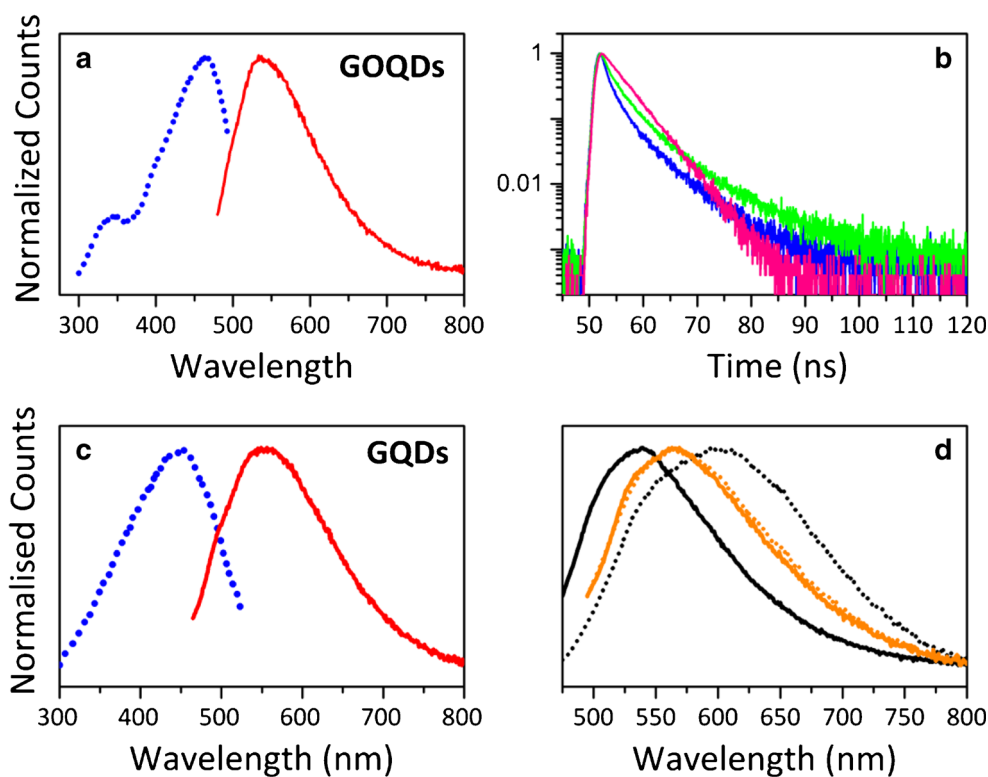


Fig. 3 Comparison of spectroscopic characterization for GOQDs (**a**) and GQDs (**c**). Photoluminescence excitation (PLE) and emission (PL) spectra are shown in blue and red respectively. PL and PLE spectra are similar but narrower for GOQDs. Fluorescence lifetime decays (**b**) of GOQDs (blue) and GQDs (green), excited at 380 nm, are shown with single-exponential fluorescein in pink for comparison. Solvatochromic shifts of GOQDs/GQDs are shown in (**d**). GQDs show no significant spectral shift on going from dimethylsulfoxide (DMSO) (dashed orange line) to DCM (solid orange line)



pulsed LED laser (Fig. 3b in green and blue respectively). The tail of the fluorescence decay was fitted using a published method [32]. We include the fluorescence decay of fluorescein in pink as a visual comparison of a molecule with near single-exponential decay. Both quantum dots show far from single exponential decay behaviour. The decay curve for GOQDs reaches the baseline faster indicating that there are faster bright transitions occurring. We fit the fluorescence decay using a log-normal model and generated a distribution of lifetimes. This distribution is weighted towards shorter lifetimes for GOQDs (Fig. S7 and S8 and Table S2). When combining this information with the quantum yields (QY) for each sample, we can build up a picture of the extent of heterogeneity of the GQDs and GOQDs. While the GOQDs have narrower emission and faster fluorescence decay profiles making them appear more uniform, they also have a lower QY of 5.28%. The GQDs, in contrast, with broader emission and slower decay profiles have a higher QY of 6.43% [48]. This suggests that there are a lower proportion of bright states for GOQDs – particularly the longer-lived bright states. We propose that during the harsh chemical synthesis, the bright states similar to those that exist in the GQDs are converted to non-emissive states.

Effect of functional groups

Figure 3d shows the solvent-dependence of GOQD emission which is absent in GQDs. To compare fluorescence spectra of

the two types of particles we resuspended both types of particle in DMSO and observed a change in luminescence (Fig. 3d, dashed lines). For the GQDs, on going from less polar dichloromethane (DCM) to more polar dimethylsulfoxide (DMSO), we see no clear shift. However for GOQDs, changing from more polar, protic water to less polar, aprotic DMSO, we observe a significant red-shift from 550 to 625 nm. We tested this shift by then resuspending the particles in their original solvents to rule out the possibility that a reaction had occurred. We observed a shift back to the original spectrum (Fig. 3d solid lines). This shift to lower energy along with the broadening of the emission spectrum of GOQDs must be largely attributed to the high proportion of oxygen functionalities in the GOQDs – as shown by XPS – that are not as abundant in the GQDs. A red-shift due to functional groups has been previously documented in the literature [49, 50]. Additionally there are many reports of pH-dependent emission behavior of graphene oxide and graphene oxide quantum dots – attributed to the protonation or deprotonation of phenolic and carboxylic acid groups in the structure [19, 51, 52]. In this case, only the GOQDs exhibit a solvent-dependant shift in emission when going from a polar protic solvent (water, solid black line) to a polar aprotic solvent (DMSO, dashed black line). We therefore postulate that, in an analogous manner to the pH-dependence of fluorescence many groups have reported, the shift here is attributed to the presence or absence of protons rather than the polarity of the solvent.

“Excitation wavelength-dependent” emission

Many groups have reported excitation wavelength-dependent emission which has also been seen in amorphous carbon dots [53–56]. Our QDs and GOQDs did not exhibit excitation wavelength-dependent emission as the emission tail does not shift as shown in Fig. S8.

The spectroscopic characterization presented for GOQDs/GQDs reflects the extent of their heterogeneity. A prevailing theory to describe the discrepancies between top-down and bottom-up produced GQDs – namely the higher energy fluorescence for GOQDs – is a conjugation island theory which was well demonstrated in a theoretical study by Sk et al. [25] They questioned why bottom-up synthesized GQDs of 2 nm in size emit red fluorescence and yet top-down synthesized GQDs emit blue or green fluorescence and suggested this was due to the introduction of defects in the harsh top-down synthetic procedures. These defects cause breaks in conjugation leading to smaller and smaller islands of conjugation that act as individual fluorophores (Fig. 4).

If that were the case for our work, we should see a shift to higher energy emission for GOQDs and this may also be accompanied by the creation of more emissive states and in turn, higher QYs. However what our work seems to demonstrate is a refinement of this theory where the very harsh synthetic method used to produce the GOQDs disrupts the conjugated lattice to an extent where a very high proportion of dark states are introduced. This results in a smaller population of fluorophores, narrower emission and shorter lifetimes than GQDs. Additionally the GOQDs have more complex emission behaviour than GQDs – presumably due to their functional groups which interact with different solvents.

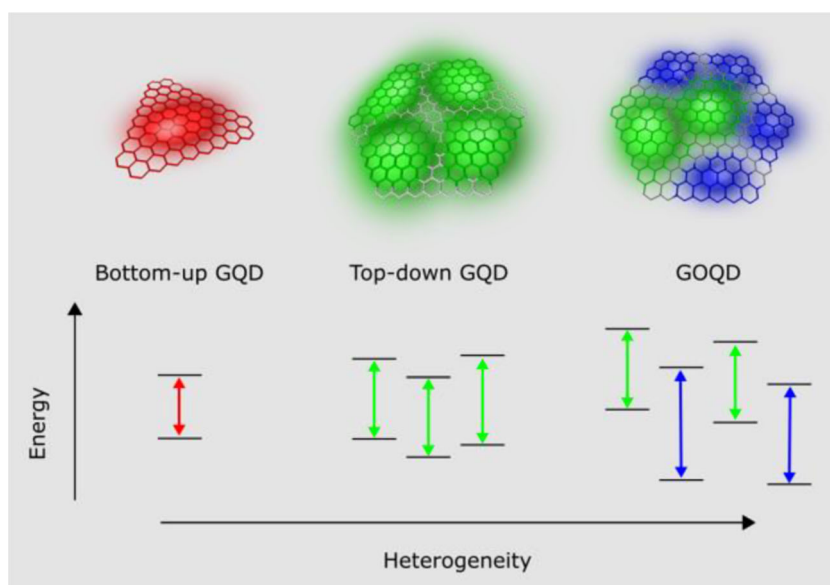
Already across two samples that differ only in their synthetic method, we see vast differences between GQDs and

GOQDs. It is therefore important to understand the complexity behind the name “GQD.” Although there are many properties that have been reported for GQDs, we wonder whether each of these properties are inherent to GOQDs/GQDs or whether this is simply a reflection of the variability of the material. Whatever the case, this work shows that this variability must be considered in future contributions to the GQD area if we are to make significant gains in understanding mechanisms of luminescence.

Conclusion

We presented a new, non-oxidative, simple synthesis method for graphene quantum dots that can be suspended in mid-polarity solvents. These particles provide a key bridge between truly pristine GQDs made from complex bottom-up methods and the extremely heterogeneous GOQDs made from oxidative, top-down processes. In characterizing the two types of particles we found the GQDs to have significantly lower oxygen content and different emission behavior. Although our particles can be considered more pristine than most published top-down GQDs based on the low O/C ratio, we demonstrated that a large degree of heterogeneity remains, as evidenced by the higher energy emission than theory predicts. We observed a large effect of solvent on fluorescence spectra of GOQDs which is absent for GQDs. GOQDs displayed negative solvatochromism when solvent polarity increased. While this may be related to the abundance of oxygen functionalities on the GOQDs and interaction with protic and aprotic solvents, further spectroscopic studies are required to reliably narrow down the origin of this spectral shift. We therefore propose that the origin of the emission in GQDs and GOQDs is a complex combination of edge group emission

Fig. 4 Schematic showing one of the theories of the origin of luminescence in GQDs. The structural differences cause spectral differences between GQDs produced using different synthetic methods. Emission is determined by the size of conjugation islands within the structure. Bottom-up GQDs such as C132 as depicted here have a pristine carbon lattice and therefore red emission [57]



and emission from conjugated areas within individual particles and that although at first glance, GOQDs appear to have simpler spectroscopic behavior, this is likely to only be true of bright states and to be related to the introduction of an abundance of dark states during the harsh top-down synthetic method. With this study, we hope to advance the understanding of the structural origin of complex photophysical processes occurring in graphene quantum dots produced using top-down techniques but also to highlight the complexity of structural and spectroscopic data derived from highly heterogeneous materials like these and to open up a discussion on heterogeneity and its effect on interpretation of characterization data in general.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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