A novel and facile method to synthesize graphene quantum dots (GQDs) from graphene oxide (GO) via sonication or UV-irradiation reaction using an acid-free oxone oxidant (potassium monopersulfate) that does not require a neutralization process with a strong base was developed. Our novel sono- and photo-oxidation approach yielded high quality GQDs after simple purification. GO sheets treated by sono- and photo-oxidation with the oxone oxidant as the free radical source broke in multiple places for efficient generation of GQDs. Sono-oxidation is a simpler and more facile method than photo-oxidation in terms of mass production and the strong fluorescence properties of the resulting GQDs. Facile synthesis by sono- and photo-oxidation represents a new route to prepare GQDs from GO in organic solvent.

Graphene quantum dots (GQDs), which comprise nanosized mono or few-layer graphene sheets, have a hexagonal lattice structure with lateral dimensions of less than 100 nm. GQDs display a strong quantum confinement effect that induces photoluminescence (PL) based on theoretical predictions and experimental studies because of their edge effect and zero dimensions (0D). Consequently, GQDs have garnered tremendous interest, especially in the fields of nanoscience and nanotechnology.7 GQDs can be applied in various fields such as optoelectronics,8 photovoltaics,9 and bio-imaging.10 GQDs have been prepared by treatment of various carbon-based materials including graphite or graphene oxide (GO), carbon nanotubes (CNTs), and carbon fibers (CFs) with high-resolution electron beams, microwave irradiation, electrochemical scissoring, chemical cutting, or hydrothermal cutting.11–18 In addition, bottom up routes have been developed to prepare GQDs via hydrothermal treatment, pyrolysis and exfoliation.19,20 One of the most effective methods to prepare GQDs is Hummers method, which is a typical protocol used to produce GO from graphite. Several methods to synthesize GQDs from GO have been introduced; however, these methods require strong acid conditions and a complicated and time-consuming purification process.10,12,21 For example, a hydrothermal route17 to provide blue photo-luminescent GQDs from GO has been reported, but a very long reaction time is required in addition to use of strong acids such as sulfuric acid and/or nitric acid. Furthermore, the synthesis of GQDs using hydrothermal cutting of GO after a series of acid treatments usually takes several days and requires a complicated purification process. Therefore, it is important to develop an entirely new GQD production reaction method that does not require a strong acid or a complicated purification process.

Advanced oxidation processes (AOPs) were well established in 1987.22 Sulfate and hydroxyl radical-based AOPs are promising methods to cleave organic and inorganic pollutants by oxidation for practical industrial applications. Oxidation is based on the formation of a reactive oxidizing agent that is able to effectively degrade pollutants.23,24 The reaction rate can be accelerated by ultraviolet (UV) light or sonication, referred to as photolysis or sonolysis, respectively.25 Recently, a photo-Fenton method to prepare GQDs from GO using ferric chloride and hydrogen peroxide was introduced.26 The reaction with ferric chloride was accelerated by UV-irradiation. Even though the photo-Fenton reaction route was employed to simplify synthesis of GQDs from GO, complex purification processes to completely remove the metal ions of ferric chloride are still required, as is neutralization treatment of the resulting acid that is produced during the reaction and workup steps. Therefore, to effectively prepare GQDs from GO, it is important to find a novel and facile method that can be used to oxidatively cleave carbon–carbon bonds from GO sheets. Furthermore, it would be ideal if the GQDs produced could be purified without the use of acid so that no neutralization process with a strong base is required.

Oxone (potassium monopersulfate) is a metal-free, neutral salt oxidant that does not require a neutralization step. It is
commonly used as an oxidizing agent because of its stability, simple handling, non-toxic nature, and low cost. Sulfate (SO$^{4-}$) or hydroxyl (OH$^-$) radicals generated by oxone have been used in the degradation of aromatic organic pollutants. Oxidation of organic components is thought to occur by free radical (sulfate radical and hydroxyl radical) attack of carbon bonds.\textsuperscript{27,28} However, sono- and photo-oxidation of GO using an acid-free oxone oxidant has not previously been reported. Based on the results presented in this study, we suggest that oxone-based sono- and photo-oxidation of GO is a straightforward and effective synthetic method to prepare GQDs.

Herein, we report a new and facile synthesis method to produce GQDs from GO via sono- or photo-oxidation using an acid-free oxone oxidant. By giving the oxidation potential, sulfate radicals (SO$^{4-}$) or hydroxyl radicals (OH$^-$) can be generated by the oxone oxidant. These radicals are responsible for the oxidation and scission of carbon–carbon bonds in the graphene oxide structure to produce oxidized GQDs that have various oxygen functional groups including hydroxyl, epoxy and carboxylic acid groups, which have a quite similar graphene oxide structure. Our approach is shown in Fig. 1, we used ultrasonation or UV-irradiation (sono- and photo-oxidation, respectively) to prepare GQDs from GO in an organic solvent system with oxone for 1 h. As proof-of-concept, GQDs were synthesized from GO with oxone in DMF by ultrasonation at 500 W or UV-irradiation at 100 W for 1 h at room temperature, respectively. After filtration, the suspended solutions of GQDs obtained by sono- and photo-oxidation were purified.

The sono- and photo-oxidation methods described above are significantly more straightforward than the photo-Fenton reaction to produce GQDs, as the latter involves the use of ferric chloride and hydrogen peroxide. Furthermore, the sono-oxidation reaction method, which is more facile than the photo-oxidation reaction, can be used for mass production of GQDs with strong fluorescence intensity. Surprisingly, after sonication or UV-irradiation of the suspended GO solution with oxone, two layers were formed; a top layer containing the GQDs, and a bottom layer containing precipitated GO (Fig. S1, ESI†). After filtration of the brownish solution of suspended GO, the resulting filtrate solution turned a transparent yellow color (Fig. S2, ESI†). Thus, sono- and photo-oxidative cleavage of the carbon–carbon bonds of the starting GO material resulted in a simple reaction setup and dramatically shortened the reaction time to 1 h. Furthermore, purification was efficient and there was no requirement for neutralization with a strong base. GO sheets used as a starting material (Fig. S3, ESI†) have numerous oxygen component groups such as hydroxyl, epoxy, and carboxylic acid groups.\textsuperscript{29}

The atomic structure of GQDs was investigated by high-resolution transmission electron microscopy (HR-TEM). GQD samples for HR-TEM were prepared by drop drying the product solution on the TEM grid. GQDs obtained by sono-oxidation of GOs with oxone were fairly uniform with a size distribution of 2–6 nm (Fig. 2a and c). GQDs shown in Fig. 2 had a lattice spacing of 0.25 nm, which corresponds to a crystal state.\textsuperscript{3,30} GQDs prepared by photo-oxidation were also uniform in size with a size distribution of 2–5 nm (Fig. 2d and f) and were crystalline (Fig. 2e). The average size of GQDs obtained by sono- and photo-oxidation was about 4–5 nm.

Topographic morphology images of typical tapping mode atomic force microscopy (AFM), shown in Fig. 3, demonstrated that most of the GQDs consisted of one to three graphene layers with a height profile mainly distributed within the narrow range of 0.7–3 nm and an average height of approximately 1.2 nm. Thus, sono- and photo-oxidation of GO to prepare GQDs was highly effective, and the resultant GQDs had a narrow size distribution. Most GQDs were single or double layer.

To validate the photophysical properties of the GQDs, we performed UV-visible absorption and PL spectral analysis of GQDs diluted in deionized (DI) water. GQDs had typical absorption peaks at 345 nm in the UV-vis spectra. Absorption peaks of GQDs generated by photo-oxidation were similar to those of GQDs obtained by sono-oxidation (Fig. 4a and b). A previous study reported that GQDs have an absorption peak centered at around 320 nm, which corresponds to the n → π* transition of C=O. This absorption peak position is dependent on the synthesis method rather than the size or shape of the GQDs.\textsuperscript{10,15,31} As shown in Fig. 4c and d, the PL emission spectra of GQDs exhibited shifts in the emission peaks with a change in excitation from 320 to 440 nm. The emission maxima of

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**Fig. 1** Representative scheme of synthesis of GQDs from GO using an acid-free oxone oxidant via sono- and photo-oxidation reactions.
solutions of sono- and photo-oxidation GQDs were 450 nm and 455 nm, respectively. The inset photograph shows blue luminescence under 365 nm UV light illumination. The photophysical properties of GQDs are well-known to be affected by a combination of factors such as size, shape, synthesis method, and functionalization.7,32 Table S1 (ESI†) shows the quantum yields (QYs) of GQDs from sono- and photo-oxidation reaction by using Rhodamine B as a reference. The time-resolved PL decay profile measurements were performed on the synthesized GQDs (Table S1, ESI†). The average PL lifetime of GQDs from sono- and photo-oxidation was about 2.49 ns and 2.17 ns, respectively (Fig. S4, ESI†).

X-ray photoelectron spectroscopy (XPS) is commonly used to measure the elemental composition of GQDs. XPS spectra showed that GO as a starting material was functionalized with hydroxyl, graphitic carbon, oxygenated carbon, and carboxylic acid groups in the form of C—C, C—O, and COOH functional groups. High-resolution XPS spectra of C1s confirmed that carbon components of GO changed completely to GQDs (Fig. S5 and S6, ESI†). Furthermore, after sono- and photo-oxidation reactions, high-resolution XPS spectra of C1s showed that functionalization increased with oxygen components of C—C, C—O, and OH groups.

Micro-Raman spectra of samples prepared by spin-casting sono- and photo-oxidized GQDs on Si wafers were obtained. The crystalline G band peak of GQDs at 1590 cm⁻¹ is related to the E₂g vibrational mode of aromatic domains in the two-dimensional hexagonal lattice structure. The amorphous D band peak of GQDs at 1370 cm⁻¹ was intense, with an intensity ratio, I_D/I_G, of ~0.90 for GQDs obtained from sono-oxidation and ~0.99 for GQDs obtained from photo-oxidation (Fig. 5a and b). I_D/I_G ratios for GQDs prepared by hydro-thermal and electrochemical methods have also been reported.16,17 These results imply that a decrease in the fraction of aromatic sp² domains and different degrees of GQDs enhances the oxygenated groups with the number of defect sites.15,31

In summary, we developed a facile and straightforward method to synthesize GQDs from GO involving sonication or UV-irradiation of GO with an acid-free oxone oxidant. GO sheets subjected to sono- and photo-irradiation in the presence of oxone as a free radical source broke in multiple places to prepare GQDs in a highly efficient manner. Sono- and photo-oxidation methods are facile, and provide eco-friendly reaction conditions for non-hazardous purification processes. To the best of our knowledge, this is the first demonstration of synthesis of GQDs via sono- and photo-oxidation using an acid-free oxone oxidant in an organic solvent. We anticipate that this approach will be widely used as it has many other potential applications.

**Experimental**

Graphene oxide (GO, 100 mg) was synthesized by Hummers method. It was completely dissolved in 100 mL DMF after which 500 mg of oxone was added and the solution was mixed. Sono- and photo-oxidation of the mixture was performed in an UV-irradiation (365 nm, 100 W) and ultrasonication bath (500 W) for 1 h at room temperature, respectively. The product suspension was filtered through a 200 nm nano-porous membrane to separate large graphene nanoparticles and GO. The final product solution was further dialyzed in a dialysis bag (retained molecular weight: 2000 Da) for 3 days.
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Notes and references

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