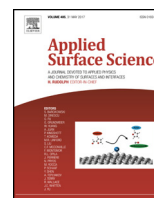




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Investigation of sulfur related defects in graphene quantum dots for tuning photoluminescence and high quantum yield

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ABSTRACT

This paper presents a comprehensive study of the impact of defects on quantum yield in doped graphene quantum dots by having sulfur containing compounds (S-GQDs). The facile and high yielding hydrothermal method was used to process the S-GQDs by selecting two different compounds such as conc. H₂SO₄ and MgSO₄·7H₂O containing sulfur. Initially, the synthesized samples were characterized by using High Resolution Transmission Electron Microscope (HRTEM), Raman Spectroscopy, Fourier Transform Infra-Red Spectroscopy (FT-IR), Thermogravimetric and Differential Thermal Analysis (TGA/DTA), UV-vis spectroscopy, and Photoluminescence (PL). HRTEM images suggest that the majority of the both samples were in the narrow range of 5–20 nm in diameter. Optical properties of the GQDs are altered as a result of S-doping with purple tunable PL at shorter wavelengths. As expected, by using the different excitation energy in PL, appearance of peak introduces additional energy levels between π and π^* that provide alternative electron transition pathways. The most remarkable finding is that the fluorescence quantum yield (FL QY) of S-doped GQDs is higher than that of the reported doped GQDs. This clearly suggests that the defects states related to S modify the electron density, tailor the PL characteristics and improvements in quantum yield of the GQDs.

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1. Introduction

Among graphene based, as two-dimensional luminescent carbon nanomaterials, GQDs have attracted tremendous research interest due to its unique properties including electrical conductivity [1], and good chemical stability [2], and novel potential applications [3–7]. Graphene is a zero band gap semiconductor with infinite exciton Bohr diameter and no optical luminescence. Quantum confinement affects in graphene fragments results in a non-zero bandgap which is tunable by the surface chemistry tuned methods, such as varying the oxidation of graphene, modifying graphene oxide (GO), reduced Graphene Oxide (r-GO), and doping in r-GO.

Doping is the most feasible method to tune the band gap in GQDs with heteroatoms to introduce more defect states to the required PL properties [8]. Generally, defects degrade the quality of materials, such as carrier mobility and conductivity, whereas doping provides a means to tune the carrier concentration in graphene,

thereby enabling the engineering of novel material systems. Doping with nonmetallic atoms like nitrogen [9], selenium [10], sulfur [11], chlorine [12], fluorine [13], boron [14], and potassium [15] into the graphene during the synthesis process of GQDs is the most practical strategy to introduce additional defects. Some researchers also demonstrated co-doped GQDs with B, N doped GQDs [12], N-S doped GQDs [13] and N-P doped GQDs [14], N, F and S doped GQDs [15], and S-N doped GQDs [16] to modify the electron density and to optimize the luminescent performance of GQDs.

Tang et al. [17] presented a simple approach for preparing glucose-derived water-soluble crystalline GQDs followed by a facile microwave-assisted hydrothermal method and reported low PL QY (~7–11%) of the GQDs. Pan et al. [18] reported a hydrothermal cutting method and their photoluminescence (PL) properties to synthesis green luminescent GQDs. Qu et al. [16] has demonstrated that S, N-GQDs processed much better absorption of visible light than pure GQDs and multicolor emission under visible light excitation. Ain et al. [19] demonstrated the red and blue shift obtained from PL by substitutional doping while using different dopants [Cl, N, Na, K, B] for the purpose of tuning the emission energy of GQDs. Zhou et al. [20] prepared a simple and efficient method of the photo-Fenton reaction after breaking C–C bond of GO to produce GQDs in large mass scale. H. Kashani et al. [21] syn-

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Table 1
The Elemental Analysis results from EDAX pattern of GO, sample-I Mg-S/GQDs and sample-II S-GQDs.

Element (wt.%)	C (%)	O (%)	S (%)	Mg (%)	O/C ratio	(O + S)/C ratio
GO	51.82	46.18	–	–	0.89	0.89
Mg-S/GQDs (sample-I)	77.95	18.11	3.41	0.51	0.23	0.28
S-GQDs (sample-II)	73.5	20.12	6.38	–	0.27	0.36

thesized nitrogen doped GQDs (N-GQDs) by pyrolysis of citric acid with blue emission and high QY. Li et al. [22] and his group have shown that reduced graphene oxide (r-GO) serves as fluorescent probe for biological applications. Li et al. [23] synthesized GQDs by electrochemical method with green luminescence for various optoelectronic devices. Li et al. [24], in 2016, developed supersaturated recrystallization (SR) method for the synthesis of inorganic perovskite quantum dots (IPQDs) with excellent PL. Here, Li et al. [25] and coworkers demonstrated highly efficient solution-processed CsPbBr₃ quantum dot light-emitting diodes (QLED) through balancing surface passivation and carrier injection through ligand density control. Bian et al. [26] observed Sulfur-doped graphene quantum dots (S-GQDs) with bright blue emission by a facile one-pot hydrothermal treatment for sensitive detection of Ag⁺ which exhibits direct fluorescence sensors. Tour et al. [27] reported a facile approach to synthesize tunable graphene quantum dots from various types of coal with 20% isolated yield from coal which are soluble and fluorescent in aqueous solution. Li et al. [28] prepared sulfur (S)-doped graphene sheets by a facile electrochemical method with effectively combined exfoliation of graphite and in situ S doping of graphene together. Luo et al. [29] and his coworkers were successful to observe high quantum yield of 41% and a diameter of 1–5 nm with a clear blue shift for nitrogen and sulfur co-doped graphene quantum dots. Gu et al. [30] and his group have used glucose as precursor material to synthesize GQDs through a one-step hydrothermal method which showed strong green PL with FL QY (~44.3%). Kharangarh et al. [31] reported the remarkable finding of nitrogen doped GQDs (N-GQDs) with FL QY (~49.8%) by using a one-step hydrothermal method. These reported methods are limited by availability of expensive materials, and accessibility of special tools. Nevertheless, the reported different synthesized methods with low quantum yield are not suitable for large-scale production. In order to improve the FLQY, a strategy needs to be defined for doping in GQDs with water-soluble inorganic salts. Although several efforts have been reported, a comprehensive understanding of the optical properties of doped GQDs is still being explored to show the excellent PL characteristics. The FLQY of doped GQDs was reported to be lower than 45% and for the co-doped GQDs; it is approximately 41% [29]. Additionally, it is quite difficult to identify the detailed PL mechanism in each case. Therefore, we need to develop a novel approach to prepare doped or co-doped GQDs with high PL characteristics and high FL-QY.

To our best knowledge, a very little attention for a top down method for preparing S-GQDs has been paid. Until now, blue or green fluorescent GQDs have been reported [33]. For practical applications in light emitting devices and short wavelengths diode lasers, we need wide band gap semiconductors [34,35]. However no purple fluorescent GQDs were reported. It will be very interesting to see the excellent PL and defect states by choosing an element that has similar electronegativity with carbon (electronegativity of C:2.55, S:2.58). In this work, initially S-GQD were synthesized and subsequently cauterised to establish a relationship between the defect states and the quantum yield. A facile hydrothermal treatment for the synthesis of S-GQDs was done by combining graphite powder and two different sulfur containing compounds: – MgSO₄·7H₂O (sample-I), and conc. H₂SO₄ (sample-II). The PL peaks of the sample-I were red shifted under a series of excitation wavelengths from 280 nm to 340 nm. However the position of the emission peak wavelengths in sample-II remained the same

with identical excitation wavelengths due to the more uniform distribution in size and presence of more sulfur related defects in comparison to the sample-I. Energy dispersive X-ray spectroscopy (EDAX) analysis as mentioned in Table 1 also indicate that the atomic ratio of C/O/S/Mg showing that the carbon is the dominant element of the Mg-S/GQDs, and the small doping element is magnesium. The sample-II exhibits small size with 6.38 at.% of S, purple PL emission, and high quantum yield (~53% FL QY). However, due to the presence of more sulfur contents, the PL of S-GQDs (sample-II) can be tailored from blue to purple. Therefore, sample-II demonstrated excellent solubility in water, intense purple emission at lower wavelengths and high FL QY (53%) in comparison to sample-I.

2. Experimental details

2.1. Materials details

Graphite powder (Graphite India), NaNO₃ (98%, Sigma Aldrich), KMnO₄ (97%, Sigma Aldrich), KOH (≥85%, Sigma Aldrich), 30% H₂O₂ (Sigma Aldrich), and HCl (≥99%, Sigma Aldrich), MgSO₄·7H₂O powder, and conc. H₂SO₄ were used as received. Double-distilled water (ρ = 18.2 MΩ cm) was used for all experiments during the preparation of GO and Sulfur doped GQDs.

2.2. Preparation of graphene oxide (GO)

Graphite Oxide (GO) was prepared by using commercially available graphite powder by the well-known Hummers and Offemmann method [36] and our earlier reported work [37,38]. In brief, 3.0 g of graphite powder was added to 69 ml concentrated H₂SO₄ with 1.50 g NaNO₃ dissolved in the solution for rephrase. The mixture was stirred for one hour at room temperature. The container was subsequently cooled in an ice-bath followed by slow addition of 9.00 g of KMnO₄ while stirring the contents vigorously by a magnetic stirrer for 15 min. The content was then allowed to warm up to room temperature naturally. Double-distilled water was then added slowly in two aliquots of 138 ml and 420 ml at about 15 min intervals. Subsequently, 7.5 ml of 30% H₂O₂ was added and the color of the suspension changed from light yellow to brown, resulting in the formation of graphite oxide (GO). The product (GO) was then separated by centrifugation, washed with warm water and ethanol several times and dried at 50 °C for 12 h.

2.3. Preparation of Mg-S/GQDs and S-GQDs

Here, some sulfur-containing compounds were used to reduce GO in water. At first, 20 mg of GO powder was dispersed in 20 ml of distilled water (1:1). The prepared solution was stirred for 30 min and ultrasonication was carried out in sonicator for another 30 min. Then 24.6 mg of MgSO₄·7H₂O powder was added to the aqueous solution under the assistance of powerful ultrasonication or stirring for next 30 min. The pH was adjusted to 9 with KOH, and the resultant solution was then transferred into a teflon lined autoclave and heated at 110 °C for 5 h by hydrothermal treatment. Furthermore, this solution was naturally brought down to room temperature and subsequently the Mg-S/GQDs were collected by filtration through a 0.22 μm teflon membrane. The final resultant solution was centrifuged at 4000 rpm before any further characterizations were

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