Effect of molar ratio of H_2 to O_2 on gaseous detonation synthesis of graphene quantum dots

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Abstract

Graphene quantum dots (GQDs) have attracted growing interest due to their interesting electrochemical and photoluminescent properties. However, it is still a challenge to establish a solvent-free and rapid method to prepare GQDs on a large scale. In this study, GQDs are fabricated using a one-pot gaseous detonation approach with benzoic acid (BA) as the carbon source and H_2-O_2 mixture as the explosion source. Furthermore, through altering the molar ratio of H_2 to O_2, three types of GQDs are obtained. Their morphology, composition and optical properties characterized by Transmission electron microscope (TEM), X-ray diffractometer (XRD), Raman spectra, Fourier transform infrared (FTIR) spectra, Elemental analyses, UV–Vis spectroscopy and Photoluminescence (PL) spectra suggest that all the GQDs possess multilayered structures and multitudes of sp^2 subdomains with oxygen-containing functional groups. Meanwhile, higher molar ratio of H_2 to O_2 is beneficial to formation of more oxygen-containing groups and has little effect on optical properties.

Keywords: gaseous detonation, graphene quantum dots, explosion source, optical properties.

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1 Introduction

Owing to their excellent quantum confinement effect and edge effect, graphene quantum dots (GQDs), being graphene nanosheets of less than 100 nm size, exhibit distinct photoluminescence (PL) behaviors, making them popular in the field of bio-imaging and sensing.[1-4] Generally, GQDs are prepared by hydrothermal method, acid oxidation, electrochemical oxidation, and microwave approach.[5-8] However, these preparation ways are generally solvent-containing and time-consuming, in which complex post-processing procedures are usually included, limiting the application of GQDs. Due to its simple operation, fast reaction and high yield, the gaseous detonation method, using combustible gas and oxygen as explosion sources to generate detonation wave which causes a complex and fast series of chemical reactions in the precursors, is employed to prepare nanomaterials, such as metallic oxides and carbon nanostructure materials.[9-11] Herein we report a one-pot gaseous detonation approach to prepare GQDs with benzoic acid (BA) as the carbon source and H_2-O_2 mixture as the explosion source. Furthermore, through altering the molar ratio of H_2 to O_2, three types of GQDs are obtained. All the GQDs possess multilayered structures and multitudes of sp^2 subdomains with oxygen-containing functional groups. Meanwhile, higher molar ratio of H_2 to O_2 is beneficial to formation of more oxygen-containing groups and has little effect on optical properties.

2 Experimental

GQDs were prepared as follows. Firstly, 4 g BA was added to a self-made detonation titanium tube. Then the tube was vacuumized and heated to 65 ºC. Thirdly, the gas mixture was detonated after hydrogen and oxygen were pumped into the tube with a molar ratio of 1:1, 1.5:1, and 2:1. Finally, when the tube cooled down to 60 ºC, black powdery GQDs were collected and marked as G-1, G-2, and G-3, respectively, as illustrated in Figure 1.

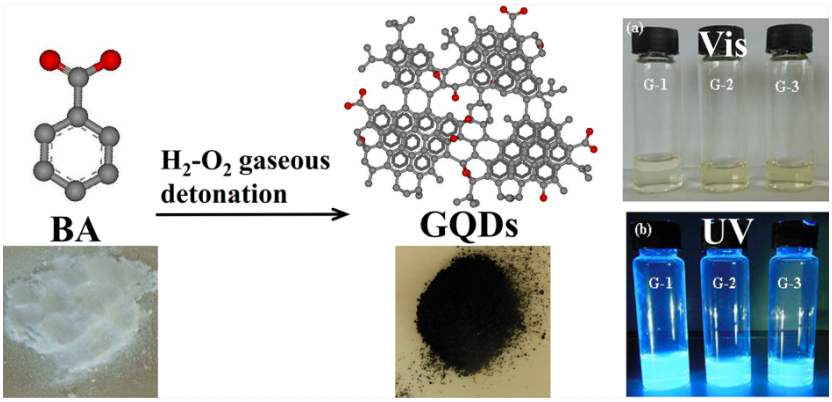

Figure 1. Preparation scheme for the GQDs

3 Results and discussion

TEM images (Figure 2) suggest G-1 and G-3 are well-dispersed with average sizes of 6.3 and 5.6 nm respectively while G-2 has apparent agglomeration with an average diameter of 28.3 nm. Their HRTEM images indicate all the samples are crystalline with spacings of 0.21 or 0.34 nm, consistent with the graphene (100) or graphite (001) planes.[12] The results are supported by XRD and Raman spectra. XRD

patterns (Figure 3a) show all the samples have two broad peaks at 24.6° and 43.4° corresponding to the graphite (002) and graphene (100) planes respectively, further indicating sp^2-hybridized structures.[13] The Raman spectra (Figure 3b) show the typical D band (1345 cm^{-1}) and G band (1590 cm^{-1}), corresponding to disordered sp^3 defects and the sp^2-hybridized structures, respectively.[2] The I_D/I_G ratios are 0.99, 0.94 and 0.96, respectively, implying that all samples have a good degree of crystallinity. FT-IR spectra (Figure 3c) suggest that all the samples have more abundant groups than BA. Compared with that of BA, two distinct new bonds at 1090 and 3425 cm^{-1} appear, assigned to C–O–C and O–H, respectively. Meanwhile, the peaks at 2850 and 2922 cm^{-1} prove the existence of C–H. The peak at 1600 cm^{-1} is attributed to aromatic CQC skeletal vibration.[14] Elemental analyses show that G-3 has the most oxygen-containing groups, then G-1, and finally G-2. All the results above indicate that all the GQDs possess multilayered structures and multitudes of sp^2 subdomains with oxygen-containing functional groups. Meanwhile, higher molar ratio of H_2 to O_2 is beneficial to formation of more oxygen-containing groups.

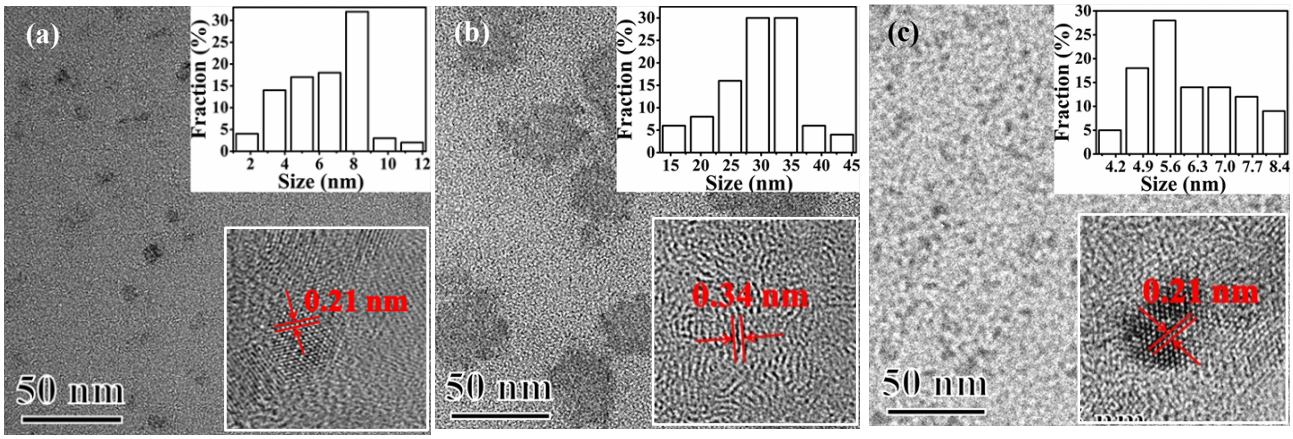

Figure 2. TEM and HRTEM images of G-1 (a), G-2 (b) and G-3 (c), with the corresponding size distribution and HRTEM inserted.

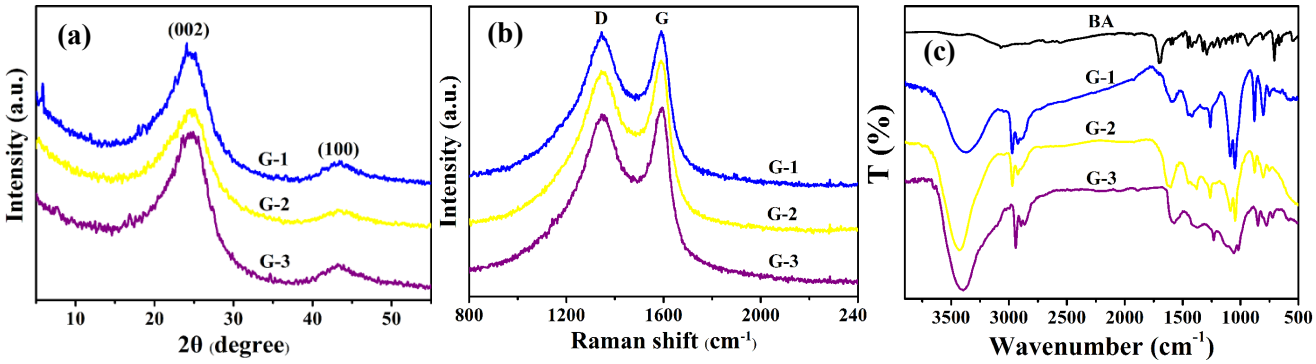

Figure 3. XRD (a), Raman (b) and FT-IR spectra (c) of G-1 to G-3.

The UV-Vis spectra (Figure 4a) exhibit two obvious absorption bands at 251 and 287 nm derived from π–π* absorption of aromatic sp^2 domains, and multiple minor peaks over 300 nm ascribed to n–π* transition of oxygen-containing functional groups.[15] The PL spectra (Figure 4b) display wavelength-independent emission with the maximum emission at 460nm. All the samples in ethyl alcohol emit bright blue fluorescence upon exposure to UV irradiation at 365 nm (Figure 1).

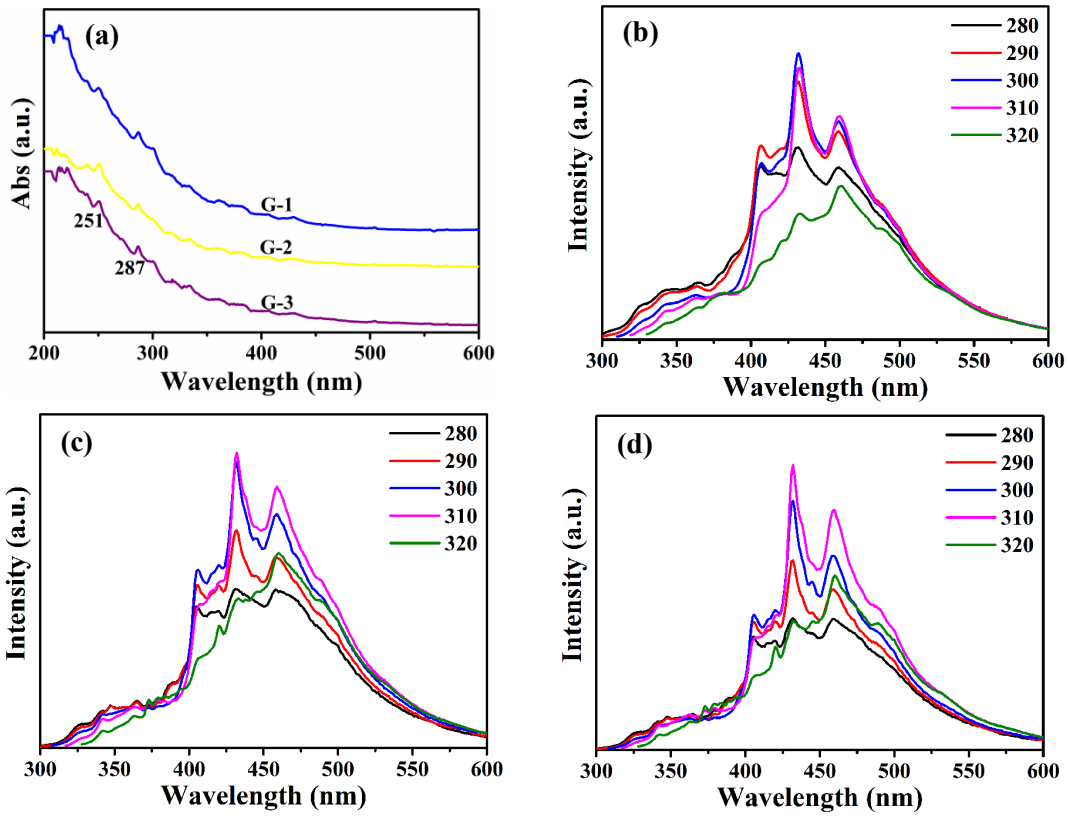

Figure 4. UV-Vis spectra (a) and PL spectra of G-1 (b), G-2 (c), and G-3 (d).

4 Conclusions

Through altering the molar ratio of H_2 to O_2, three types of GQDs are obtained. The results from characterization suggest that all the GQDs possess multilayered structures and multitudes of sp^2 subdomains with oxygen-containing functional groups. Meanwhile, higher molar ratio of H_2 to O_2 is beneficial to formation of more oxygen-containing groups and has little effect on optical properties.

References

[1] X. Hai, J. Feng, X. Chen, J. Wang, Tuning the optical properties of graphene quantum dots for biosensing and bioimaging, Journal of Materials Chemistry B 6(20) (2018) 3219-3234.
[2] X. Hai, Q.-X. Mao, W.-J. Wang, X.-F. Wang, X.-W. Chen, J.-H. Wang, An acid-free microwave approach to prepare highly luminescent boron-doped graphene quantum dots for cell imaging, Journal of Materials Chemistry B 3(47) (2015) 9109-9114.
[3] R. Guo, S. Zhou, Y. Li, X. Li, L. Fan, N.H. Voelcker, Rhodamine-Functionalized Graphene Quantum Dots for Detection of Fe(3+) in Cancer Stem Cells, ACS applied materials & interfaces 7(43) (2015) 23958-66.

[4] L. Wang, Y. Wang, T. Xu, H. Liao, C. Yao, Y. Liu, Z. Li, Z. Chen, D. Pan, L. Sun, M. Wu, Gram-scale synthesis of single-crystalline graphene quantum dots with superior optical properties, Nature communications 5 (2014) 1-9.
[5] D. Pan, J. Zhang, Z. Li, M. Wu, Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots, Advanced materials 22(6) (2010) 734-8.
[6] J. Peng, W. Gao, B.K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, L. Song, L.B. Alemany, X. Zhan, G. Gao, S.A. Vithayathil, B.A. Kaipparettu, A.A. Marti, T. Hayashi, J.J. Zhu, P.M. Ajayan, Graphene quantum dots derived from carbon fibers, Nano letters 12(2) (2012) 844-9.
[7] S. Chen, X. Hai, C. Xia, X.W. Chen, J.H. Wang, Preparation of excitation-independent photoluminescent graphene quantum dots with visible-light excitation/emission for cell imaging, Chemistry 19(47) (2013) 15918-23.
[8] Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou, L. Qu, An Electrochemical Avenue to Green-Luminescent Graphene Quantum Dots as Potential Electron-Acceptors for Photovoltaics, Advanced materials 23(6) (2011) 776-780.
[9] L. Wu, H. Yan, J. Xiao, X. Li, X. Wang, Characterization and photocatalytic properties of SiO 2 –TiO 2 nanocomposites prepared through gaseous detonation method, Ceramics International 43(12) (2017) 9377-9381.
[10] T. Zhao, X. Li, Y. Wang, J.H.S. Lee, H. Yan, Growth mechanism and wave-absorption properties of multiwalled carbon nanotubes fabricated using a gaseous detonation method, Materials Research Bulletin 102 (2018) 153-159.
[11] N. Luo, H. Jing, Z. Ma, R. Chen, Gaseous detonation chemical synthesis of onion-like carbons, Mendeleev Communications 27(2) (2017) 195-197.
[12] X. Miao, D. Qu, D. Yang, B. Nie, Y. Zhao, H. Fan, Z. Sun, Synthesis of Carbon Dots with Multiple Color Emission by Controlled Graphitization and Surface Functionalization, Advanced materials 30(1) (2018).
[13] Y. Wang, Y. Li, L. Tang, J. Lu, J. Li, Application of graphene-modified electrode for selective detection of dopamine, Electrochemistry Communications 11(4) (2009) 889-892.
[14] T.V. Khai, H.G. Na, D.S. Kwak, Y.J. Kwon, H. Ham, K.B. Shim, H.W. Kim, Comparison study of structural and optical properties of boron-doped and undoped graphene oxide films, Chemical Engineering Journal 211-212 (2012) 369-377.
[15] S. E, Q.X. Mao, X.L. Yuan, X.L. Kong, X.W. Chen, J.H. Wang, Targeted imaging of the lysosome and endoplasmic reticulum and their pH monitoring with surface regulated carbon dots, Nanoscale 10(26) (2018) 12788-12796.