

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Photochemical synthesis of doped graphene quantum dots and their photoluminescence in aqueous and solid states

Received 00th January 20xx,
Accepted 00th January 20xx

Dezhi Tan,^a Xiaofeng Liu^a and Jianrong Qiu^{*a}

DOI: 10.1039/x0xx00000x

www.rsc.org/

A facile photochemical approach to prepare nitrogen doped graphene quantum dots (NGQDs) has been presented. NGQDs exhibit strong photoluminescence (PL) in both colloid and solid states. Abnormal emission behavior is observed and the mechanism is discussed. The unique solid-state PL of NGQDs inspires new thoughts for novel applications in micro-solid devices.

Graphene quantum dots (GQDs) exhibit unique size-dependent and edge-sensitive photoluminescence (PL) properties as well as excellent biocompatibility, photostability and chemical inertness, which promise great potential for many applications.^{1–3} Until now, tremendous efforts have been stimulated for synthesis of GQDs with different sizes and functionalities by various methods. Unfortunately, strongly acidic or alkaline environment or a time-consuming multi-step process is usually needed.^{1,4} On the other hand, though there are intensive investigations on the optical properties of GQDs and several proposals have been suggested, such as, quantum size effects, edge/surface effects and defect states related radiative recombination, the PL mechanism is still under debate.^{5, 6} The discovery of the novel remarkable optoelectronic and structural properties of GQDs as well as determining the underlying mechanism may revolutionize the scientific and technological community.⁵ Furthermore, most of the PL was detected from the colloid GQDs in past studies and fluorescence quenching may occur in the dry and aggregated state.^{7,8} However, strong PL in solid stated GQDs is necessary for fabrication of advanced devices and other uses (e.g., inks and luminescence pattern printing). In addition, chemical doping is an effective way to tune the optical, chemical, and electronic properties of GQDs. For example, the functional modification with the incorporation of heterogeneous atoms (e.g., nitrogen (N) atoms) in the carbon lattice of GQDs (forming N doping GQDs, NGQDs) can give rise to significantly

enhanced luminescence quantum yield and a widely tunable band gap as well as offering more active sites, which is important for a variety of practical applications in electrocatalysis, photovoltaic and light emitting devices, sensors, biology and biomedicine.^{1,9–11} Interesting upconversion PL was detected from fluorinated GQDs and NGQDs.^{12,13} Tuning PL of GQDs by controlling the oxygen content was also achieved.⁶

Photochemical engineering provides a simple and facile route to fabricate nanostructures and modify their properties.^{14,15} Especially, femtosecond (fs) laser induced photochemical engineering has been used to prepare a series of functional nanomaterials with tunable size, structures, and properties, by adjusting the targets and solutions, recently.^{15–18} Herein, NGQDs are prepared by fs laser irradiating graphene oxide in ammonia aqueous solution. Strong PL is detected from colloid and solid NGQDs. Our results presented here imply the possibility to fabricate GQDs doped, as well as co-doped, with various heterogeneous atoms with tunable contents.

Our strategy in this work is inspired by the extreme local conditions in the fs laser induced photochemical processing, in which complex physical and chemical reactions may happen. For example, due to the ultra-high irradiance of fs laser, a local high temperature and high pressure condition followed by fast cooling can be created, resulting in creation of bubbles and high strain rate, which can cut graphene nanosheets into species (GQDs).^{19, 20} Furthermore, heterogeneous atoms doping is achievable in the photochemical processing of graphene oxide.¹⁸ Therefore, we recognized that it could be possible to prepare doped GQDs using this general and easy method. To validate the research idea, N atom was chosen as the prototypical dopant for its ability to render various intriguing and improved optical functions. Fig. 1a represents the typical transmission electron microscopy (TEM) image of the products, which shows that the size of particles is smaller than 10 nm with the average diameter of 3.5 nm (Fig. S1). The clear atomic lattice structure shown in the high resolution TEM (HRTEM) image (Inset: Fig. 1a) indicates that the NGQDs are crystalline with a lattice spacing of about 0.21 nm (100).²¹

^a School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China. Email: qjr@zju.edu.cn

Electronic Supplementary Information (ESI) available: Experimental details. See DOI: 10.1039/x0xx00000x

Therefore, GQDs were fabricated successfully. X-ray photoelectron spectroscopy (XPS) measurements were

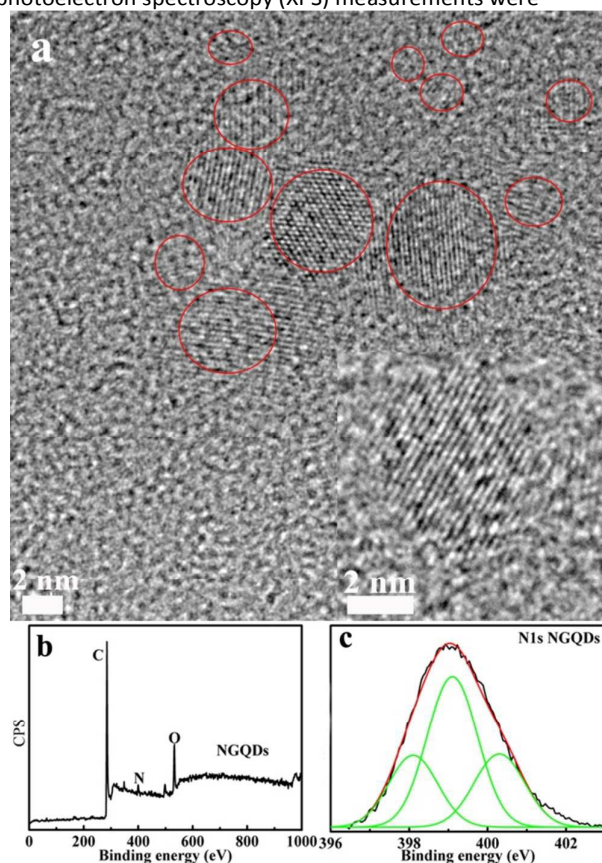


Fig. 1 (a) Typical TEM image, (b) wide XPS spectrum and (c) N 1s spectrum of NGQDs. Inset of a: HRTEM image.

performed to determine the composition of the as-produced NGQDs. The XPS survey spectrum of NGQDs shows a predominant graphitic C 1s peak at about 284 eV, an O 1s peak at about 532 eV and a N 1s peak at about 399 eV (Fig. 1b), which evidence the successful incorporation of N atoms in NGQDs. The calculated C, O and N contents are about 83.1 %, 11.3 % and 5.6 %, respectively. In comparison, the C, O and N contents in the initial parent GO are about 84 %, 16% and 0 %, respectively. The high resolution N 1s XPS spectrum (Fig. 1c) reveals that the existence of pyridinic (398.1 eV), pyrrolic (399.1 eV), and graphitic N atoms (400.3 eV).¹⁸ These results imply that fabrication of NQGDs with tunable N contents may be promising by controlling the ammonia concentration in the solution.²² Choosing appropriate solutions (e.g., H₂S aqueous solution), preparation of QGDs doped by other atoms (e.g., S), as well as multiple kinds of atoms (e.g., N and S), is also potential. The Fourier transform infrared spectroscopy (FTIR) was also used to characterize the surface functional groups, as revealed in Fig. S2. The characteristic bands of the C=C can be found at 1590 cm⁻¹.²³ The C=O groups may be also present at 1600-1700 cm⁻¹.²⁴ The absorption peaks at 3360 cm⁻¹ is due to the stretching vibration of O-H bonding.¹⁶ The bands at around

1260 and 1380 cm⁻¹ are assigned to O-C/N-C stretching vibrations.^{24,25} 1100 cm⁻¹ is attributed to C-OH stretching vibrations.^{16,23} The FTIR results indicate that the NGQDs are functionalized by several kinds of functional groups, which make the NGQDs stable in the solution and induce defects in NGQDs.

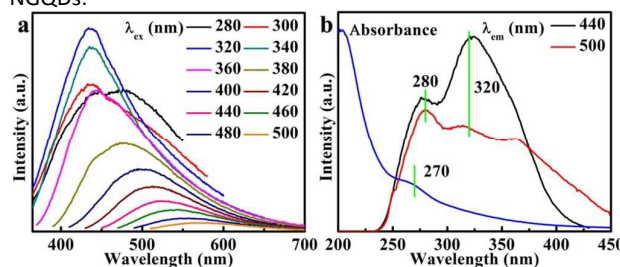


Fig. 2 (a) Emission spectra and (b) absorption spectra and emission spectra at 440 nm and 500 nm of NGQDs.

To explore the optical properties of the NGQDs, we performed a detailed PL study by using different excitation wavelengths. Fig. 2a shows the emission spectra of NGQDs. In contrast to usual excitation-dependent/-independent emission properties, NGQDs prepared in our case exhibit interesting unusual emission behaviors. The emission spectrum is broad with the peak at about 480 nm along with a shoulder at 440 nm, when excited at 280 nm. Their emission peak wavelengths are almost invariant at around 440 nm with respect to the excitation wavelengths from 300 to 360 nm. In contrast, the PL of NGQDs is redshifted with increase of excitation wavelengths from 360 to 500 nm. The observed unusual emission properties suggest that there are different radiative recombinations. As mentioned above, though there several mechanisms are suggested as the PL origin of NGQDs, the exact mechanism is still not fully understood. To get insight into this issue, the absorption and excitation spectra were shown in Fig. 2b. A shoulder at around 270 nm is found in the absorption spectrum of NGQDs, which can be attributed to characteristic $n \rightarrow \pi^*$ transition of the C=N bond.²⁶⁻²⁸ This indicates the presence of defect energy states in NGQDs due to the incorporation of N.^{7,26} Obvious excitation peaks at 280 and 320 nm are observed in the excitation spectra with monitoring emission at 440 and 500 nm, which indicates the presence of two excited energy states determining the emission. For the emission of 440 nm, there is a strong excitation peak at 320 and a relatively smaller peak at 280 nm. Whereas, the excitation peak at 280 nm is stronger than that at 320 nm in the emission spectrum of 500 nm. The change of excitation behaviors reveal that radiative recombinations from these two excited energy states contribute differently to the emission at 440 and 500 nm. Furthermore, it is worth noting that the excitation peak of 280 nm is very close to the absorption shoulder (270 nm). Therefore, we propose that the emission at 440 nm, which is nearly independent of the excitation wavelength, a feature of molecular fluorescence, originates from the radiative electronic transition between the $n \rightarrow \pi^*$ states of the C=N structure conjugated to aromatic

carbons.²⁹ Furthermore, radiative recombination can also happen in the oxidation defect states, resulting from the confirmed presence of oxygen-functional groups, and edge states, which could be the origins of the excitation-dependent PL in this case.^{16,21,23} The PL quantum yield of NGQDs is determined to about 16.7%. We also confirmed that the PL of initial grapheme oxide is negligible, which is rational considering the low content of oxygen.

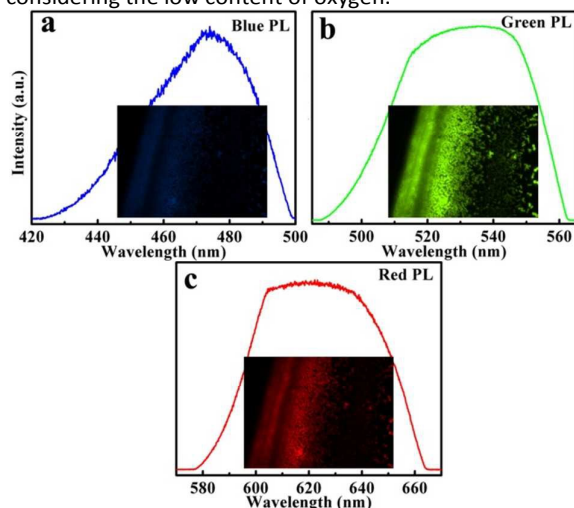


Fig. 3 Emission spectra of dried NGQDs excited by the light with wavelength of 350 ± 25 (a), 470 ± 20 (b), and 545 ± 15 nm (c). Inset: corresponding fluorescence images.

Due to the PL quenching resulting from the aggregation in the dried solid state photoluminescent nanoparticles, the applications of GQDs are significantly limited.^{8,30} So far, there have been very few reports about PL from solid GQDs, especially GQDs not embedded in other matrix.⁸ To underline the potential applications of NGQDs prepared here in micro-optoelectronic devices, printing inks and so on, emission properties were further investigated from NGQDs in the solid state. Colorful PL can be visualized clearly from the fluorescence images by excitation at different wavelengths. Emission spectra of dried NGQDs are shown in Fig. 3 excited by the light with wavelength of 350 ± 25 (a), 470 ± 20 (b), and 545 ± 15 nm (c), which indicate that the prepared NGQDs can also emit strong PL in the solid state, opening the door to more applications, especially in the solid devices. Furthermore, the blue PL excited by 350 ± 25 nm light shows a peak at around 474 nm, which is not in agreement with the result (440 nm) obtained from the NGQDs in the solution. We suggest that this disagreement stems from the aggregation induced PL quenching in the deep blue region, which makes the blue emission with wavelength longer than 440 nm dominate the emission property and is consistent with the previous report.²⁹

In summary, NGQDs have been conveniently prepared by means of a simple and facile method of photochemical engineering. The obtained NGQDs emit tunable PL in both solid and aqueous states. NGQDs exhibit a feature of molecular fluorescence with an invariant emission peak at

around 440 nm excited by the light with wavelength in the range from 280 to 360 nm. Redshifted emission is observed with increase of excited wavelength from 360 to 500 nm. The excitation-independent PL is proposed to originate from the $n\rightarrow\pi^*$ electronic transition of C=N bond and the excitation-dependent PL may result from the radiative recombination determined by defect energy states, resulting from the oxidation and edge structures. Furthermore, decrease of the PL intensity from solid NGQDs in the deep blue region is observed, which is suggested to originate from the aggregation induced quenching. The outstanding characteristics of solid-state PL properties promise highly potential of NGQDs in micro-optoelectronic devices. Our observation and discussions also have general significance in understanding the optical properties of other fluorescent carbon materials.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 51072054, 51132004, and 51102209) and the National Basic Research Program of China (2011CB808100). The authors would like to thank Prof. M. Meunier and Dr. C. Boutopoulos for the PL measurements of solid NGQDs.

Notes and references

- 1 S. Y. Lim, W. Shen and Z. Gao, *Chem. Soc. Rev.*, 2015, **44**, 362.
- 2 L. Wang, Y. Wang, T. Xu, H. Liao, C. Yao, Y. Liu, Z. Li, Z. Chen, D. Pan, L. Sun and M. Wu, *Nat. Comm.*, 2014, **5**, 5357.
- 3 Z. Fan, S. Li, F. Yuan and L. Fan, *RSC Adv.*, 2015, **5**, 19773.
- 4 C. B. Ma, Z. T. Zhu, H. X. Wang, X. Huang, X. Zhang, X. Qi, H. L. Zhang, Y. Zhu, X. Deng, Y. Peng, Y. Han and H. Zhang, *Nanoscale*, 2015, **7**, 10162.
- 5 S. Zhu, Y. Song, X. Zhao, J. Shao, J. Zhang and B. Yang, *Nano Research*, 2015, **8**, 355.
- 6 F. Liu, T. Tang, Q. Feng, M. Li, Y. Liu, N. Tang, W. Zhong and Y. Du, *J. Appl. Phys.*, 2014, **115**, 164307.
- 7 C. Shen, J. Wang, Y. Cao and Y. Lu, *J. Mater. Chem. C*, 2015, **3**, 6668.
- 8 G. S. Kumar, U. Thupakula, P. K. Sarkar and S. Acharya, *RSC Adv.*, 2015, **5**, 27711.
- 9 J. Moon, J. An, U. Sim, S. P. Cho, J. H. Kang, C. Chung, J. H. Seo, J. Lee, K. T. Nam and B. H. Hong, *Adv. Mater.*, 2014, **26**, 3501.
- 10 J. Shen, Y. Zhu, X. Yang and C. Li, *Chem. Commun.*, 2012, **48**, 3686.
- 11 H. X. Wang, J. Xiao, Z. Yang, H. Tang, Z. T. Zhu, M. Zhao, Y. Liu, C. Zhang and H. L. Zhang, *J. Mater. Chem. A*, 2015, **3**, 11287.
- 12 Q. Feng, Q. Cao, M. Li, F. Liu, N. Tang and Y. Du, *Appl. Phys. Lett.*, 2013, **102**, 013111.
- 13 M. Li, W. Wu, W. Ren, H. M. Cheng, N. Tang, W. Zhong and Y. Du, *Appl. Phys. Lett.*, 2012, **101**, 103107.
- 14 F. Liu, N. Tang, T. Tang, Y. Liu, Q. Feng, W. Zhong and Y. Du, *Appl. Phys. Lett.*, 2013, **103**, 123108.
- 15 D. Z. Tan, S. F. Zhou, J. R. Qiu and N. Khusro, *J. Photochem. Photobiol. C*, 2013, **17**, 50.
- 16 D. Z. Tan, S. Zhou, B. Xu, P. Chen, Y. Shimotsuma, K. Miura, and J. R. Qiu, *Carbon*, 2013, **62**, 374.

- 17 G. W. Yang, *Prog. Mater. Sci.*, 2007, **52**, 648.
- 18 D. Z. Tan, X. Liu, Y. Dai, G. Ma, M. Meunier and J. R. Qiu, *Adv. Optical Mater.*, 2015, **3**, 836.
- 19 T. N. Lin, K. H. Chih, C. T. Yuan, J. L. Shen, C. A. J. Lin and W. R. Liu, *Nanoscale*, 2015, **7**, 2708.
- 20 D. Z. Tan, Y. Yamada, S. F. Zhou, Y. Shimotsuma, K. Miura and J. R. Qiu, *Nanoscale*, 2013, **5**, 12092.
- 21 W. Kwon, Y. H. Kim, C. L. Lee, M. Lee, H. C. Choi, T. W. Lee, and S. W. Rhee, *Nano Lett.*, 2014, **14**, 1306.
- 22 L. Guo, Y. L. Zhang, D. D. Han, H. B. Jiang, D. Wang, X. B. Li, H. Xia, J. Feng, Q. D. Chen and H. B. Sun, *Adv. Optical Mater.*, 2014, **2**, 120.
- 23 J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, Li Song, L. B. Alemany, X. Zhan, G. Gao, S. A. Vithayathil, B. A. Kaipparattu, A. A. Marti, T. Hayashi, J. Zhu and P. M. Ajayan, *Nano Lett.*, 2012, **12**, 844.
- 24 S. Sahu, B. Behera, T. K. Maiti and S. Mohapatra, *Chem. Commun.*, 2012, **48**, 8835.
- 25 H. Li, W. Kong, J. Liu, N. Liu, H. Huang, Y. Liu and Z. Kang, *Carbon*, 2015, **91**, 66.
- 26 H. Ding, J. S. Wei and H. M. Xiong, *Nanoscale*, 2014, **6**, 13817.
- 27 J. Moon, J. An, U. Sim, S. P. Cho, J. H. Kang, C. Chung, J. H. Seo, J. Lee, K. T. Nam and B. H. Hong, *Adv. Mater.*, 2014, **26**, 3501.
- 28 L. Tang, R. Ji, X. Li, G. Bai, C. P. Liu, J. Hao, J. Lin, H. Jiang, K. S. Teng, Z. Yang and S. P. Lau, *ACS Nano*, 2014, **8**, 6312.
- 29 Y. Deng, X. Chen, F. Wang, X. Zhang, D. Zhao and D. Shen, *Nanoscale*, 2014, **6**, 10388.
- 30 X. Li, S. Zhang, S. A. Kulinich, Y. Liu and H. Zeng, *Sci. Rep.*, 2014, **4**, 4976.