Up-conversion and Tunable Up-conversion Emission from Nitrogen Functionalized Graphene Quantum Dots

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Abstract. In amidst of conflicts of opinion regarding the presence of up-conversion in carbonaceous nanostructure. We have critically and precisely asserted that there is a real up-conversion in the nitrogen functionalized graphene quantum dots (NGQDs), which is found to be its inherent feature and not a measurement artefact. We have demonstrated that NGQDs exhibit real up-conversion in the blue-green region. To define the perspective of the study a variant of GQDs, NGQDs was synthesized using facile, one-pot synthetic methods. We have critically examined the up-conversion emission in NGQDs, interestingly, N-GQDs exhibited very superior optical properties such as high quantum yield of 97%, up-conversion emission at 535 nm and tunable up-conversion that exhibited a red shift of 12 nm. The two-photon excitation process is the governing phenomenon behind the real up-conversion in NGQDs which is suggested by the quadratic dependence of the integrated intensity on excitation power. Up-conversion can enhance the efficiency of the photovoltaic solar cell by even converting infrared region of sunlight to electricity. Moreover, tunable up-conversion open the door for promising applications of NGQDs in tunable fibre lasers, multicolour displays and multiphoton optical data storage.

Keywords: up-conversion, tunable up-conversion, UPCL, GQDs, NGQDs
1. The Introduction

Carbon quantum dots are one of the most sought carbon nanostructures for research, especially graphene quantum dots (GQDs). Recently, GQDs have appealed the global attention not only for their novel photo-physical features [1] but also for the versatile applications. A significant number of applications of GQDs structures have already been demonstrated in the past decade. Most of the demonstrated applications of GQDs relates to the field of biology due to the benign nature of these nanostructures. Thorough reviews of bioanalytical applications of GQDs can be found in the review articles by Zuo et al.,[2] Wang et al.,[3] and Namdari et al.[4] Luminescence quenching based detection/sensing of analytes is also widely reported for GQDs and NGQDs. Two recent reviews, by Li et al.[5] and Liu et al.[6] summarize the major advances in sensing applications using carbon and graphene based dots. Besides sensing and bio-related applications, GQDs, primarily the GQDs have been used in solar photovoltaics,[7] photodetectors,[8] and light emitting devices,[9-13]. Commencing from the initial reviews on GQDs to the most recent ones [14, 15] it has been noticed that fluorescence property has permanently remained the most striking feature of each and every variety of GQDs. All variants of GQDs display intense PL with extraordinarily high PL quantum yield (PLQY). Remarkably, despite the structural and compositional differences, several variants of GQDs exhibited similar photophysical properties.[16,17] In addition to that there are significant number of reports that claim to observe up-conversion photoluminescence for a variety of carbon dots and GQDs.[1,18-21] However, till date there are many contradictory arguments regarding the up-conversion PL in GQDs, in which one side of the researchers claim it to be the materials property, whereas counterparts argue it to be measurement artefact. In this paradigm, the reliability of up-conversion PL in GQDs has been debateable. Some of the claims of up-conversion PL measured with the white light in GQDs have been refuted by careful successive studies.[22-24] Wen et al. have carefully studied up-conversion in five variants of GQDs and considered this property to be measurement artefact.[25] However, there are significant reports that argue the presence of real up-conversion in GQDs that can be experimentally measured with pulsed laser excitation.[24,26] This work not only critically examine and consolidate up-conversion in GQDs with the help of spatially resolved laser source but it also claims that the observed up-conversion is tunable with the excitation energy. To the best of our knowledge, there is no report on the tunable up-conversion PL in nitrogen functionalized GQDs. To define the perspective of the study a variant of GQDs—that is N-functionalized GQDs (NGQDs) was synthesized using facile, one-pot synthetic methods. We have critically examined the up-conversion PL in NGQDs, interestingly, N-GQDs exhibited very superior optical properties such as high quantum yield, up-conversion emission (two-photon process) and tunable up-conversion.

2. Experimental

2.1 Materials:
Citric acid (Merck, India) and ethylene diamine (SRL) were used for preparation of NGQDs. All chemicals were of high purity and suitable for the synthesis purpose. DI water having 18.2 MΩ·cm resistivity procured from Millipore was used for all experimental requirements.

2.2 Preparation of N-GQDs:
The N-GQDs were synthesized by mixing 2.1 g of CA and 1.8 g ethylene diamine in 50 ml DI water, the solution was mixed properly to make the clear solution before transferring to the Teflon lined 150 mL autoclave. The airtight closed autoclave was heated to 180°C in oil bath and kept for continous 8 hours. Finally, N-GQDs were collected and stored in refrigerator after being centrifuged at 5,000 rpm for 10 min.

2.3 Characterization:
The nano size of the synthesized material was examined by HR-TEM model JEM-2200 FS by JEOL which is armed with 200-kV field emission gun, energy filter (Omega) and Gatan software. In order to do the HR-TEM measurements, the NGQDs samples were diluted to deposit 3 μL of samples on the
carbon coated copper grids and dried. We used a GATAN energy filtered TEM integrated with HR-TEM for EELS study of our samples. The transition of carbon was identified from the spectrum obtained from electron energy loss spectroscopy of the NGQDs. The dried samples of NGQDs were used for doing Fourier transform infrared (FTIR) measurement by using JACSO 4700 LE in ATR mode. Omicron Multiprobe spectrometer (Omicron NanoTechnologyGmbH, UK) was employed to do the X-ray photoelectron spectroscopy (XPS) measurements of the dried sample. This unit is tailored with an EA125 (Omicron) hemispherical analyzer. It is worth noting here that any amount of moisture in the sample may lead to degassing in the vacuum chamber. The absolute PLQY was measured by Horiba made spectrofluorometer having model number as Nanolog model FL3-11. During the measurement the both the slits were fixed at 1nm and integrating time at 0.5 s. PL spectra were recorded using integrating sphere mounted that was mounted inside Nanolog-3 spectrofluorometer and absolute PLQY was estimated by Suzuki et al. [27]. Pulsed excitation measurement was done by using a tunable Ti-Sapphire pulsed laser, named Tsunami from Spectra-Physics. It has maximum power of excitation of 2W and repetition rate of 80 MHz with pulse width ~100 femtoseconds. For spectroscopic measurement with pulsed laser, we have used an Andor Shamrock 303i spectrograph attached with an ultra-sensitive EM-CCD named iXon, also from Andor.

3. Results and Discussion

![Image](image-url)

**Figure 1.** NGQD structural characterization: (a) bright field HRTEM image, inset: the size distribution histogram; (b) high magnification image; (c) SAEDP corresponding to the image in (a); (d) EELS profile of the NGQDs; (e) FTIR spectrum of NGQDs; (f) XPS wide scan spectrum; deconvoluted (g) C1s; (h) N1s spectra and (i) O1s.

The structural and surface features of the prepared NGQDs have been characterized by the above-mentioned techniques and the overall features were summarized in Figure 1. The localized clusters of carbon atoms are confirmed by the appearance of distinguishable dark spots shown in the bright field HR-TEM image of NGQDs in Figure 1a. The histogram shown as an inset exhibited the well distributed size variation of NGQDs from ~1-5 nm with average size of 2.75±0.4 nm. The crystalline
nature of NGQD is revealed by the high magnification image of NGQD shown in Figure 1b, which clearly shows the fringes of 0.31 nm that corresponds to (002) graphitic planes. In addition to that SAEDP corresponding to Figure 1a, also consolidate on its crystallinity by the presence of bright spots that corresponds to the same (002) graphitic planes as shown in Figure 1c.

The electron energy loss spectroscopy (EELS) of the prepared sample, gave the clearer understanding about the NGQDs structure. The low-loss EELS spectrum revealed a π* surface plasmon peak at 5.5 eV and exhibited a peak at 14.2 eV that corresponds to π* + σ* bulk plasmon transition, showed in the Figure 1d. The occurrence of these peaks at obtained location direct towards the formation of graphene layers. Additionally, the peak at 14.2 eV even suggests the formation of 2D layers of graphene.[28, 29] Moreover, the broad but a weak peak at 43.5 nm manifest the incorporation of nitrogen in the graphene layer, confirms the functionalization of GQDs with nitrogen.[30] The outcomes of structural study that is HR-TEM and EELS consequently substantiate the formation of NGQDs. However, to get more insight into the surface of NGQDs, FTIR and XPS analysis was done.

The FTIR spectrum in Figure 1e, confirms the stretching vibrations of N-H and O-H exhibited by the band peaking between 3300-3600 cm\(^{-1}\). The band peaking at 1730 cm\(^{-1}\) and 1560 cm\(^{-1}\) corresponds to the vibrations of C=O and C=C respectively.[31, 32] The efficacious insertion of nitrogen atom in the graphitic structure were revealed by the presence of the bending vibration of C-NH at 1376 cm\(^{-1}\) and by the stretching vibrations of C-N at 1220 cm\(^{-1}\).[33, 34]. To further understand the presence of various surface functional groups and chemical bonding, we have done the XPS measurement of the NGQD dry sample.

The wide scan XPS spectrum exhibited three strong peaks at 285 eV, 400 eV and 530 eV that correspond to C1s, N1s and O1s, respectively, shown in Figure 1f.[35] The peaks exhibited at 284.5eV, 285.8 eV and 287.55 eV correspond to C=C (sp\(^2\) carbon), C-C (sp\(^3\) carbon) and nitrous-carbon,[36]which were exhibited as the deconvoluted components of C1s as shown in Figure 1g. Similarly, XPS spectra of N1s deconvoluted to two components at 399.25 and 400.25 eV corresponds to aromatic-N and surface-NH\(_2\) respectively shown in Figure 1h.[37] In addition to that the high resolution of O1s spectrum also de-convoluted to two components C-O and C=O peaking at 531.1 and 532.2 eV respectively.[9] The presence of Surface NH\(_2\) in N1s peak of high resolution XPS and the peak of N-H bonding vibration in the FTIR could ensure the passivation and functionalization of nitrogen with GQD. The detailed description about the structural and surface features gives the direction to study its controversial property that is up-conversion PL in NGQD.

We have estimated the PLQY of NGQDs sample with help of integrating sphere mounted in the Nanolog spectrofluorometer. The absolute PL QY of the samples was 97% estimated by recording the PL spectra using an integrating sphere following the method proposed by Suzuki et al.[27] which is in agreement with other report.[38] Due to such a unprecedented PLQY and high absorption cross-section,[39] it is anticipated that leakage of even a weak magnitude of lower excitation wavelength is sufficient to produce normal emission output, which could be taken as the up-conversion emission. Thus, remarkably high photon conversion efficiency and unusually high absorption makes NGQDs vulnerable to wrong interpretation of up-conversion emission. Moreover, in order to proclaim on up-conversion emission even with laser excitations, it is necessary to negate the possibilities of exciting the samples with leaking of lower wavelengths. In order to repudiate any possibility of leakage, a spatially resolved excitation of 800 nm was used from Ti–Sapphire, tuneable femtosecond pulsed laser. To precisely negate any possibility of the presence of any other component except 800 nm in the excitation channel, the spatial distance between the 800 nm and any other component happened to be present was increased by using three mirrors as reflectors.
However, in order to understand the mechanism responsible for up-conversion which is intense. It is also important to add here that, the up-conversion signal was observed only with pulsed mode highly concentrated laser beam and not with same laser in continuous wave mode. In order to strengthen our claim, we have also varied the excitation power (P), and estimated the integral intensity to plot the graph of P (log scale) versus integral intensity (log scale) as shown in Figure 2b. The slope of this linearized plot came out to be ~2, that strongly suggest the presence of up-conversion having a two-photon excitation process. [40] Remarkably, it was noticed that with the 800 nm pulsed excitation, NGQDs not only exhibit up-conversion emission but also these emission were found to be tunable with the excitation energy shown in Figure 2c. The up-converted peak at 535 nm clearly shows the red-shift with the increase in the excitation wavelength. The excitation wavelength and up-converted emission peak position is plotted in Figure 2d, that shows distinguishable red-shift and assert tunable up-conversion. This is for the first time that we have observed such interesting features in NGQDs, that open the new door for research in the most explored topic of the time. The outcome of this work is summarized and compared with other related work in the Table 1. Tunable up-conversion is promising for the potential application in tunable fiber lasers, multicolor displays and multiphoton optical data storage. However, in order to understand the mechanism responsible for up-conversion and tunable up-conversion observed in NGQDs warrant a separate investigation.

Figure 2. (a) Up-conversion spectra in NGQDs under excitation with the 800 nm femtosecond pulsed laser; (b) Integral intensity versus Excitation power (log-log scale); (c) Up-converted emission spectra of NGQDs measured with 800 nm femtosecond laser; (d) Excitation wavelength and up-converted emission peak position.
Table 1. Comparison of summary of present work with other related work

| Sample          | PLQY | Laser Excitation/ White light | Up-converted Emission | Up-conversion red shift | Ref |
|-----------------|------|-------------------------------|-----------------------|-------------------------|-----|
| NGQDs           | 97%  | Laser 800 nm                  | Up-converted peak 535 nm | 12 nm                  | This work |
| NGQDs           | 99%  | -                             | No Upconversion       | -                       | [38] |
| Carbon dots/ GQD| -    | Laser and white light         | Upconversion refuted  | -                       | [22-25] |
| Carbon dots/ GQD| -    | Laser                         | Real Upconversion reported | -                       | [24, 26] |

4. Conclusions

In amidst of conflicts of opinion regarding the presence of up-conversion in carbonaceous nanostructure. We have critically and precisely asserted that there is a real up-conversion in the NGQDs, which is its inherent feature and not a measurement artefact. The prepared N-GQDs exhibited very superior optical properties such as high PL quantum yield of 97%, up-conversion emission at 535 nm and tunable up-conversion that exhibited a red shift of 12 nm. However, the up-conversion signal was observed only with pulsed mode highly concentrated laser beam and not with same laser in continuous wave mode. The two-photon excitation process is the governing phenomenon behind the real up-conversion in NGQDs which is suggested by the quadratic dependence of the integrated intensity on excitation power. To understand the mechanism responsible for up-conversion and tunable up-conversion observed in NGQDs warrant a separate investigation. Up-conversion can enhance the efficiency of the photovoltaic solar cell by even converting infrared region of sunlight to electricity. Moreover, tunable up-conversion open the door for promising applications of NGQDs in tunable fibre lasers, multicolour displays and multiphoton optical data storage.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Yan Y, Gong J, Chen J, Zeng Z, Huang W, Pu K, Liu J and Chen P 2019 Recent advances on graphene quantum dots: from chemistry and physics to applications Adv. Mater. 31 1808283
[2] Zuo P, Lu X, Sun Z, Guo Y and He H 2016 A review on syntheses, properties, characterization and bioanalytical applications of fluorescent carbon dots Microchim. Acta 183 519-42
[3] Wang J and Qiu J 2016 A review of carbon dots in biological applications J. Mater. Sci. 51 4728-38
[4] Namdari P, Negahdari B and Eatemadi A 2017 Synthesis, properties and biomedical applications of carbon-based quantum dots: An updated review Biomed. Pharmacother. 87 209-22
[5] Li M, Chen T, Gooding J J and Liu J 2019 Review of carbon and graphene quantum dots for sensing ACS sensors 4 1732-48
[6] Liu M L, Chen B B, Li C M and Huang C Z 2019 Carbon dots: Synthesis, formation mechanism, fluorescence origin and sensing applications Green Chem. 21 449-71
[7] Essner J B and Baker G A 2017 The emerging roles of carbon dots in solar photovoltaics: a critical review Environ. Sci. Nano 4 1216-63

[8] Mihalache I, Radoi A, Pascu R, Romanian C, Vasile E and Kusko M 2017 Engineering graphene quantum dots for enhanced ultraviolet and visible light p-Si nanowire-based photodetector ACS Appl. Mater. Interfaces 9 29234-47

[9] Tang L, Ji R, Cao X, Lin J, Jiang H, Li X, Teng K S, Luk C M, Zeng S and Hao J 2012 Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots ACS nano 6 5102-10

[10] Zheng M, Liu S, Li J, Qu D, Zhao H, Guan X, Hu X, Xie Z, Jing X and Sun Z 2014 Integrating oxaliplatin with highly luminescent carbon dots: an unprecedented theranostic agent for personalized medicine Adv. Mater. 26 3554-60

[11] Zhang X, Zhang Y, Wang Y, Kalytchuk S, Kershaw S V, Wang Y, Wang P, Zhang T, Zhao Y and Zhang H 2013 Color-switchable electroluminescence of carbon dot light-emitting diodes ACS nano 7 11234-41

[12] Li C-X, Yu C, Wang C-F and Chen S 2013 Facile plasma-induced fabrication of fluorescent carbon dots toward high-performance white LEDs J. Mater. Sci. 48 6307-11

[13] Wang F, Kreiter M, He B, Pang S and Liu C-y 2010 Synthesis of direct white-light emitting carbogenic quantum dots Chem. Commun. 46 3309-11

[14] Baker S N and Baker G A 2010 Luminescent carbon nanodots: emergent nanolights Angew. Chem. Int. Ed. 49 6726-44

[15] Mintz K J, Zhou Y and Leblanc R M 2019 Recent development of carbon quantum dots regarding their optical properties, photoluminescence mechanism, and core structure Nanoscale 11 4634-52

[16] Cao L, Meziani M J, Sahu S and Sun Y-P 2012 Photoluminescence properties of graphene versus other carbon nanomaterials Acc. Chem. Res. 46 171-80

[17] Siddique A B, Pramanick A K, Chatterjee S and Ray M 2018 Amorphous Carbon Dots and their Remarkable Ability to Detect 2, 4, 6-Trinitrophenol Sci. Rep. 8 9770

[18] Cao L, Wang X, Meziani M J, Lu F, Wang H, Luo P G, Lin Y, Harruff B A, Veca L M and Murray D 2007 Carbon dots for multiphoton bioimaging J. Am. Chem. Soc. 129 11318-9

[19] Hutton G A, Martindale B C and Reisner E 2017 Carbon dots as photosensitisers for solar-driven catalysis Chem. Soc. Rev. 46 6111-23

[20] Wang H, Revia R, Wang K, Kant R J, Mu Q, Gai Z, Hong K and Zhang M 2017 Paramagnetic properties of metal-free boron-doped graphene quantum dots and their application for safe magnetic resonance imaging Adv Mater 29 1605416

[21] Li J-Y, Liu Y, Shu Q-W, Liang J-M, Zhang F, Chen X-P, Deng X-Y, Swihart M T and Tan K-J 2017 One-pot hydrothermal synthesis of carbon dots with efficient up-and down-converted photoluminescence for the sensitive detection of morin in a dual-readout assay Langmuir 33 1043-50

[22] Zhuo S, Shao M and Lee S T 2012 Upconversion and downconversion fluorescent graphene quantum dots: ultrasonic preparation and photocatalysis ACS nano 6 1059-64

[23] Tan D, Zhou S and Qiu J 2012 Comment on upconversion and downconversion fluorescent graphene quantum dots: ultrasonic preparation and photocatalysis ACS nano 6 6530-1

[24] Shao M and Zhuo S 2012 Reply to Comment on Upconversion and Downconversion Fluorescent Graphene Quantum Dots: Ultrasonic Preparation and Photocatalysis ACS nano 6 6532

[25] Wen X, Yu P, Toh Y-R, Ma X and Tang J 2014 On the upconversion fluorescence in carbon nanodots and graphene quantum dots Chem Comm. 5 4703-6

[26] Gan Z, Wu X, Zhou G, Shen J and Chu P K 2013 Is there real upconversion photoluminescence from graphene quantum dots? Adv. Opt. Mater. 1 554-8
[27] Suzuki K, Kobayashi A, Kaneko S, Takehira K, Yoshihara T, Ishida H, Shiina Y, Oishi S and Tobita S 2009 Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector Phys. Chem. Chem. Phys. 11 9850-60
[28] Gass M H, Bangert U, Bleloch A L, Wang P, Nair R R and Geim A 2008 Free-standing graphene at atomic resolution Nat. Nanotechnol. 3 676
[29] Jiang D-e, Du M-H and Dai S 2009 First principles study of the graphene/Ru (0001) interface J. Chem. Phys. 130 074705
[30] Tang L, Ji R, Li X, Teng K S and Lau S P 2013 Energy-level structure of nitrogen-doped graphene quantum dots J. Mater. Chem. C 1 4908-15
[31] Tetsuka H, Nagoya A, Fukusumi T and Matsui T 2016 Molecularly designed, nitrogen-functionalized graphene quantum dots for optoelectronic devices Adv. Mater. 28 4632-8
[32] Ţucureanu V, Matei A and Avram A M 2016 FTIR spectroscopy for carbon family study Critical reviews in analytical chemistry 46 502-20
[33] Zhang H, Chen Y, Liang M, Xu L, Qi S, Chen H and Chen X 2014 Solid-phase synthesis of highly fluorescent nitrogen-doped carbon dots for sensitive and selective probing ferric ions in living cells Anal. Chem. 86 9846-52
[34] Qu D, Zheng M, Du P, Zhou Y, Zhang L, Li D, Tan H, Zhao Z, Xie Z and Sun Z 2013 Highly luminescent S, N co-doped graphene quantum dots with broad visible absorption bands for visible light photocatalysts Nanoscale 5 12272-7
[35] Qu D, Zheng M, Zhang L, Zhao H, Xie Z, Jing X, Haddad R E, Fan H and Sun Z 2014 Formation mechanism and optimization of highly luminescent N-doped graphene quantum dots Sci. Rep. 4 5294
[36] Liu S, Tian J, Wang L, Zhang Y, Qin X, Luo Y, Asiri A M, Al-Youbi A O and Sun X 2012 Hydrothermal treatment of grass: a low-cost, green route to nitrogen-doped, carbon-rich, photoluminescent polymer nanodots as an effective fluorescent sensing platform for label-free detection of Cu (II) ions Adv. Mater. 24 2037-41
[37] Yang Y, Cui J, Zheng M, Hu C, Tan S, Xiao Y, Yang Q and Liu Y 2012 One-step synthesis of amino-functionalized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan ChemComm. 48 380-2
[38] Khan F and Kim J H 2018 N-Functionalized Graphene Quantum Dots with Ultrahigh Quantum Yield and Large Stokes Shift: Efficient Downconverters for CIGS Solar Cells ACS Photonics 5 4637-43
[39] Sun J, Xin Q, Yang Y, Shah H, Cao H, Qi Y, Gong J R and Li J 2018 Nitrogen-doped graphene quantum dots coupled with photosensitizers for one-/two-photon activated photodynamic therapy based on a FRET mechanism ChemComm. 54 715-8
[40] Pollnau M, Gamelin D R, Lüthi S, Güdel H and Hehlen M P 2000 Power dependence of upconversion luminescence in lanthanide and transition-metal-ion systems Phys. Rev. B 61 3337