

Supporting/Supplementary Information

Title: Amino-functionalized Graphene Quantum Dots: Origin of Tunable Heterogeneous Photoluminescence

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Supplementary Information

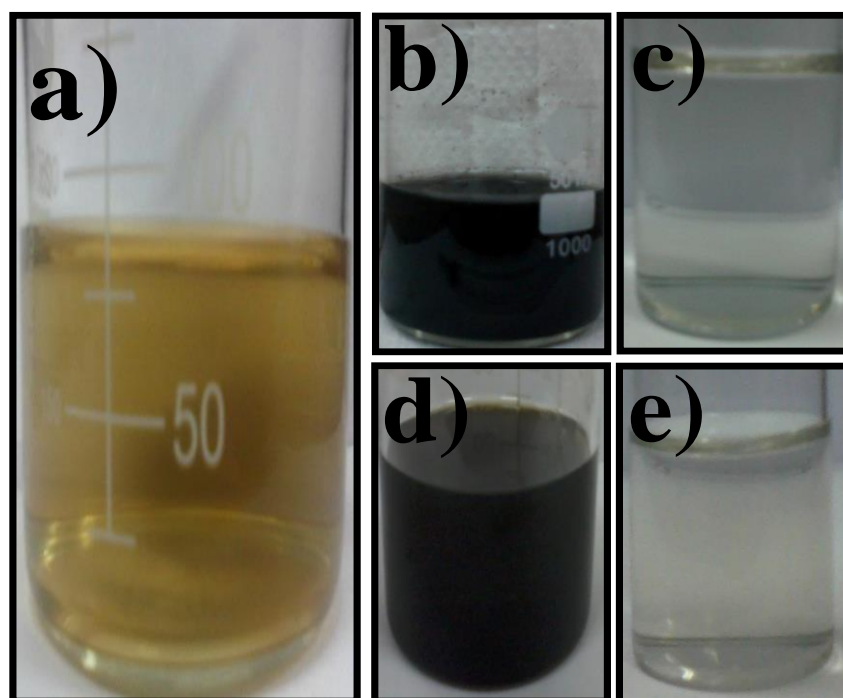


Figure S1. Digital photographs of (a) GO, (b, c) GQDs and (d, e) QGFs solutions at different stages of synthesis. (b) represents GQDs synthesis after hydrothermal reaction from starting GO. (c) obtained final resultant GQD solution. (d) represents QGFs synthesis after open atmosphere heat treatment from starting GO. (e) obtained final resultant QGFs solution

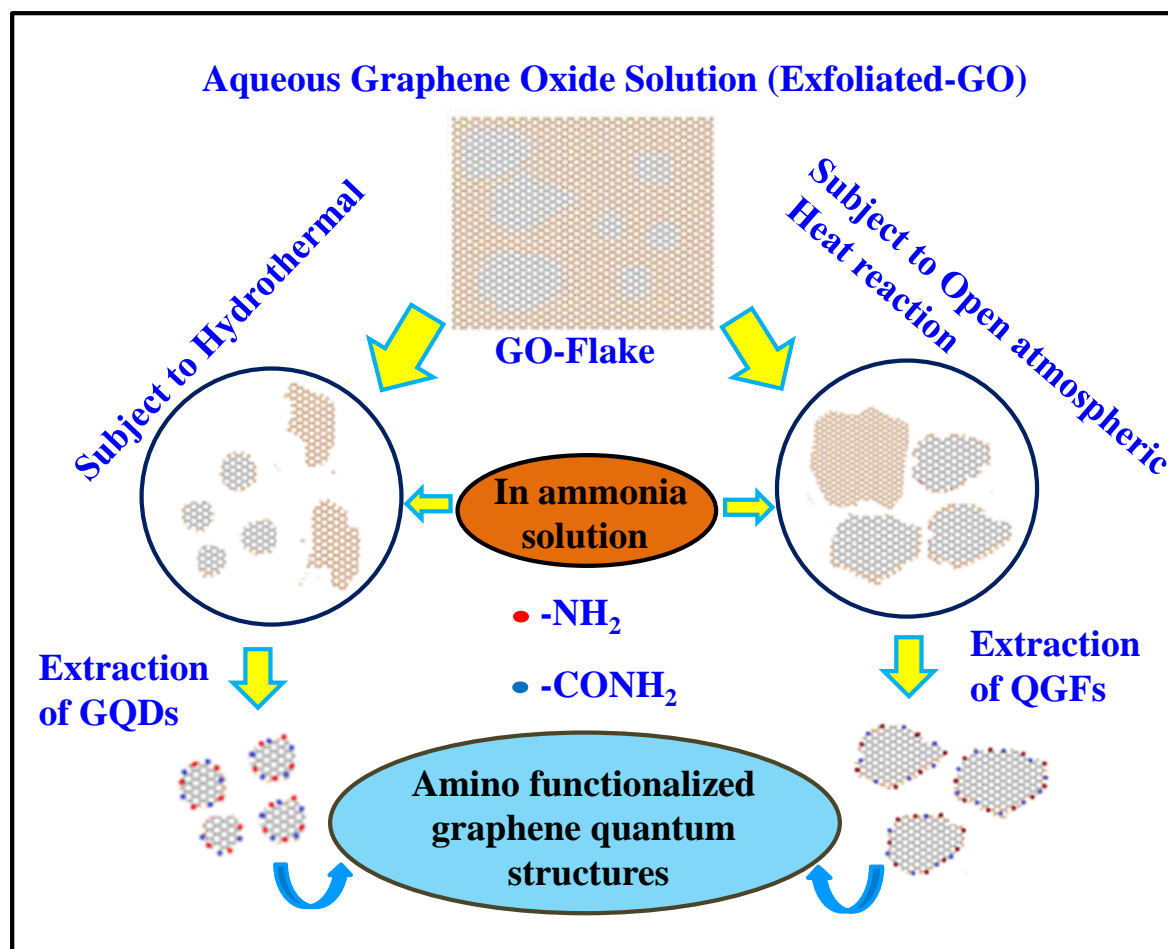


Figure S2. Schematic representation of the synthesis mechanism to obtain the amino-functionalized quantum graphene structures (GQDs and QGFs)

Characterizations

The synthesized GQDs and QGFs solution samples have been characterized for structural, compositional and optical analysis. HRTEM analysis was done (JOEL-2100) to ascertain the structural attributes and lattice parameter of the materials. FTIR analysis was carried out by using Shimadzu-IR Prestige-21 spectrometer and XPS (monochromatic Al K_{α} ($h\nu = 1486.6$ eV) X-ray source and a hemispherical analyzer by SPECS, HSA 3500. The recorded spectra were charge corrected using the C1s line of the adventitious carbon at 284.4 eV as a reference was done to determine the nature of bonding and the different functional groups being present in the quantum structures and for elemental compositional analysis. Similarly RAMAN spectroscopy was conducted using (WITEC alpha, 300R) to confirm the successful synthesis of the carbon materials. Finally UV-Vis (Shimadzu UV 1700 spectrophotometer) characterizations were conducted to observe the optical absorption edge in the quantum structures. Photoluminescence (Horiba Jobin Yvon Fluoromax-4) and time decay analysis (picosecond diode laser in IBH Fluorocube apparatus JY-IBH-5000M) were carried out to investigate the excitation wavelength

dependent tunable heterogeneous photoluminescence conversion along with computation of time decay profiles for corresponding band to band and interstate to band transitions.

Our first-principles calculations were performed by CASTEP code¹ which implements a supercell approach to density functional theory (DFT). Perdew–Burke–Ernzerhof (PBE) functional² within the generalized gradient approximation (GGA) was used to deal with exchange and correlation term. Vanderbilt ultrasoft pseudo potential³ was used to represent the carbon atoms and plane waves up to energy cut off 500 eV was used in the calculation. Brillouin zone integrations were performed within the Monkhorst Pack scheme⁴ using $1 \times 1 \times 1$ k-point mesh. For geometrical optimization, the system was allowed to fully relax using BFGS (Broyden-Fletcher-Goldfarb-Shanno) scheme⁵ until the total energy converged to less than 2×10^{-5} eV/atom, the maximum force converged to lower than 0.05 eV/Å and the maximum displacement was 0.002 Å. All calculations were performed in spin-unrestricted manner. Graphene surface was built by cleaving the optimized graphite (space group P63/MMC) structure. Thus obtained graphene unit cell consisted of two carbon atoms and had lattice parameter of $a = b = 2.461$ Å. A vacuum slab of length 15 Å was used along c axis to ward off the spurious interaction with its own periodic image. A graphene flake containing 52 atoms was built from the above structure using a $6 \times 6 \times 1$ unit cell. For such configuration, nearest C-C distance between a flake and its periodic image was found to be ~ 17 Å, which is large enough to not induce any false interaction. A DV 5 8 5 defect was introduced in the model of the graphene flake by removing two adjacent carbon atoms and subsequently relaxing the structure. Subsequently we modified our graphene flake under the following conditions to simulate the quantum structures. 1. Periodic pristine graphene structure with DV 5 8 5 defect. 2. DV 5 8 5 defect with H-termination at the zig-zag edges (52 C and 18 H atoms) and 3. DV 5 8 5 defect with amino-group termination (NH_2 , $\text{O}=\text{C}-\text{NH}_2$: 58 C, 36 H, 18N and 6 O atoms).

FTIR and XPS analysis

Figure S3 (a) represents the FTIR absorption spectra for all the samples. For better analysis to determine the various structural vibrational modes, we have compared the two quantum structures with that starting GO material used for synthesis. It was revealed that in GO the absorption peaks at 1082 cm^{-1} , 1444.6 cm^{-1} & 1535.5 cm^{-1} , 1641 cm^{-1} & 1705 cm^{-1} , $3200-3450 \text{ cm}^{-1}$ can be assigned to C-O, C-O-C (epoxy), C=O (carbonyl) and OH (hydroxyl) groups respectively. After the reaction with ammonia, new peaks appeared for both GQDs and QGFs at 1159.2 cm^{-1} , 1525 cm^{-1} and $2900-3200 \text{ cm}^{-1}$ which can be attributed to C-N (nitril), N-H (amino)

out of plane and N-H in plane stretching of the amine groups. Additionally amide-carbonyl (–NH-CO–) stretching vibration was observed at 1652 cm^{-1} in both GQDs and QGFs. This indicated towards the formation of amide groups through interactions with the carboxylic groups as Lewis acids. From FTIR Plot, it was also revealed that hydroxyl groups from starting GO are absorbed at $\sim 3200\text{-}3450\text{ cm}^{-1}$. After the reaction with ammonia, “NH in plane” groups were observable at $\sim 2900\text{-}3200\text{ cm}^{-1}$ and formed through nucleophilic substitution reaction with ammonia by ring opening reaction.⁶ This implies primary amine insertion took place at the edges in place of oxygenated moieties in both the structures.

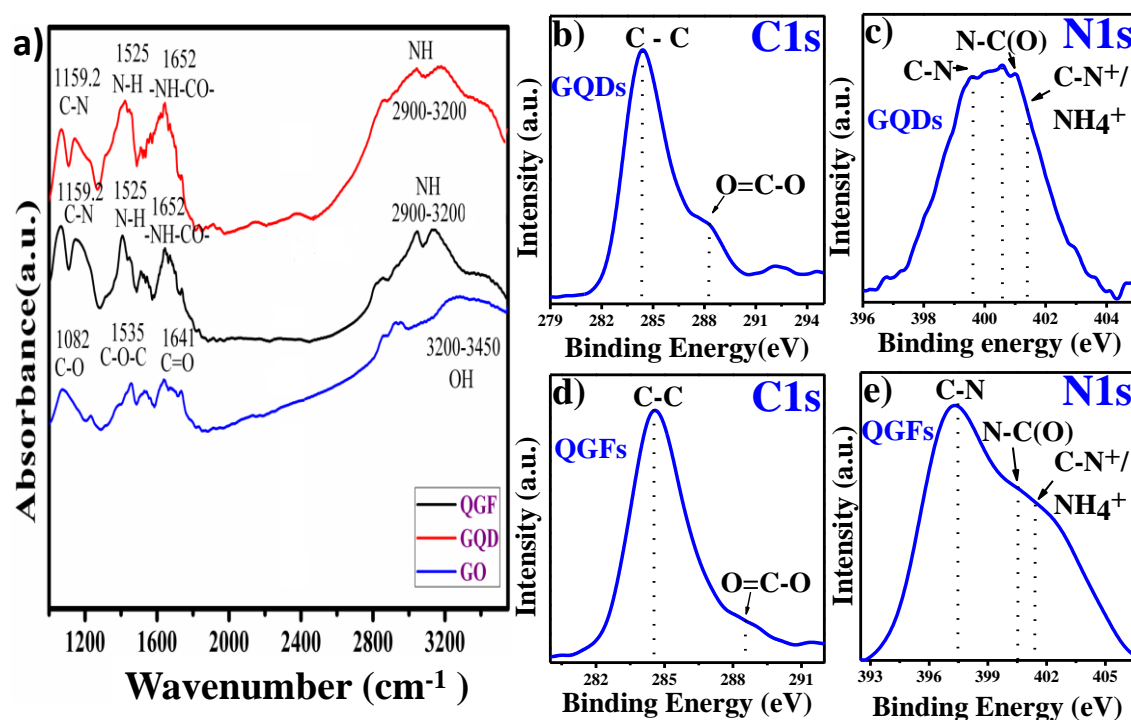


Figure S3. (a) FTIR absorption spectra for GO, GQDs and QGFs. (b, d) represents C1s core level XPS spectra for GQDs and QGFs and (c, e) represents N1s core level XPS spectra for GQDs and QGFs respectively

Figure S3 (b, d) and (c, e) represents C1s and N1s core level XPS spectra for GQDs and QGFs respectively. In GQDs, the presence of main peak at 284.4 eV can be attributed to C-C corresponding to sp^2 domains. This implied that most of the C atoms in the graphene are arranged in a conjugated honeycomb lattice. The small peak at higher binding energy indicates the existence of small amount of oxygenated groups, containing the O=C-(O) at 288.26 eV. The disappearance of the secondary C 1s signal at 286.4 eV, which is assigned to epoxide groups, is a manifestation of the loss of epoxide groups through nucleophilic substitution reaction with ammonia. Similarly the presence of amino functional groups is confirmed by N1s spectra. The

peak present at the 399.66 eV is assigned to the amino group (NH_2) and 400.6 eV is assigned to the amide carbonyl group ($\text{O}=\text{C}-\text{NH}_2$)⁶⁻⁸ represent the amino and amide-carbonyl functionalization at the edges of the graphene quantum dots. This functionalization of the amino functional groups NH_2 and $\text{O}=\text{C}-\text{NH}_2$ are also confirmed by the FTIR spectra.

For the QGFs, the primary peak at 284.58 eV in C1s can be attributed C-C corresponding to sp^2 domains. At higher binding energy the small humps indicates the existence of small amount of oxygenated groups, containing the $\text{O}=\text{C}-\text{O}$ at 288.43 eV. We also found the absence of the epoxide moieties at 286.4 eV after nucleophilic substitution reaction with ammonia like in the GQDs. From the N1s spectra, the peak present at the 397.43 eV is assigned to amino group (NH_2) and 400.6 eV is assigned to the amide-carbonyl group ($\text{O}=\text{C}-\text{NH}_2$) in the quantum graphene flakes. Although the primary N1s peak position belonging to the amino groups in GQDs and QGFs are different, however this subtle shift from 399.6 eV to 397.43 eV can be expected due to the changes in the synthesis conditions.

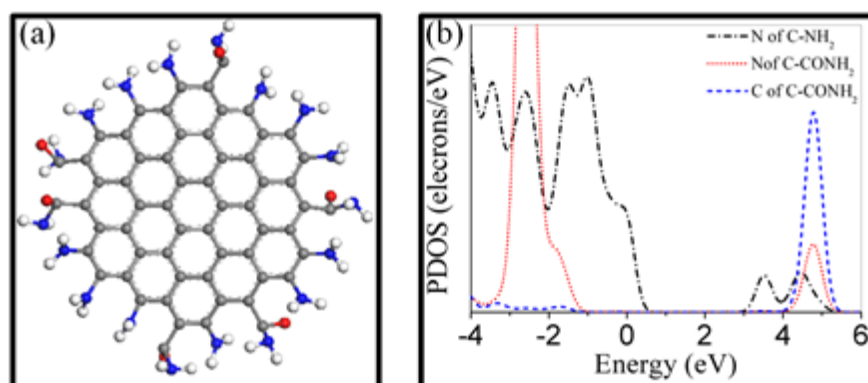


Figure S4. (a, b) represents the model and DOS of the amino functionalized graphene quantum structure model without the presence of DV 5 8 5 defect

Figure S4 represents the model and the DOS of our graphene quantum structure with amino functionalization without the presence of DV 5 8 5 defect: We propose that the PL emission with higher time decay is due to the formation of interband as a result of amino functionalization. Primarily the amine edge termination was responsible for this. It was observed further that even without the presence of DV 5 8 5 in the structure the interband formation took place and its position remained unchanged. The DV 5 8 5 represented the more realistic model of graphene quantum dot, necessary to understand the role of defect. For this particular phenomenon the model can be considered as generic.

TABLE T1: The weighting parameters of fitted Time decay curves are listed below:

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A ₁	A ₂	A ₃	χ^2	Average Decay Time (τ_{avg}) (ns)
GQDs at 310 Ex.	2.897	8.822	0.704	39.16	35.03	25.81	1.047	6.68
GQDs at 410 Ex.	2.954	9.091	0.653	35.45	59.39	5.15	1.002	8.10
QGFs at 310 Ex.	3.068	8.843	0.686	44.78	36.16	19.06	1.021	6.92
QGFs at 410 Ex.	2.317	8.750	0.287	24.16	71.81	4.03	1.132	8.21

References (Supplementary)

- 1 M. D. Segall, J. D. L. Philip, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C Payne, First-principles simulation: ideas, illustrations and the CASTEP code, *Journal of Physics: Condensed Matter*, 2002, **14**, 2717-2744.
- 2 J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Physical Review Letters*, 1996, **77**, 3865-3868.
- 3 D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Physical Review B*, 1990, **41**, 7892-7895.
- 4 J. D. Pack, H. J. Monkhorst, "Special points for Brillouin-zone integrations"-a reply, *Physical Review B*, 1977, **16**, 1748-1749.
- 5 B. G. Pfrommer, M. Côté, S. G. Louie, M. L. Cohen, Relaxation of Crystals with the Quasi-Newton Method, *Journal of Computational Physics*, 1997,**131**, 233-240.
- 6 H. Tetsuka, R. Asah, A. Nagoy, K. Okamoto, I. Tajima, R. Ohta, A. Okamoto, Optically Tunable Amino-Functionalized Graphene Quantum Dots, *Adv.Mater.*, 2012, **24**, 5333-5338.
- 7 M. Li, S. K Cushing, X. Zhou, S. Guo, N. Wu, Fingerprinting photoluminescence of functional groups in graphene oxide, *J. Mater. Chem.* 2012, **22**, 23374-23379.
- 8 O. C. Compton, D. A Dikin, K. W. Putz, L. C Brinso, S. T. Nguyen, Electrically Conductive "Alkylated" Graphene Paper via Chemical Reduction of Amine-Functionalized Graphene Oxide Paper, *Adv. Mater.*2010, **22**,892-896.