Electronic Supplementary Information (ESI)

Efficient synthesis of rice based graphene quantum dots and their fluorescent properties

Hemen Kalita[a,1], Jeotikanta Mohapatra[b,1], Lina Pradhan[b], Arijit Mitra[a], Dhirendra Bahadur[c], Mohammed Aslam[a,*]

[a]*Department of Physics,* [b]*Centre for Research in Nanotechnology & Science (CRNTS)*

[c]*Department of Metallurgical Engineering and Materials Science,*

IIT Bombay, Powai, Mumbai, India 400076

[1]*These authors contributed equally to this work*

[*]*Author to whom correspondence should be addressed: m.aslam@iitb.ac.in*

Experimental section

Synthesis of GQDs from rice:

Cleaned rice powder extracted from rice grain is fried in a hot plate at around 200 ^{0}C. Different batches of rice powder are taken and heated for different time. The size of GQDs was controlled by varying the heating time as 3 min (2 nm), 5 min (4 nm), 7 min (5.2 nm) and 10 min (6.5 nm), respectively. To disperse out different batches GQDs in the solution, the fried rice powder samples are sonicated in DI water for about 30 min to get a light brownish to dark brownish color solution. Sample is then filtered through the millipore porous membrane (0.22 μm pore size) by using vacuum filtration technique and the filtrate was collected. The filtrate was then washed and dialyses for 2-3 days in an acidic medium to remove any unwanted carbohydrates and then the purified samples were used for further characterizations.

Functionalization of GQDs with oleylamine:

To functionalize GQDs with amine, 200 mg of GQDs powder were added to 5 ml of oleylamine. The mixture was first heated to 120 °C for 30 min. Then temperature was increased to 180 °C for 4 hrs. Like pristine GQDs, amine functionalized GQDs (amine-GQDs) also show excitation dependent PL emission (Fig. S5).

Photoluminescence (PL) quantum yield measurements:

The PL quantum yield is defined as the ratio of photons absorbed to photons emitted was measured using rhodamine B as a reference. [1] The quantum yield of GQDs in water was calculated according to:

$$\varphi = \varphi_r \times \frac{A_r}{A} \times \frac{I}{I_r} \times \frac{\eta^2}{\eta_r^2}$$

Where φ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index (1.33 for water) and A is the optical density. The subscript 'r' refers to the reference standard with known quantum yield. In order to minimize absorption effects, absorbencies for 10 mm fluorescence cuvette were kept below 0.1 at the excitation wavelength of 340 nm. Rhodamine B in water (QY = 0.31) is chosen as the standard.

Table S1. Peak position and integrated intensity values (%) of the deconvoluted components of the C1s core level of as prepared GQDs

De-convoluted peak positions (eV)							
Sample	sp^2C	sp^3C	C-O (286.5)	C=O (287.4)	COOH (288.4)	π-π* (289.6)	O/C ratio
GQDs	43	19	10	10	12	6	0.44

Table S2. Relative QYs of different sized GQDs and amine-GQDs with Rhodamine B as reference.

Sample specification	Integrated emission intensity (I)	Abs. at 340 nm (Å)	Refractive index of solvent (η)	Quantum Yield (φ)
Rhodamine B	31608	0.027	1.33	0.31
GQDs -6.5 nm	29939	0.05	1.33	0.16
GQDs-5.2 nm	32698	0.05	1.33	0.17
GQDs-4 nm	43948	0.05	1.33	0.23
GQDs-2 nm	46261	0.05	1.33	0.24
Amine-GQDs (6.5 nm)	26566	0.014	1.37	0.54

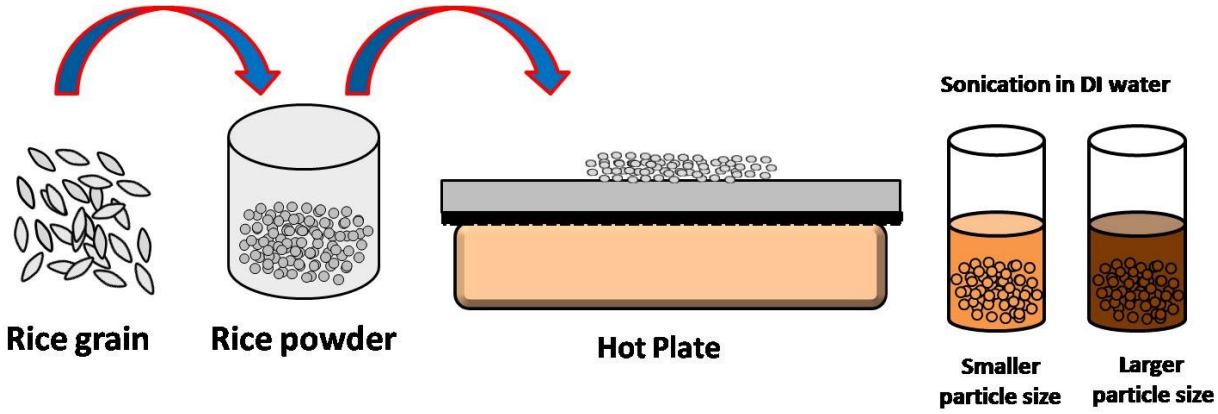

Fig. S1 Schematic of the experimental set-up

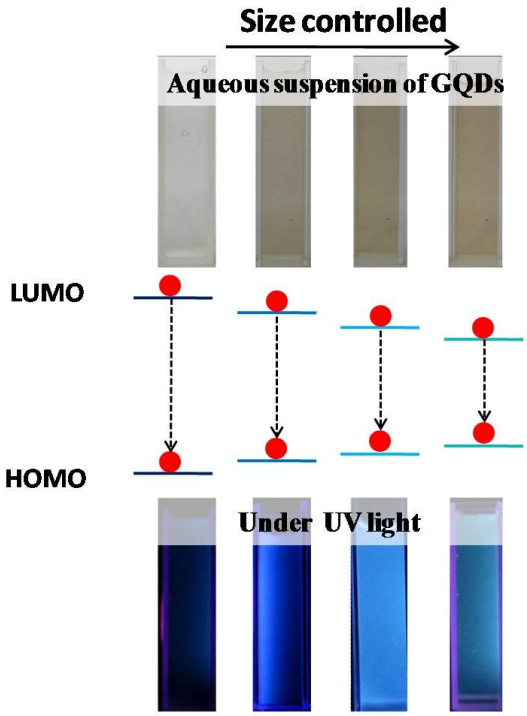

Fig. S2 Shows the optical image of the GQDs alongwith the change in luminescence from blue to cyan under the UV light illumination (λ = 336 nm) with the increase in size under the scheme of band gap change with size.

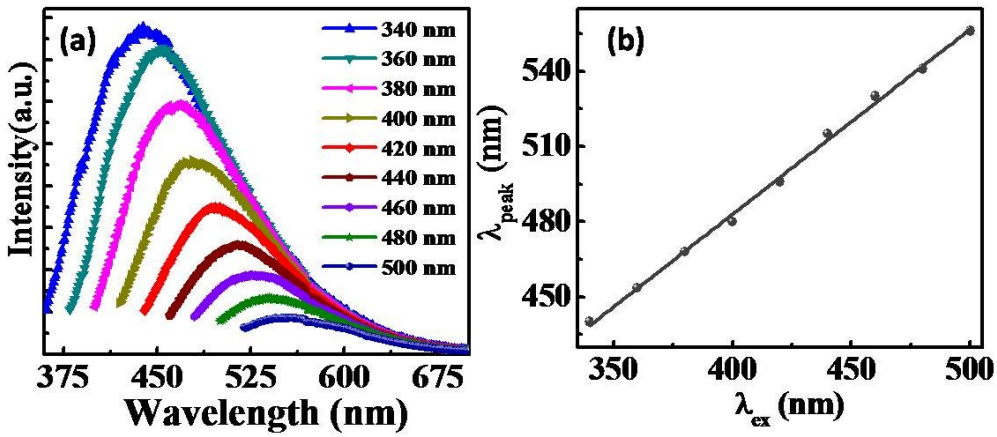

Fig. S3 (a) Excitation dependence PL spectra of GQDs of size 4 nm and (b) Respective linear relationship between the emission wavelength λ_{em} and excitation wavelength, λ_{exc} of the GQD.

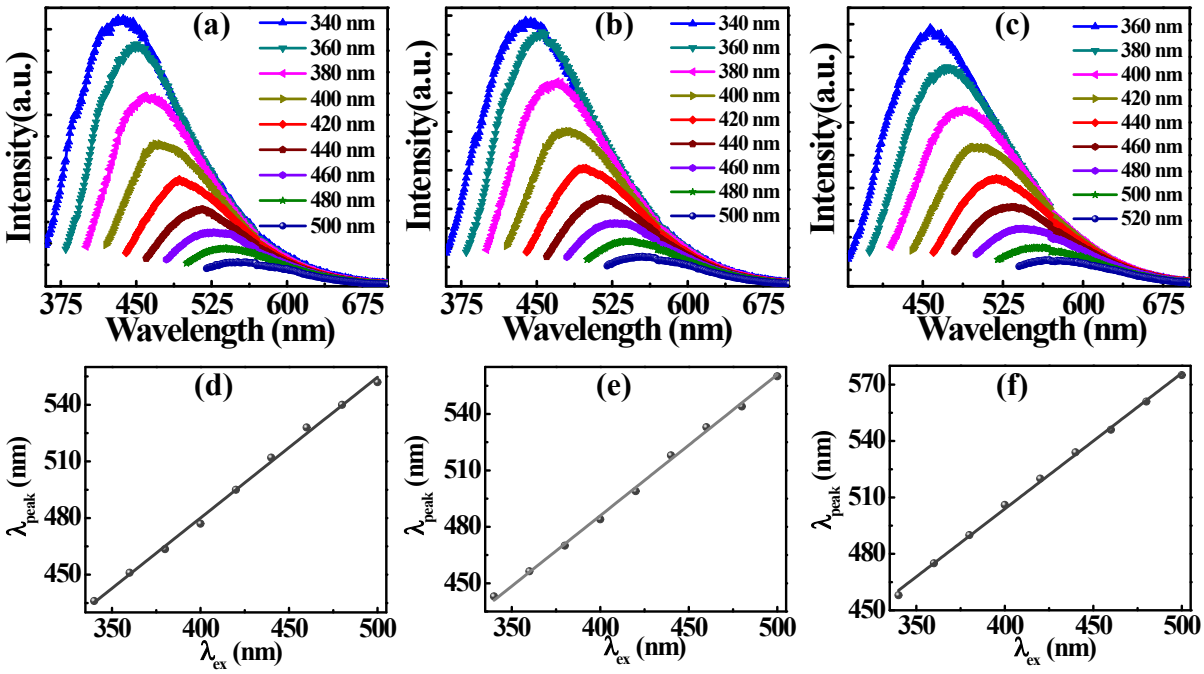

Fig. S4 Excitation dependence PL spectra of GQDs of size: (a) 2 nm (b) 5.2 nm (c) 6.5 nm. Respective linear relationship between the emission wavelength λ_{em} and excitation wavelength, λ_{exc} of the GQD of size (d) 2 nm, (e) 5.2 nm and (f) 6.5 nm.

Gram scale synthesis:

In a typical synthesis of large scale (1.4 g scale) GQDs, 2.5 g cleaned rice grain are taken and powder is made out of it and then fried it in a hot plate for 10 min. To disperse out the GQDs in the solution, the fried rice samples are sonicated in DI water for about 30 min to get a light brownish color solution. The rest procedure is same as discussed in the experimental section.

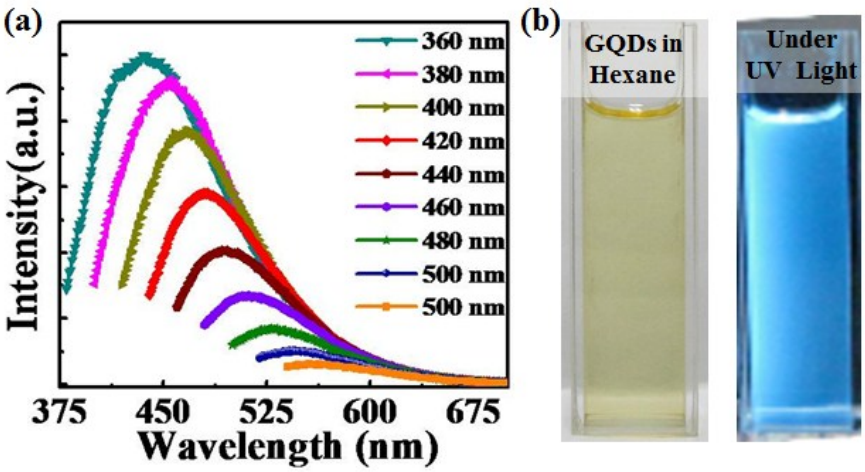

Fig. S5 (a) The PL spectra of amine-GQDs at 340-480 nm excitation wavelengths. The photographs of the hexane dispersion of GQDs suspension: (b) without and (c) with illumination of UV light (λ = 336 nm).

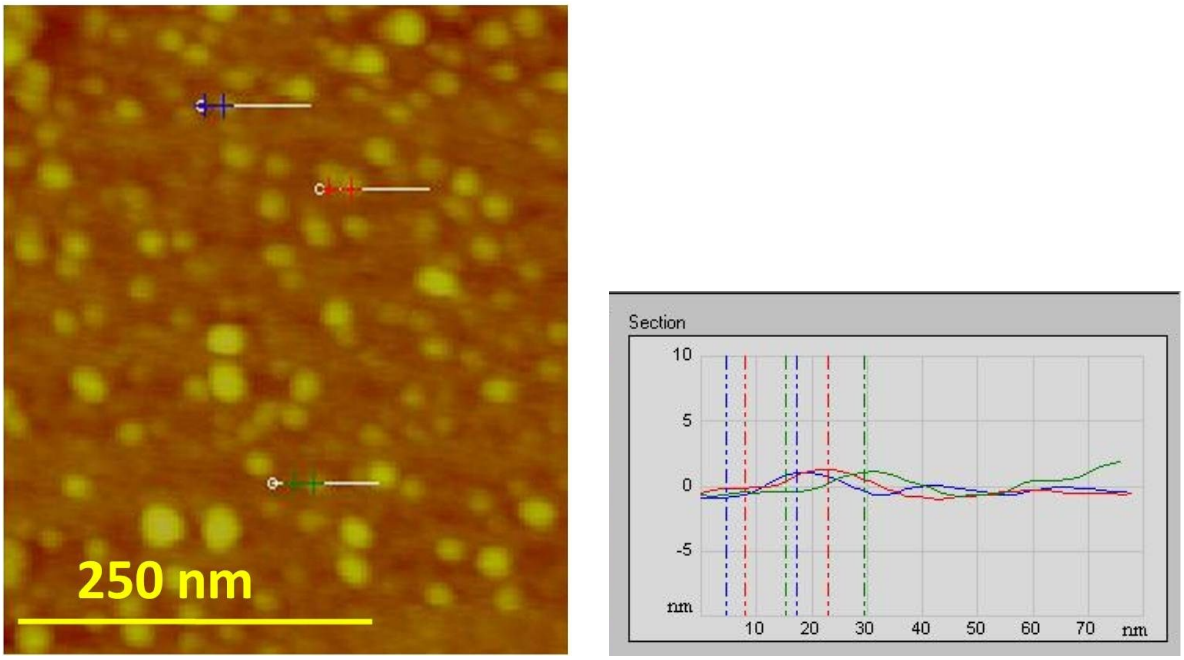

Fig. S6 AFM images of 4 nm sized GQDsand (c) the corresponding cross-sectional analysis showing the average height of the GQDs to be 1-2 nm.

References:

1. J. Shen, Y. Zhu, C. Chen, X. Yang and C. Li, *Chem. Commun.*, 2011 , **47**, 2580.