Electronic Supplementary Information for

Facile bulk production of highly blue fluorescent graphitic carbon nitride quantum dots and its application as a highly selective and sensitive sensor for the detection of mercuric and iodide ions in aqueous media

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1. Experimental

The characterizations of g-CNQDs were done using tapping mode of AFM (Asylum MFP-3D Atomic Force Microscope) and transition electron microscopy (TEM, JEOL JEM2010, operated at 200 kV). Powder X-ray Diffraction (p-XRD) patterns were performed on a Bruker DAVINCI D8 ADVANCE diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm). XPS measurements on the sample were done using a monochromatic Mg Kα X-ray source (XPS VG Microtech). XPS sample were prepared by drop casting few drops of aqueous solution of g-

CNQDs on silicon substrate and drying at room temperature. UV-Visible spectra were recorded using a UV-Visible Spectrophotometer (Varian Cary 100 Bio). Fluorescence studies of g-CNQDs were carried out using a spectrofluorimeter (Perkin Elmer, LS 55). Time resolved fluorescence life time measurements were performed using a time-correlated single photon counting (TCSPC) spectrometer (Edinburgh, OB920). ^{13}C and ^{1}H NMR spectra were recorded using a NMR Spectrometer (Bruker biospin 400MHz). ATR-FTIR measurements of aqueous solution of g-CNQDs were performed using a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer equipped and a ZnSe crystal. The ATR-FTIR spectrum of g-CNQDs was determined by using few drops of aqueous solution of g-CNQDs on the ZnSe ATR surface. For ATR-FTIR titration measurements, aqueous solution of g-CNQDs was prepared by sonicating 5mg of g-CNQDs with 10 ml of water for 1hr. The concentration of mercuric and iodide ions in the aqueous solution of g-CNQDs for the ATR-FTIR titration were 0.002 (M) and 0.004 (M) respectively. The CHN analysis for the composition of g-CNQDs was recorded using TruSpec CHNS analyzer.

2. Quantum Yield Measurements

Quantum yield of g-CNQDs in different solvents were calculated according to following equation[1]:

$$\Phi_S = \Phi_S \times (I_S/I_R) \times (\eta^2_S/\eta^2_R) \times (A_R/A_S)$$

Where the Φ is the quantum yield, I is the integrated photoluminescence intensity (excitation wavelength is 340 nm), A is the optical density and η is the refractive index of the solvent. The subscript "S" refers to the sample, g-CNQDs and "R" for reference. Quinine sulfate in 0.1M H_2SO_4 was taken as a reference. It is known from literature that quantum yield of Quinine sulfate in 0.1M H_2SO_4 is 54%. The absorbance of the solution of g-CNQDs in different solvents and reference were kept below 0.10 at 340 nm.

3. ^{1}H NMR Titration

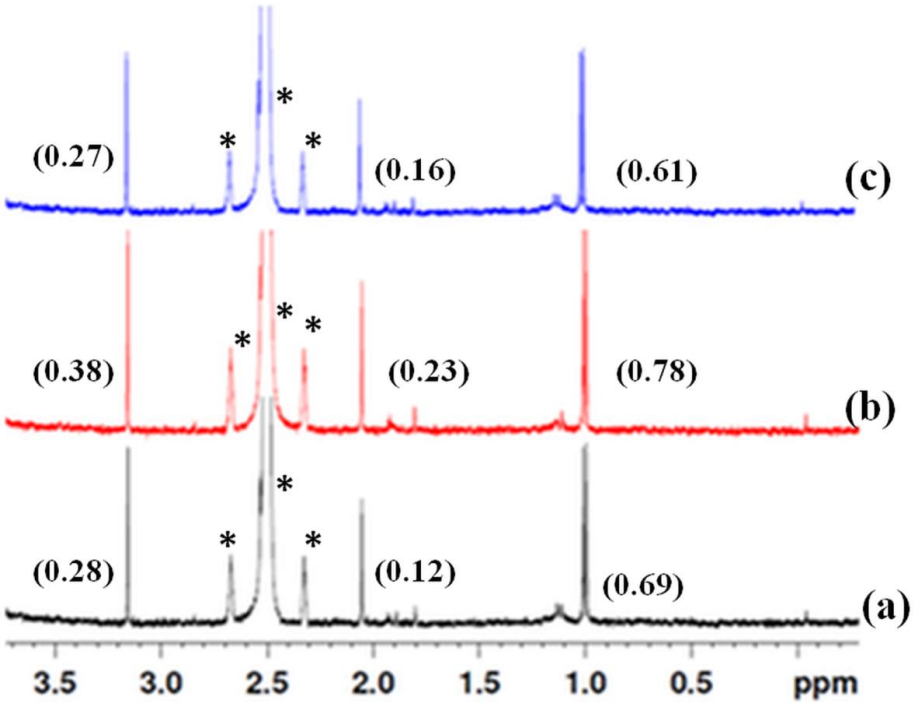

Fig. S1. ^{1}H NMR spectra in the aliphatic region of (a) free g-CNQDs (4mg/mL) in DMSO-water (2:3, v/v) solution, (b) in the presence of mercuric percholrate salts (0.002M), (c) in the presence of mercuric perchlorate (0.002M) and potassium iodide(0.006M). The asterisks (*) denote the solvent peaks. The values with a bracket are the areas under the peaks.

4. Fluorescence life time of g-CNQDs in different solvents

Fluorescence life times were determined using time correlated single photon counting technique. The emission decay curves of g-CNQDs in different solvents are shown in Figure 3d and Figure S2. Decays were recorded for g-CNQDs at 400 nm emission at excitation of 330 nm. Decay curves were fitted using multi exponential model[1] using the following:

$$I(t) = \sum^{n} A_i \exp(-t / \tau_i)$$

Where I(t) is the intensity usually assumed to decay as the sum of individual single exponential decays, A_i are the pre-exponential factors, τ_i are the decay times. The fluorescence decay curves of g-CNQDs in different solvents are fitted to triple exponential functions. The average life time (τ_{avg}) of g-CNQDs were determined by

$$\tau_{avg} = \frac{\sum_i A_i \tau_i^{\,2}}{\sum_i A_i \tau_i}$$

Following Fig. S2 and Table S1 prove the strong effects of the solvents on the fluorescence life time of g-CNQDs. This is due to the effect of polarity of solvent on energy states of the molecules.

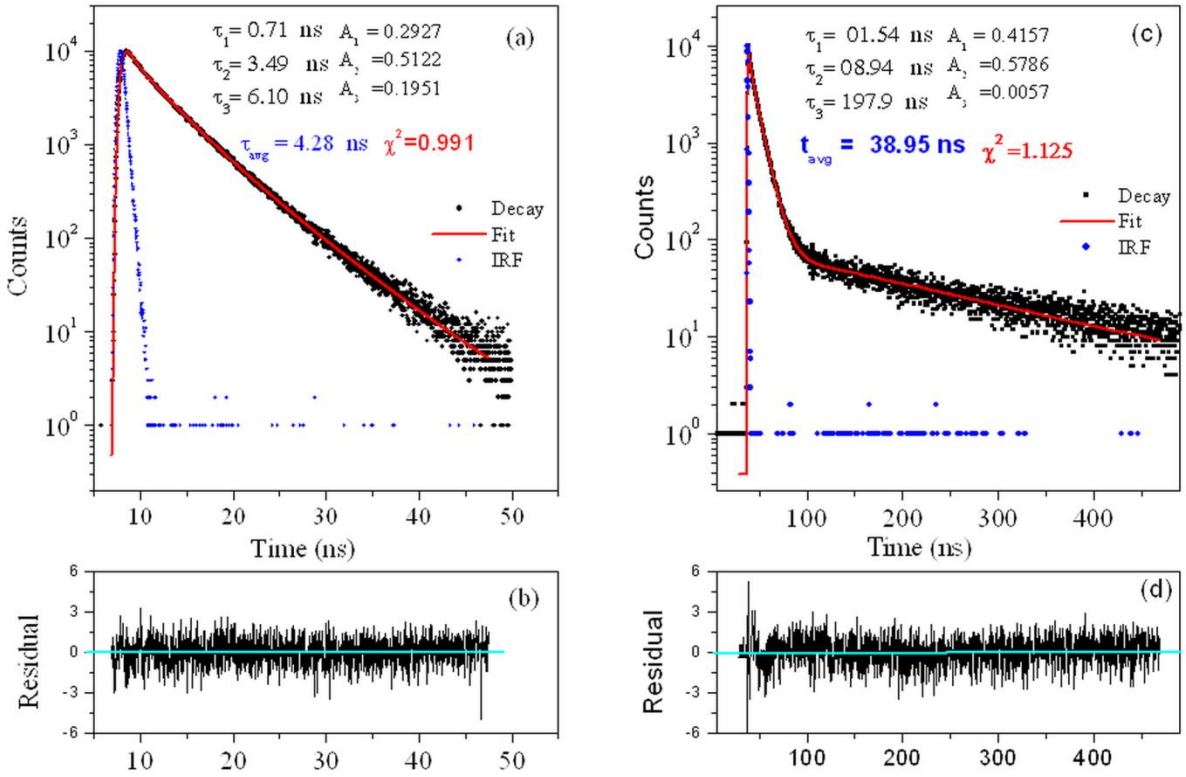

Fig. S2. Fluorescence decay curve and exponential fitting curve of g-CNQDs in (a) polar, water and in (c) non-polar, toluene. IRF is instrument response function.

Table S1: Fluorescence decay time (τ) and pre-exponential factor (A) of g-CNQDs in various solvents.

Solvent	$\tau_1(A_1)$	$\tau_2(A_2)$	$\tau_3(A_3)$	τ_{avg}	χ^2
Formamide	1.58 ns (0.666)	4.18 ns (0.3325)	20.23ns (0.0015)	**3.27 ns**	0.97
Water	0.71 ns (0.2927)	3.49 ns (0.5122)	6.10 ns (0.1951)	**4.28 ns**	0.99
Ethanol	2.67ns (0.7902)	6.03ns (0.2085)	83.93ns (0.0013)	**6.43 ns**	1.125
Benzene	1.52ns (0.4645)	8.94ns (0.5311)	184.5ns (0.0044)	**30.84 ns**	1.17
Toluene	1.55ns (0.4157)	8.94ns (0.5786)	197.9ns (0.0057)	**38.95 ns**	1.16

5. Effect of pH on Fluorescence Emission of g-CNQDs

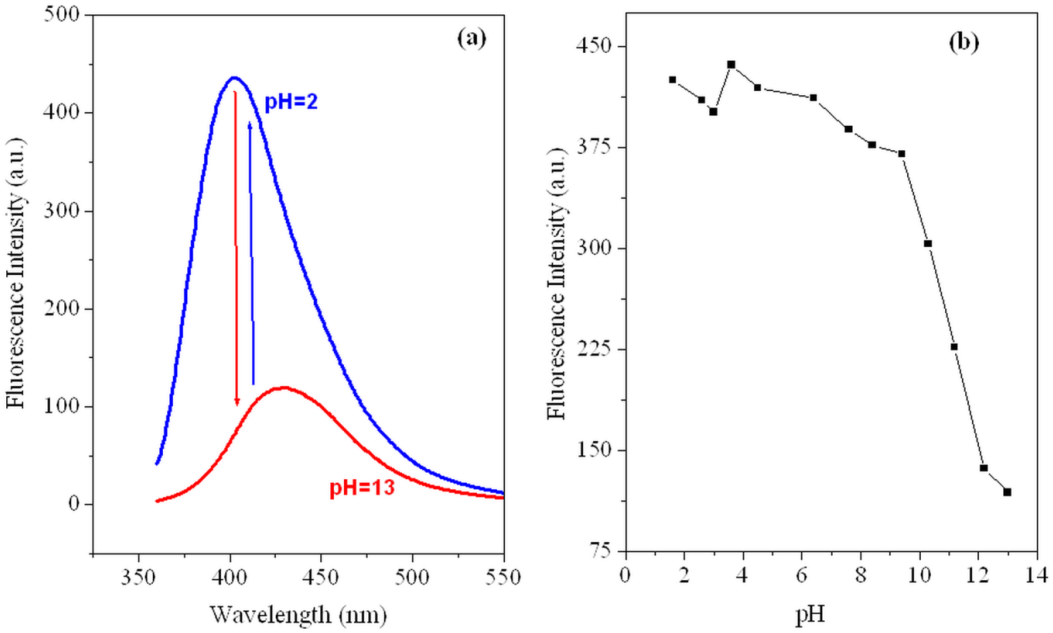

Fig. S3 (a) pH dependent fluorescence spectra of g-CNQDs displaying the change of fluorescence intensity when pH is switched between 2 and 13; (b) plot of fluorescence intensity vs. pH of the medium; (Excitation wavelength =340nm).

6. Effect of ionic strength on Fluorescence Emission of g-CNQDs

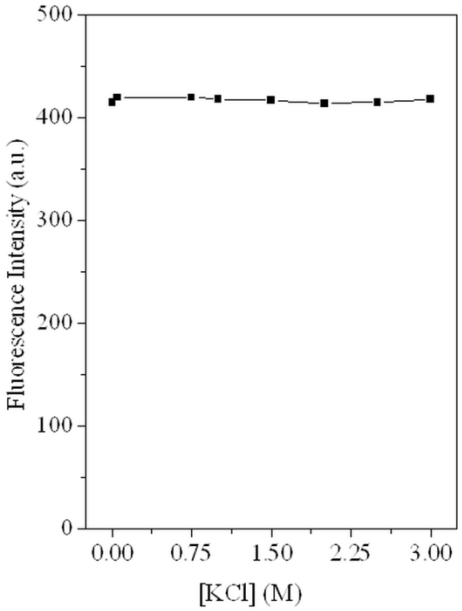

Fig. S4 Plot shows the effects of Ionic Strength on Fluorescent intensity of g-CNQDs in water. pH of the solution is 6.0. The fluorescence intensity is invariant with added KCl solution.

7. Fluorescence Quenching Measurements

Hg^{2+} ions quench the fluorescence emission of g-CNQDs in aqueous medium**.** The quenching of g-CNQDs by Hg^{2+} ions can easily be understood by a Stern-Volmer analysis. The Stern-Volmer constant, K_{SV} is related to fluorescence intensities by the following Stern-Volmer equation[1]:

$$F_0/F = 1 + K_{SV}[Q]$$

Where F_0 and F are the fluorescence intensities in absence and presence of quencher, respectively and [Q] is the concentration of quencher.

The Stern-Volmer plot of F_0/F versus [Q] is given in Fig. 5b and K_{SV} ($=2.4 \times 10^7$ M^{-1}) was calculated from the slope.

Fluorescence decay curves of g-CNQDs in presence Hg^{2+} ions of different concentrations are given in following Fig. S5. This plot shows the fluorescence life times of g-CNQDs are constant with added mercuric ions.

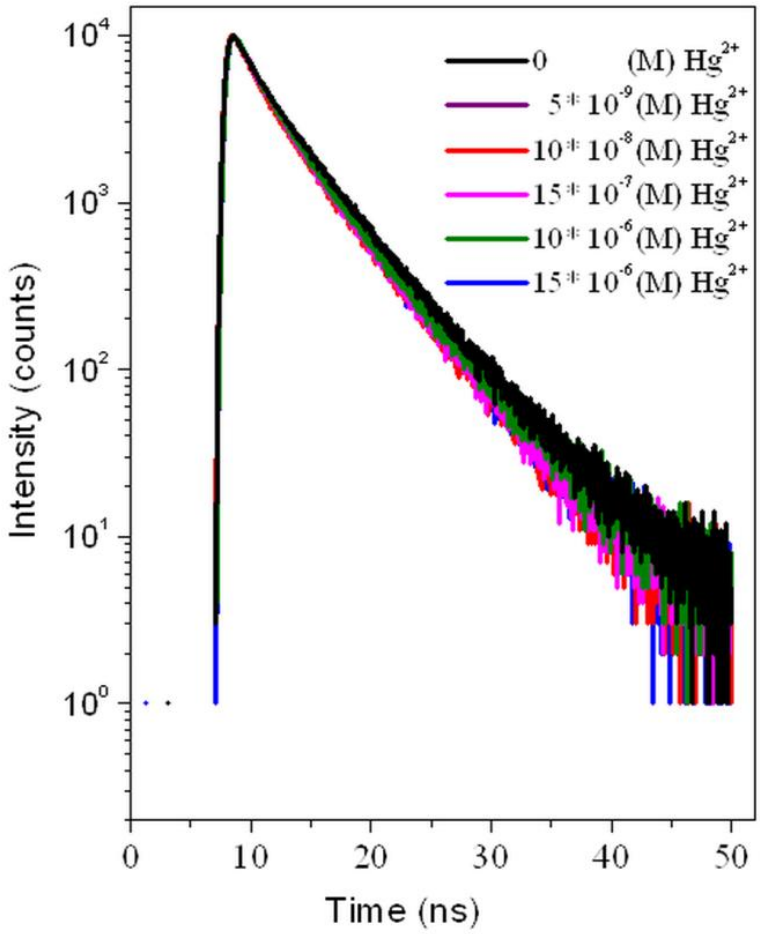

Fig. S5 Fluorescence decay profiles of g-CNQDs in presence of different concentration (5-30μM) of Hg^{2+} ions in aqueous medium. ($\lambda_{Excitation}$ = 330 nm and $\lambda_{emission}$ = 400 nm.)

8. ATR-FTIR and UV-Visible Spectroscopic Studies

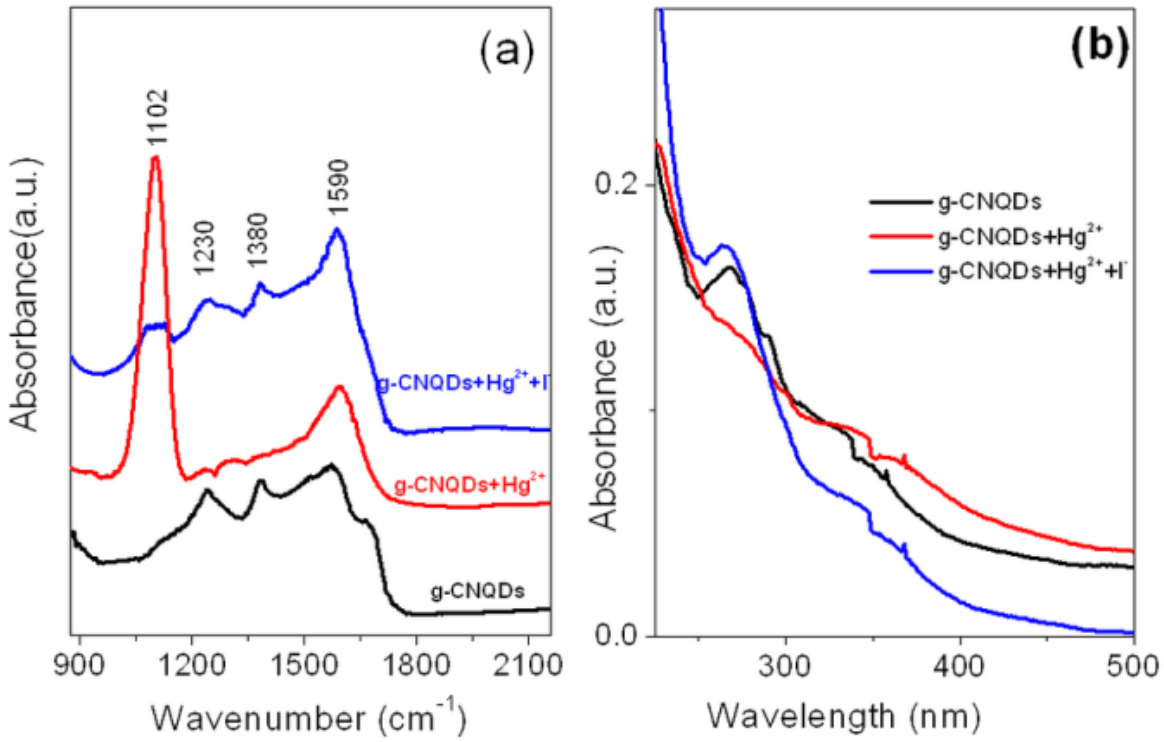

Fig. S6 (a) ATR-FTIR (b) UV-Visible spectra of free g-CNQDs, in the presence of Hg^{2+} ions and in the presence of both Hg^{2+} and iodide ions.

9. C1s XPS Spectra of g-CNQD-$(Hg^{2+})_x$

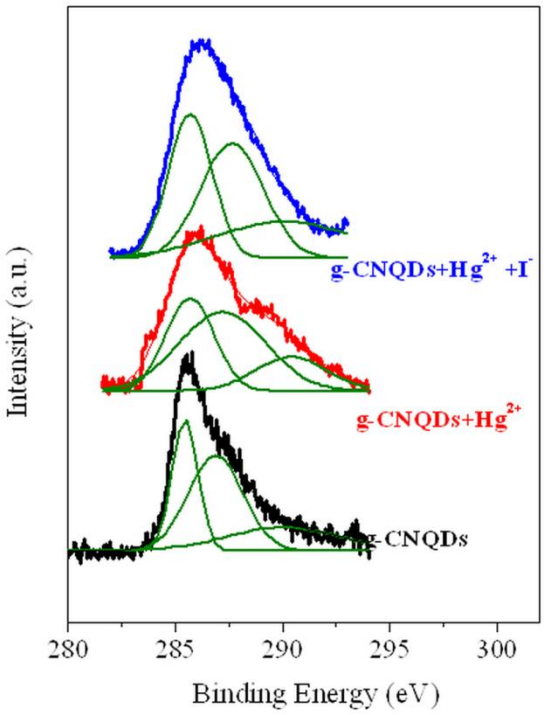

Fig. S7 XPS spectra in the C 1s region of (a) free g-CNQDs, (b) after treatment with $Hg^{2+,}$ (c) after addition of Hg^{2+} and iodides.

References

1. J. R. Lakowicz, *Principle of Fluorescence Spectroscopy* **1999**, Third Edition.