Electronic Supplementary Information (ESI)

Graphene Quantum Dots from Graphite by Liquid Exfoliation showing Excitation-Independent Emission, Fluorescence Upconversion and Delayed Fluorescence †

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1. Description Fluorescence Up-Conversion System & TCSPC System

Description of femtosecond laser apparatus was described in previous reports.¹ In brief, for fluorescence up-conversion study, FOG 100-DX system (CDP System Corp. Moscow, Russian Federation) was used. Fundamental laser output (~500 mW at 800 nm) of Ti:sapphire oscillator (Mai Tai HP, Spectra Physics) was steered into CDP2015 frequency conversion unit to have second harmonic (SH). A beam splitter (BS) is used to split the input beam (SH of fundamental) to excitation and gate (fundamental residual pulses) beams. The excitation beam directed to a rotating sample cell with the help of six mirrors and one BS. A lens (f = 40 mm) was used to focus the excitation beam into the sample. A neutral density (ND) filter was used for the excitation attenuation. The gate beam was directed by two mirrors to goldcoated retro-reflector mirror connected to 8 ns optical delay line before being focused together with the fluorescence (collected by an achromatic doublet, f = 80 mm) on 0.5 mm type-I BBO crystal. The angle of the crystal was adjusted to phase matching conditions at the fluorescence wavelength of interest. The up-converted signal (in the UV range) was focused with a lens (f = 60 nm) to an input slit of the monochromator (CDP2022D). The intensity of the up-converted radiation was measured with a photomultiplier tube operating in the photon counting mode. Proper filters were used before the detector to eliminate parasitic light from the up-converted signal if any. The polarization of the excitation pulses was set at magic angle relative to that of the gate pulses using Berek's variable wave plate. The sample solutions were placed in a 0.6 or 1 mm rotating cell, and absorbance of about 0.6 at excitation wavelength was generally used (yielding a concentration around 100–200 μ M). The FWHM of the instrument response function (IRF) in this setup was calculated about 240 fs in the 0.4 mm cell and 280 fs in the 1 mm cell. Hence, a time resolution of <200 fs could be achieved. For data analysis, the fluorescence time profile at a given emission wavelength $I(\lambda,t)$ was reproduced by the convolution of a Gaussian IRF with a sum of exponential trial function representing the pure sample dynamics S(t). Gaussian term was added to account for fast nonexponential processes, if any, owing to vibrational or other solvent relaxation process. In order to measure nanosecond range fluorescence lifetime we have used SPC-130 TCSPC module (Becker and Hickl). The femtosecond pulses at required repetition rate were obtained from fractional part of Mai Tai HP (Spectra Physics) output passing through femtosecond Pulse Selector (3980-5S, Spectra Physics, single shot to 8 MHz). The excitation pulses at desired wavelength were generated by frequency doubling with 0.5 mm BBO crystal using CDP2015 frequency conversion unit. These excitation pulses are focused to the sample using our fluorescence up-conversion set up described above. The time distribution data of fluorescence intensity were recorded on a SPC-130 TCSPC module (Becker and Hickl). Excitation pulses are focused to the sample using our fluorescence up-conversion set up described above. The time distribution data of fluorescence intensity were recorded on a SPC-130 TCSPC module (Becker and Hickl).

2. Effect of Sonication time on GQDs yield





Figure S1. (a) GQD yield vs. applied frequency and (b) corresponding optical images (c) Effect of sonication time on GQD yield (using constant frequency of 10 kHz) and (d) corresponding optical images.

3. Effect of sonication time on degree of exfoliation and crystalinity of graphite



Figure S2. Effect of sonication time on degree of exfoliation and crystalinity of graphite.

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4. Comparison of normal emission and Up-converted emission of GQDs at room temperature in DMF.



Figure S3. A typical Comparison of normal emission and Up-converted emission of GQDs at room temperature.



5. Excitation dependent emission spectra of GQDa at 77K in DMF

Figure S4. Excitation dependent emission spectra of GQDs at low temperature in DMF.

6. Low temperature excitation spectra in DMF,



Figure S5. Excitation spectra monitored at 550 nm in emission spectra of GQDs at low temperature in DMF.

7. Excitation dependent low temperature Up-converted PL emission



Figure S6. Excitation dependent Up-converted emission spectra of GQDs at 77K in DMF



8. Excitation dependent room temperature Phosphorescence spectra,

Figure S7. Excitation dependent Phosphorescence spectra of GQDs at room temperature.

9. Excitation dependent Low temperature phosphorescence spectra,



Figure S8. Excitation dependent phosphorescence spectra of GQDs at 77K in DMF and Excitation spectra monitored at 530 nm.

10. Phosphorescence decay both at 300 K and 77 K,



Figure S9. Phosphorescence decay at different wavelength both at 300 K and 77 K in DMF





Figure 10. Comparison of fluorescence and phosphorescence both at 300K and 77 K when excited at 390 nm, in DMF

12. Comparison of fluorescence and phosphorescence both at 300K and 77 K when excited at 450nm



Figure S11. Comparison of fluorescence and phosphorescence both at 300K and 77 K when excited at 450nm.

References:

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