Supporting Information

# Enhanced Photoluminescence of Pyrrolic-Nitrogen Enriched Graphene Quantum Dots

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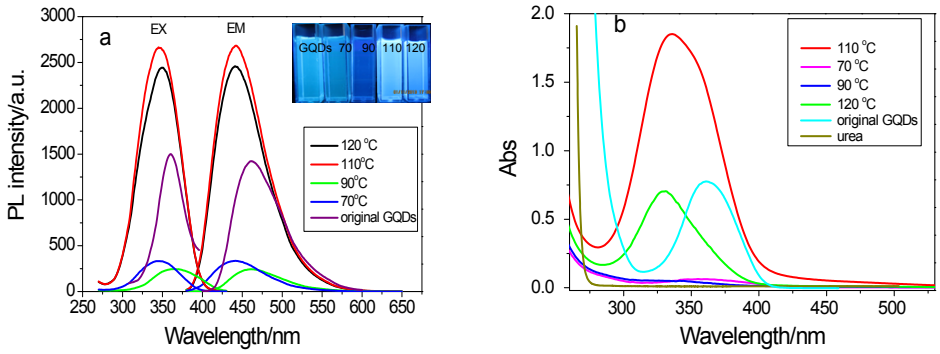


**Figure S1.** The PL emission and PL excitation (a) and UV-vis absorption (b) spectra of original GQDs and N-GQDs solutions prepared under different temperature (70, 90, 110, 120 °C). The inset in (a) shows photographs the solutions of N-GQDs under UV irradiation at 365 nm.

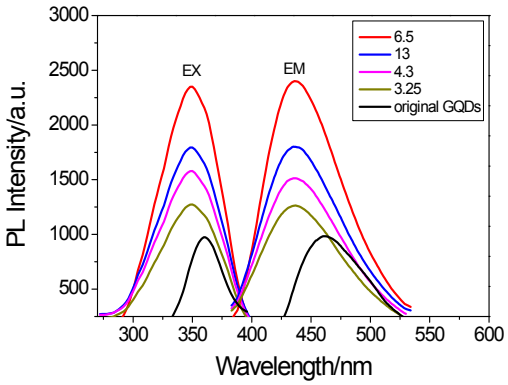


**Figure S2.** The PL emission and PL excitation spectra of N-GQDs solutions prepared at different urea concentration (3.25, 4.3, 6.5, 13 mol $L^{-1}$).

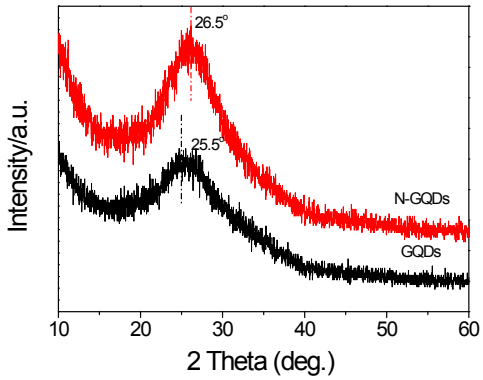


**Figure S3.** XRD patterns of GQDs and N-GQDs.

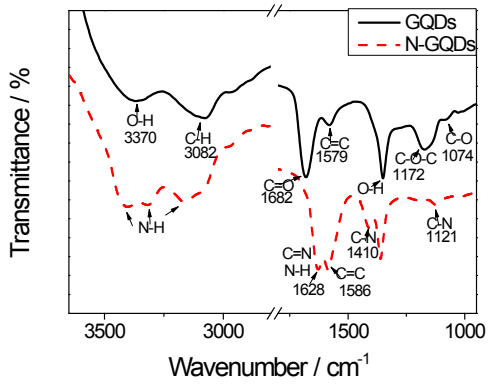


**Figure S4**. FT-IR spectra of GQDs and N-GQDs.

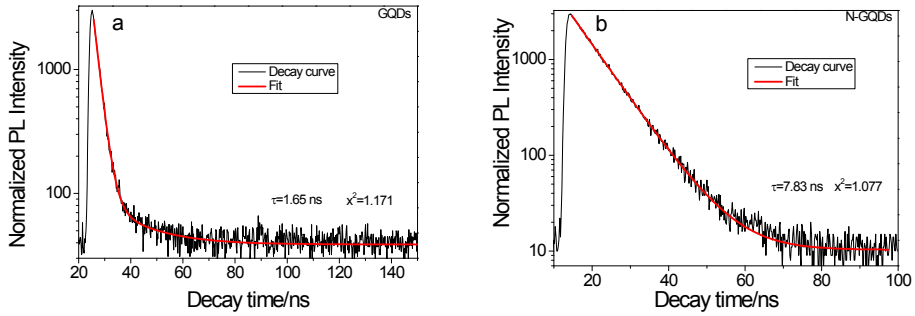


**Figure S5.** PL decay of GQDs (a) and N-GQDs (b) after dialysis.

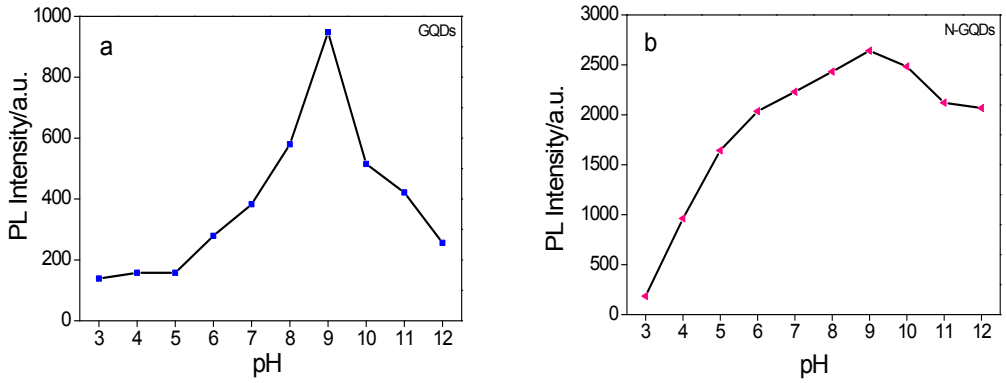


**Figure S6.** PL response of GQDs (a) and N-GQDs (b) under different pH values.

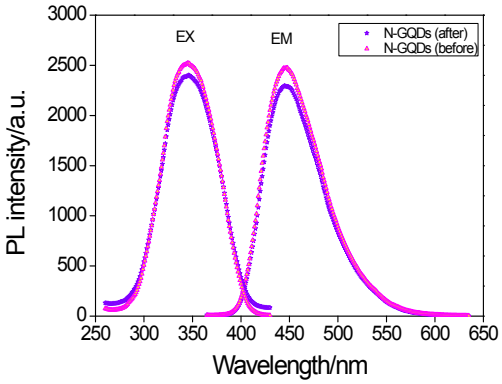


**Figure S7** The PL spectra of N-GQDs solution stored before and after one month.

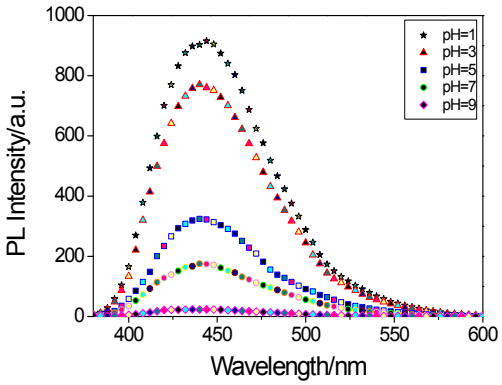


**Figure S8.** The PL spectra of the mixture solutions of citric acid and urea heated in the oven at 110 °C for 3 h. Before heating, the mixture solutions were firstly adjusted to different pH values using 0.25 mol $L^{-1}$ NaOH.

**Table S1.** A summary of the morphologies, nitrogen/carbon atomic ratio content and quantum yield of N-doped GQDs and C-dots synthesized via typical synthetic routes.

| Routes | Methods | Samples | Materials | Temperature (°C)/Time(h) | Size (nm) | Height (nm) | N/C atomic ratio | Zeta (mV) | Color with UV lamp irradiation | QY (%) | $\tau_{ave}$ (ns) | ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Up-down | Hydrothermal treatment followed by thermal annealing. | $NH_2$-GQDs* | OGSs [a], ammonia | 70-150/5 | 2.5 | 1.13 | 0.022 ~ 0.12 | — | violet to yellow | 19-29 | $5.1\times10^8$, $2.2\times10^8$ | S1 |
| | Hydrothermal | GQDs* | OGSs [b], ammonia | 200/10~12 | 1.5~5 | 1.5~1.9 | No present | — | green | ~7.5 | — | S2 |
| | Hydrothermal | $NH_2$-GQDs*, | GQDs [d], ammonia | 200/10 | 3~9 | 0.4~2 | 0.1205 | + 3 | blue | ~16.4 | — | S3 |
| | Hydrothermal | N-GQDs | GO, ammonia | 180/12 | 2-6 | 0.5-3 | 0.1788 | — | blue | 24.6 | — | S4 |
| | Hydrothermal | N-C-dots | Monkey grass | 180/6 | 1~4 | — | No present | + 30.2 | bright blue | — | — | S5 |
| | Refluxing | rGQDs*,[c] | GQDs, $N_2H_4$ | 95/1~60(min) | 2~5.5 | 0.6~2 | 0.0792 | — | — | 10.3 | — | S6 |
| | Electrochemical | N-GQDs* | Graphene film, TBAP [f] | ±3.0(V)/ 0.5(V/s) | 2~5 | 1~2.5 | 0.0428 | — | blue | — | — | S7 |
| | Solvothermal | GQDs* | GO, DMF | 200/8 | 2~5.5 | 0.6~2 | 0.1926 | — | Blue in DMF; yellowish-green in water | 5.1 | — | S6 |
| | Solvothermal | N-GQDs | GO, DMF | 200/4.5 | 1-6 | 0.5-1 | — | -21 | green | 31 | 6.27 | S8 |
| Bottom-up | Hydrothermal | GQDs-U-4** | CA, urea | 160/4 | 1.8 ~ 3.4 | 0.5~2 | ~0.2 | — | blue | 78 | 8 | S9 |
| | Microwave | C-dots* | CA, urea | 750(W)/ 4~5(min) | 1~5 | 1~4 | 0.429 | + 88.1 | blue~yellow | ~14 | 2.11(15.9%); 5.97(84.1%) | S10 |
| | Pyrolysis followed by hydrothermal | N-GQDs** | CA, urea | 110/3 | 5~9 | 1~2 | 0.06 | -24.9 | blue | ~24 | 7.83 | This work |

* Emission wavelength excitation-dependent; ** Emission wavelength excitation-independent.

[a] OGSs ( oxidized graphene sheets) were obtained by Hummers' method at 80 °C for 8h. [b] GSs (graphene sheets) were derived from thermal reduction of graphene oxide (GO) sheets, and then the GSs were oxidized in concentrated $H_2SO_4$ and $HNO_3$ to form OGSs. [c] rGQDs, reduced GQDs. [d] GQDs were obtained by microwave assisted refluxing of GO suspension mixed with $H_2SO_4$ and $HNO_3$. [e] TBAP, tetrabutylammonium perchlorate.

**Table S2**. Quantum yields of GQDs and N-GQDs (before and after centrifugation) using quinine sulfate as a reference.

| Sample | Integrated emission intensity ($I$) | Abs. at 360 nm ($A$) | Refractive index of solvent ($\eta$) | Quantum Yield ($QY$) |
|---|---|---|---|---|
| Quinine sulfate | 147637 | 0.057 | 1.33 | 54% (known) |
| GQDs (before centrifugation) | 32580 | 0.070 | 1.33 | 9.7% |
| GQDs (after centrifugation) | 25525 | 0.057 | 1.33 | 9.3% |
| N-GQDs (before centrifugation) | 87448 | 0.074 | 1.33 | 24.6% |
| N-GQDs (after centrifugation) | 77382 | 0.065 | 1.33 | 24.8% |

**Quantum yields (QY) measurements**

Quinine sulfate in 0.1 M $H_2SO_4$ (QY=0.54) was chosen as standards. The quantum yields of GQDs and N-GQDs were calculated according to:

$$\phi_x = \phi_{st}(I_x / I_{st})(\eta_x^2 / \eta_{st}^2)(A_{st} / A_x)$$

Where $\Phi$ is the quantum yield, $I$ is the measured integrated emission intensity, $\eta$ is the refractive index of the solvent, and $A$ is the optical density. The subscript "st" refers to the reference standard with known quantum yield and "x" for the sample. In order to minimize re-absorption effects, absorbencies in the 10 mm fluorescence cuvette were kept under 0.10 at the excitation wavelength (360 nm).

**References**


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