Supporting information

Langmuir-Blodgett self-assembly of ultrathin graphene quantum dots films with modulated optical properties

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AFM images of GQDs

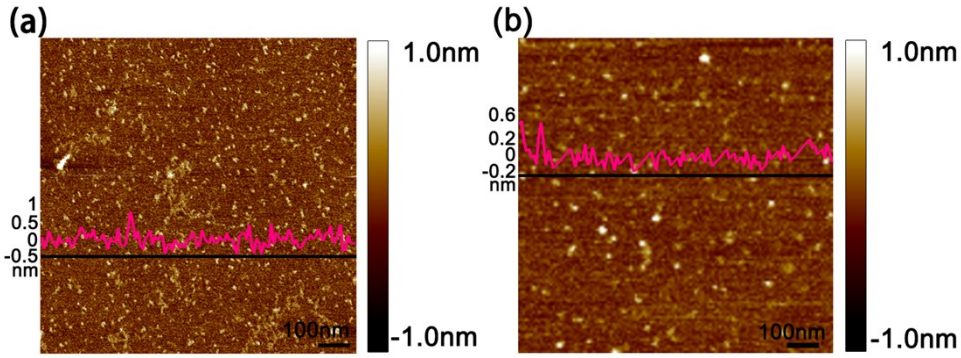

Figure S1 AFM images of (a) OH-GQDs, and (b) NH_2-GQDs, respectively.

Detailed characterization of GQDs

As shown in Fig.S2, different functionalized GQDs (OH-GQDs and NH_2-GQDs) was characterized and analyzed by XRD, FTIR, Raman and XPS spectra. For XRD spectra (Fig. S2 (a)), XRD pattern for both of them was characteristic of graphite with a (002) layer spacing, which was identical to that of bulk graphite (3.34 Å). For the FTIR spectra, Fig. S2 (b) showed the FTIR spectrum of the dried OH-GQDs and dried NH_2-GQDs respectively. A strong vibration at 1,590 cm^{-1} corresponded to the C═C bonds, and another vibration at 3,400 cm^{-1} was ascribed to the O—H bonds. The vibration of C—OH at 1,270 cm^{-1} mainly represented the hydroxyl functionalization of the GQDs. Moreover, for NH_2-GQDs, there were two vibration at 3,200 and 1,620 cm^{-1} corresponding to the N-H bond. For Fig. S2 (c) Raman spectra, it had shown the high graphitization of our GQDs which the ordered G band at 1,582 cm^{-1} was much stronger than the disordered D band at 1,372 cm^{-1}. XPS spectra of two different GQDs was

shown in Fig. S2 (d) and (e). For OH-GQDs, the high-resolution C1s spectrum showed the signals of C═C at 284.8 eV, C—O at 286.4 eV. The high-resolution O1s spectrum showed the signals of -OH bond at 532.1 eV. For the C1s high- resolution spectrum of NH_2-GQDs (Fig. S2 (e)), the signals of C═C, C—O, C═O, C—N were at 284.8 eV, 286.4 eV, 288.4 eV and 285.9 eV respectively. The N1s high-resolution spectrum showed the signal of pyridinic N (N—C) at 398.9eV and $–NH_2$ at 400.1 eV. Besides, high-resolution of O1s spectrum of NH_2-GQDs revealed the signal of –OH at 531.3 eV, O═C at 533.3 eV and a minimum signal of H_2O at 535.5 eV.

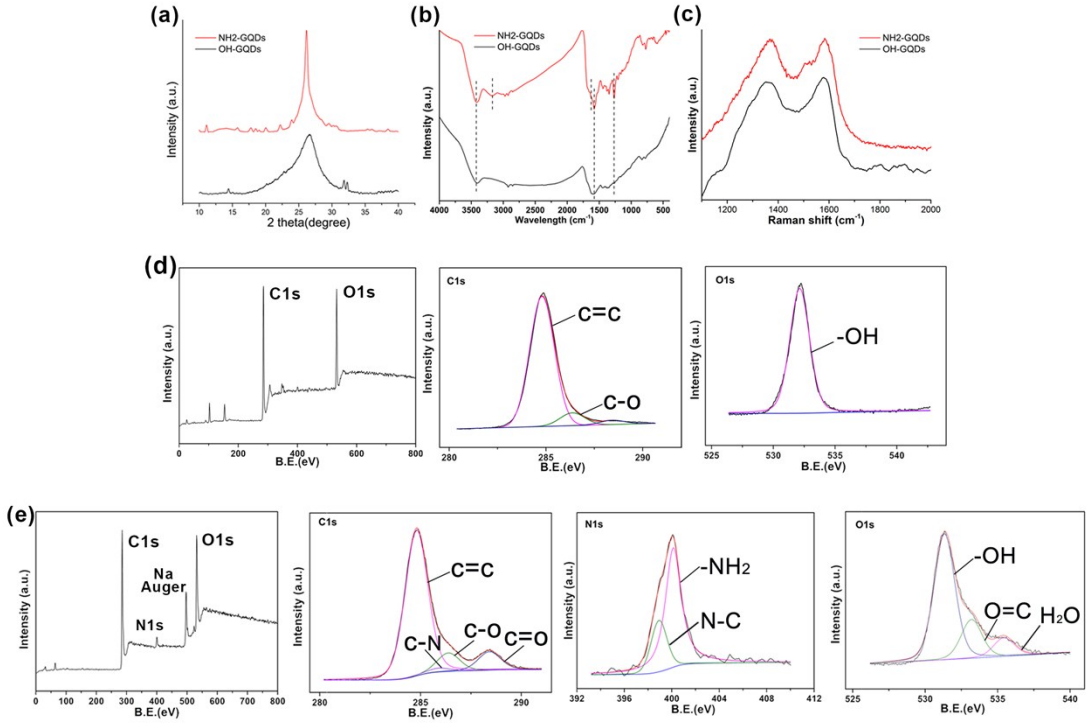

Figure S2 Structural characterization of prepared GQDs. (a) XRD pattern. (b) FTIR spectrum. (c) Raman spectrum. (d) XPS spectrum of OH-GQDs. (Left) High-resolution C1s spectrum of OH-GQDs. (Middle) High-resolution O1s spectrum of OH-GQDs. (Right) (e) XPS analysis of NH2-GQDs. Spectrums from left to right are full spectrum, High-resolution C1s spectrum, High- resolution N1s spectrum and High- resolution

O1s of NH2-GQDs.

Theoretical calculation of GQDs solution and ultra-thin GQDs films bandgap

Accurate E_g estimation of our GQDs was calculated with the general equation as follow:

$$\alpha(hv) \approx B(hv - E_g)^n$$

The n=1/2 was for the direct semiconductor bandgap. So the equation was written as $\alpha(hv) \approx B(hv - E_g)^{1/2}$. Because the $\alpha \propto$ A (absorbance), general formula can be conversed as follow:

$$A(hv)^2 \propto (hv - E_g)$$

Then we plotted $A(hv)^2$ versus E_g. The bandgap value of our GQDs can be obtained by extrapolating the slope to A = 0 as shown in Fig. 2(d).

Excitation/Emission 3D View of full spectrum scanning

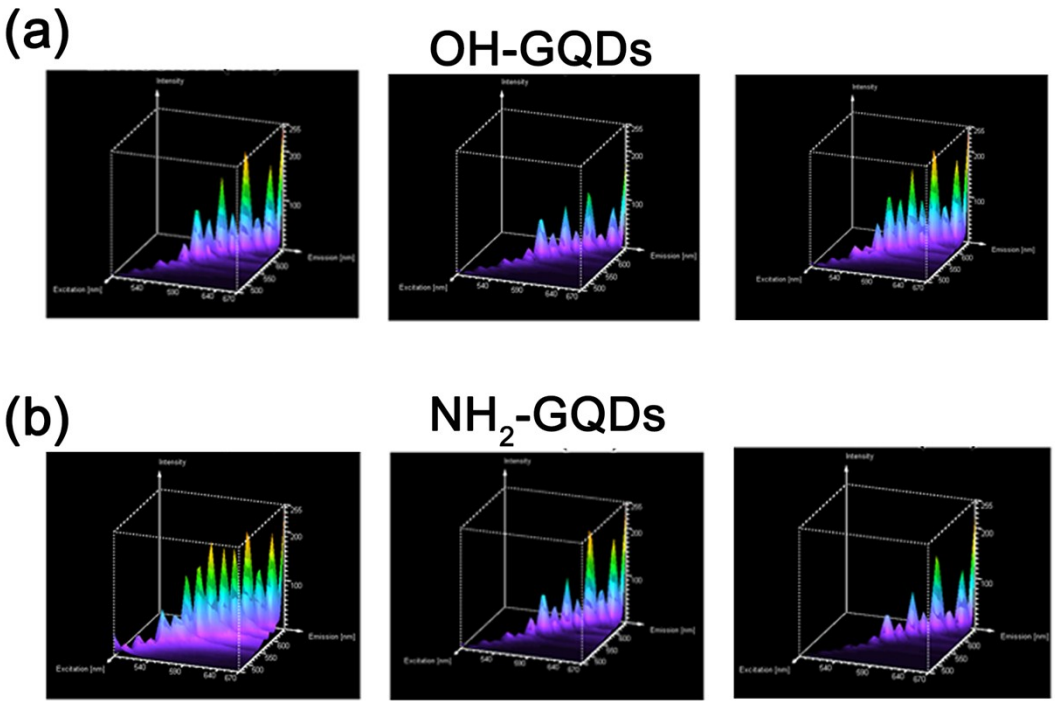

Figure S3 Excitation/Emission 3D View of multi-layer GQDs films. (a) Excitation/Emission 3D View of OH-GQDs ultra-thin films. Images from left to right are from the monolayer, tri-layer films and five layers of OH-GQDs. (b) Excitation/Emission 3D View of NH_2-GQDs ultra-thin films. Images from left to right are from the monolayer, tri-layer films and five layers of NH_2-GQDs.