Supplementary Information

Acid-free and Oxone Oxidant-assisted Solvothermal Synthesis of Graphene Quantum Dots using Various Natural Carbon Materials as Resources

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Experimental Section

Synthesis of G-GQDs, M-GQDs, CF-GQDs and C-GQDs: GQDs were synthesized from graphite powder (325 mesh Bay Carbon), MWCNTs (Iljin Nanotech Co., Ltd), carbon fiber (VGCF^{TM}, Showa Denko Europe GmbH), and charcoal (Activated charcoal, Sigma-Aldrich Co. LLC) by a one-pot solvothermal redox reaction. Graphite (1 g), MWCNTs (1 g), CF (1 g), and charcoal (1 g) powder were first individually mixed in concentrated DMF (100 mL) with oxone (2 g). The mixture solution was sonicated for 1 h. Then, the mixture was transferred to an autoclave (100 ml) and was heated up to 200 ℃ for 10 h. The resulting product was then cooled to room temperature and was filtered through a 100 nm nano-porous membrane to separate the carbon based materials. The resulting product solution was further dialyzed in a dialysis bag (retained molecular weight: 2000 Da) for 3 days. To demonstrate the recycling of insufficiently reacted starting material, we carried out the same reaction using the re-collected G, M, CF and C in DMF with oxone. Then, the resulting solutions were again filtered and further dialyzed.

Characterization of graphene quantum dots: The morphologies of GQDs were observed by using a high resolution transmission electron microscope at an accelerating voltage of 200 kV (JEOL JEM-2100 Field Emission Gun HR-TEM) and an AFM in tapping-mode. The height profile of GQDs was obtained using an XE-100 AFM system (Park Systems, Inc., Korea). The AFM samples were prepared by spin-coating at 4000 rpm on a pre-cleaned Si wafer. Raman spectroscopy measurements were taken using a confocal Raman system (WiTec, Alpha 300R) with a 532-nm laser. XPS measurements were taken in a SIGMA PROBE (ThermoVG) using a monochromatic Al-Kα X-ray source at 100 W. Surface analyses of graphite, MWCNT, CF, and charcoal were collected by field emission scanning electron microscopy (SEM) (JSM-6701F/INCA Energy, JEOL). FT-IR spectra were obtained on a Bruker Vertex 70 spectrometer. Fluorescence lifetime decay was measured using a

confocal microscope (MicroTime-200, Picoquant, Germany) with a 20x objective. A pulsed diode laser (375 nm with a pulse width of ~240 ps and an average power of ~1 μW) was used as an excitation source. An avalanche photodiode detector (PDM series, MPD) was used to collect whole emissions from the samples. Time-correlated single-photon counting (TCSPC) technique was used to count fluorescence photons. All UV-vis absorption spectra were recorded using an 8453 UV-Vis spectrophotometer (Agilent, Technologies, America). Photoluminescence (PL) spectra were obtained on a Cary eclipse fluorescence spectrophotometer (Agilent, Technologies, America).

Table. S1 Comparison of acid-assisted and acid-free GQDs methods from raw materials including a graphite, multiwall carbon nanotube, carbon fiber and charcoal.

Previous methods	Chemical route	Chemical route	Chemical route	Thermal plasma jet route	K intercalation route	Our route
Starting materials	Coal	Carbon fiber	Graphite	Graphite	Graphite, MWCNT	Graphite, MWCNT, carbon fiber, charcoal
Scale	No mass	No report	Mass	Mass	No mass	Mass
Reaction condition	Acid condition	Acid condition	Acid condition	Mild condition	Mild condition	Acid-free condition
Reference	Ref 5	Ref 6	Ref 21	Ref 16	Ref 26	

Quantum yields (QYs) measurements:
Rhodamine B in water (QYs=0.31) was chosen as a standard. The quantum yields of GQDs in water were calculated according to:

$$\Phi = \Phi_r \times \frac{\mathrm{I}}{\mathrm{I}_r} \times \frac{\mathrm{A}_r}{\mathrm{A}} \times \frac{n^2}{n_r^2}$$

Where Φ is the quantum yield, I is the measured integrated emission intensity, n is the refractive index of the solvent, and A is the optical density. The subscript “r” refers to the reference standard with known quantum yield. In order to minimize re-absorption effects,

absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength (340 nm).

Table. S2 QYs of the GQDs by using Rhodamine B as a reference.

Sample	Integrated emission intensity *(I)*	Abs. at 340 nm *(A)*	Refractive index of solvent *(η)*	Quantum Yield *(φ)*
Rhodamine B	21503	0.072	1.33	0.31
G-GQDs	2242	0.046	1.33	0.050
M-GQDs	2816	0.051	1.33	0.056
CF-GQDs	2683	0.053	1.33	0.052
C-GQDs	3180	0.041	1.33	0.080

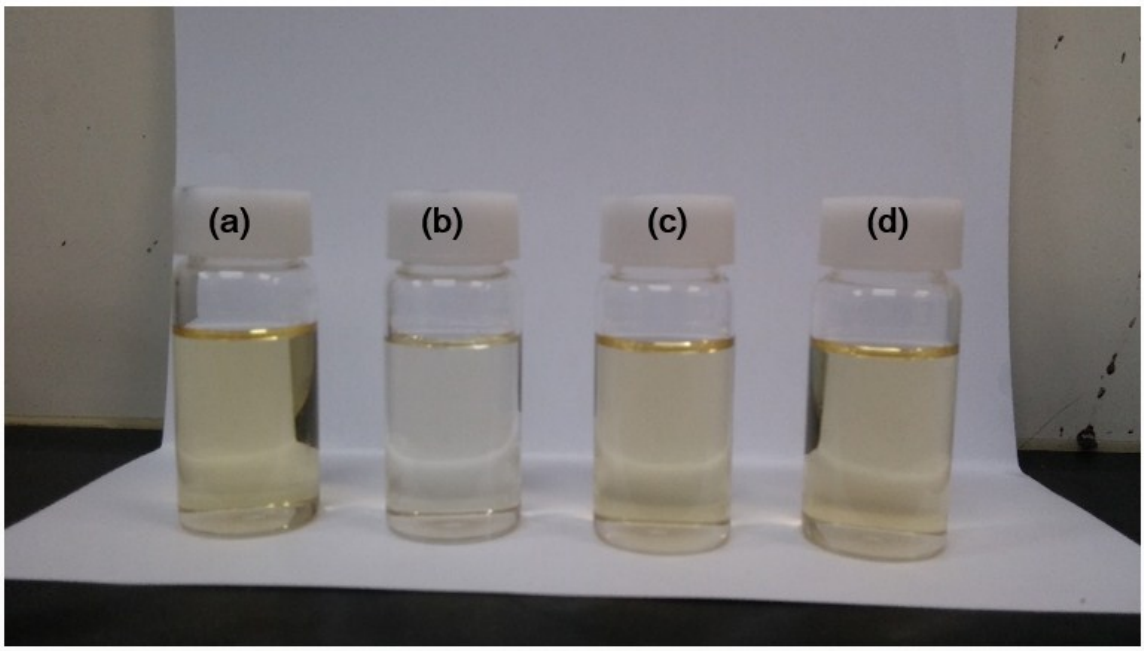

Figure S1. Photographs of GQDs: (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs and (d) C-GQDs synthesized via an acid-free solvothermal redox reaction.

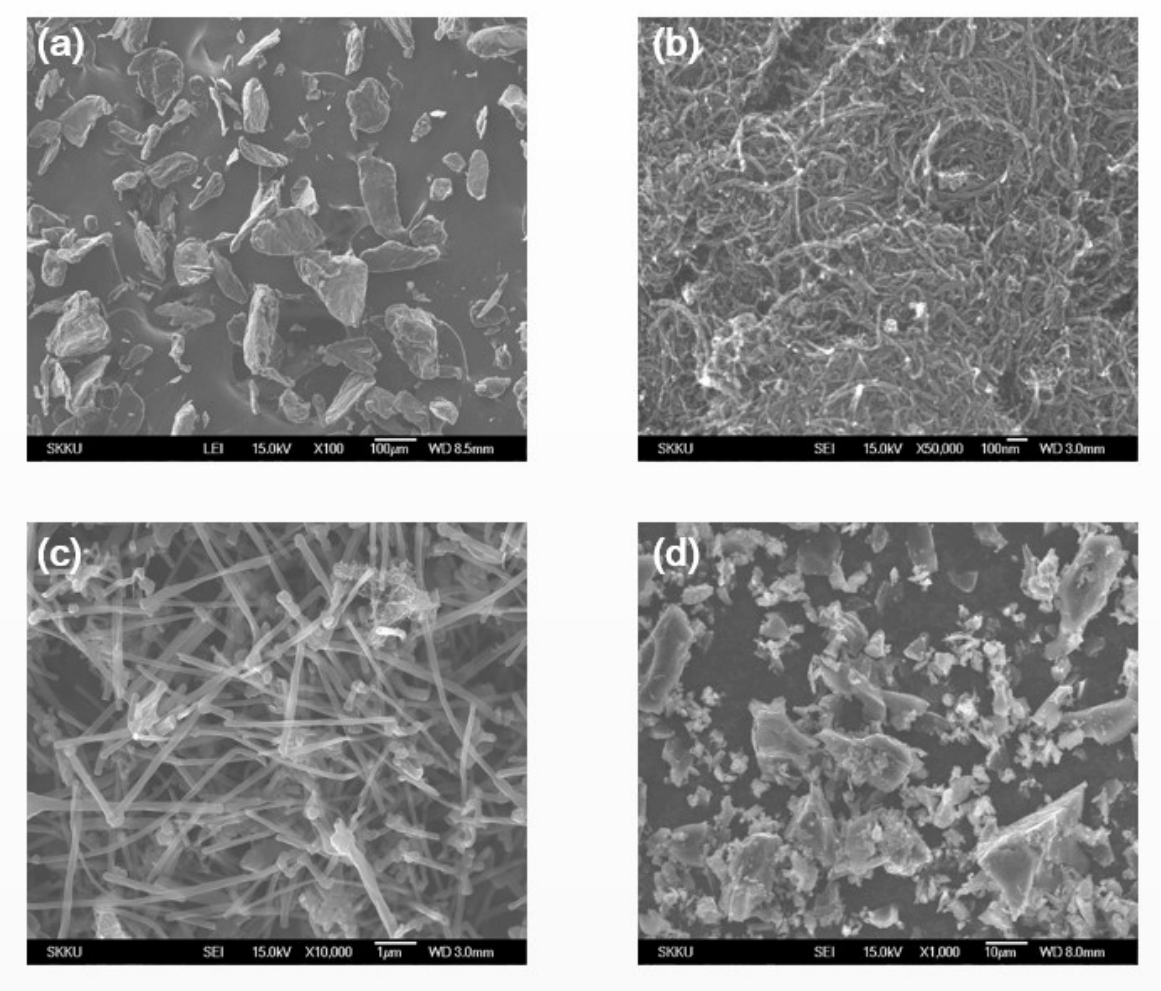

Figure S2. SEM images of carbon based starting materials including (a) graphite, (b) MWCNTs, (c) carbon fiber, and (d) charcoal.

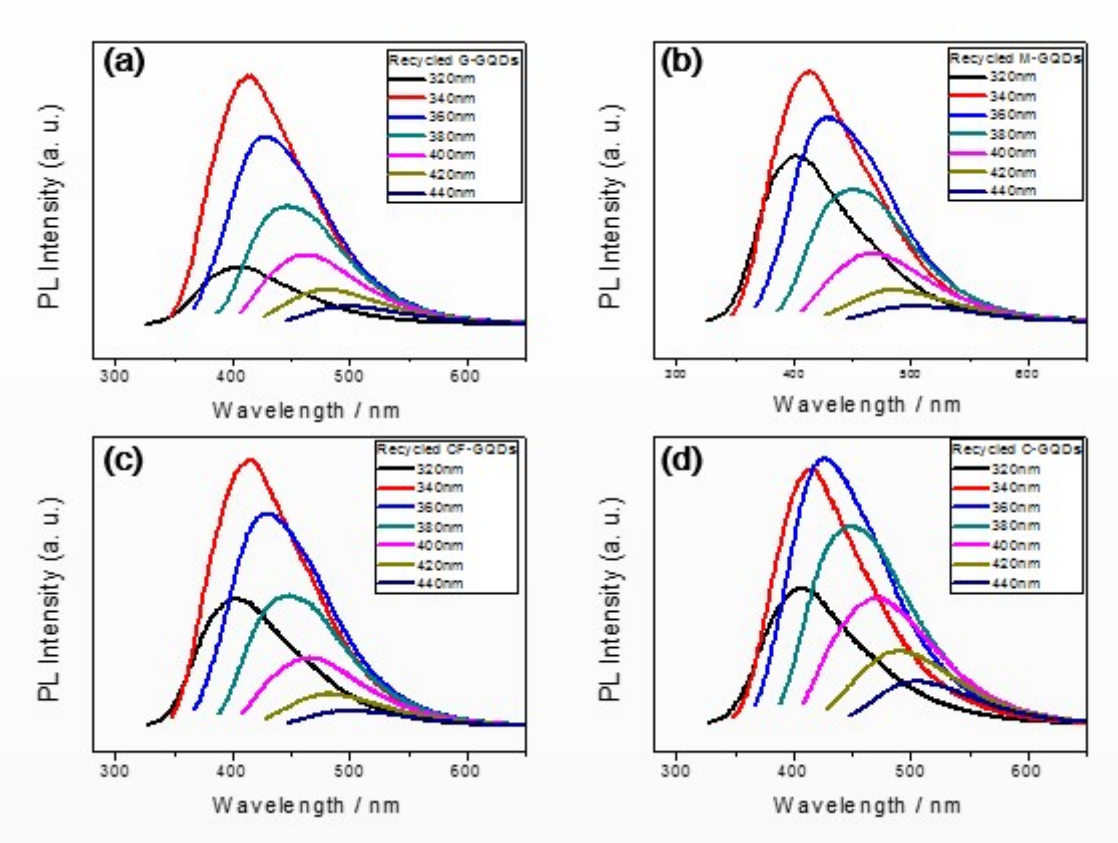

Figure S3. PL spectra of (a) recycled G-GQDs, (b) recycled M-GQDs. (c) Recycled CF-GQDs and (d) recycled C-GQDs measured at different excitation wavelengths from 320 to 440 nm.

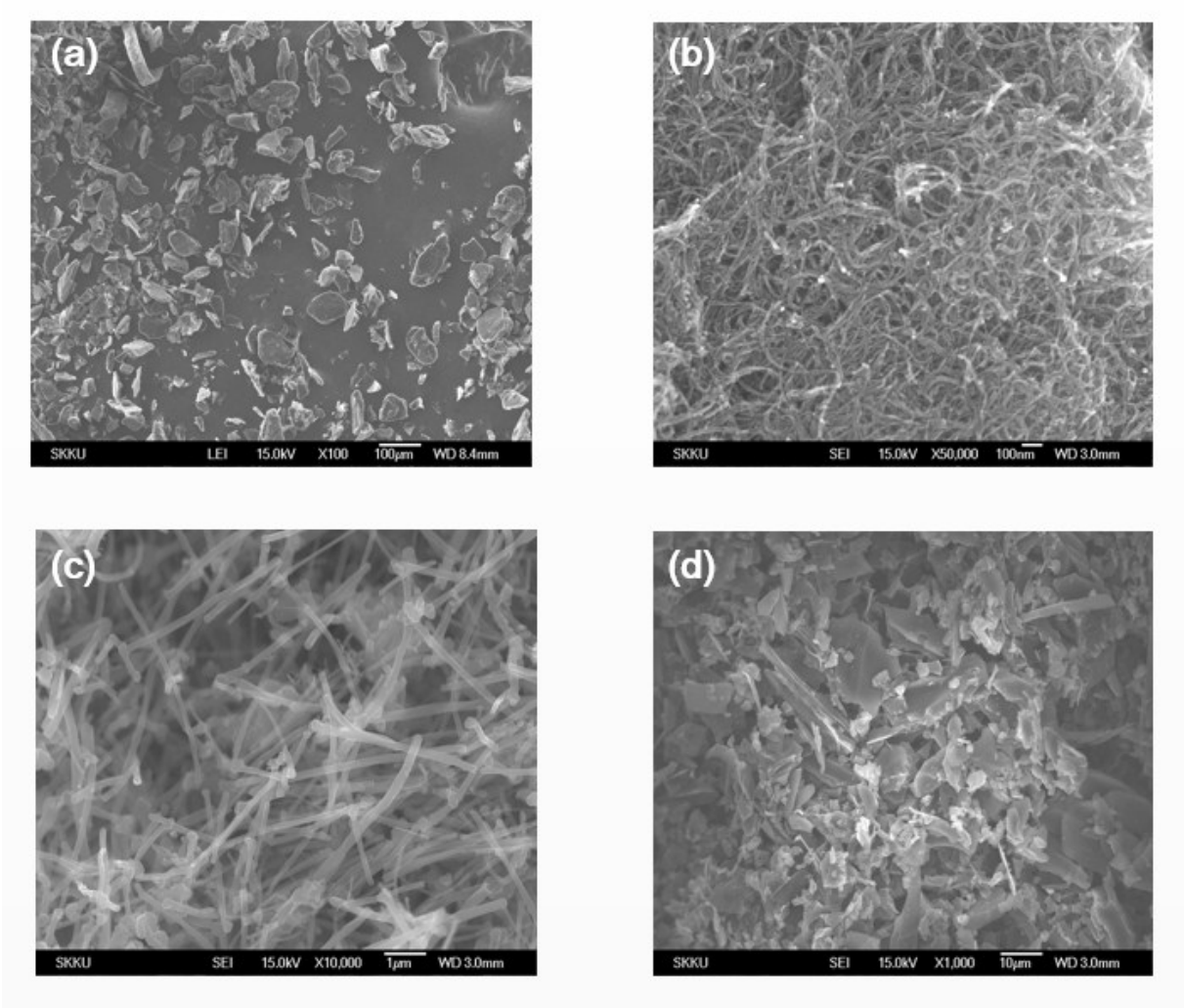

Figure S4. SEM images of (a) graphite, (b) MWCNT, (c) carbon fiber, and (d) charcoal after the 1st solvothermal redox reaction.

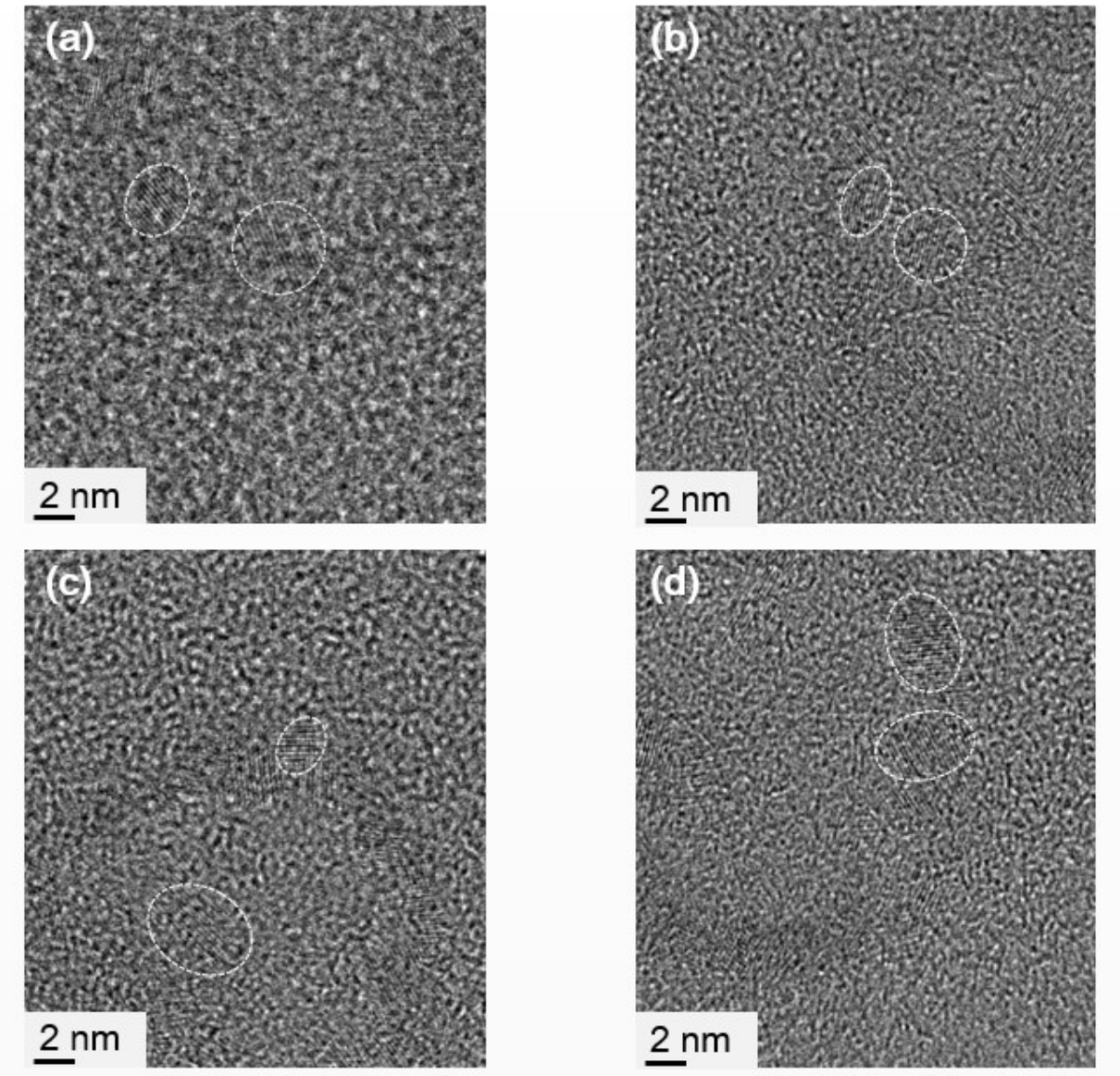

Figure S5. HR-TEM images of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs showing many nano-sized crystalline domains highlighted with white dotted circles.

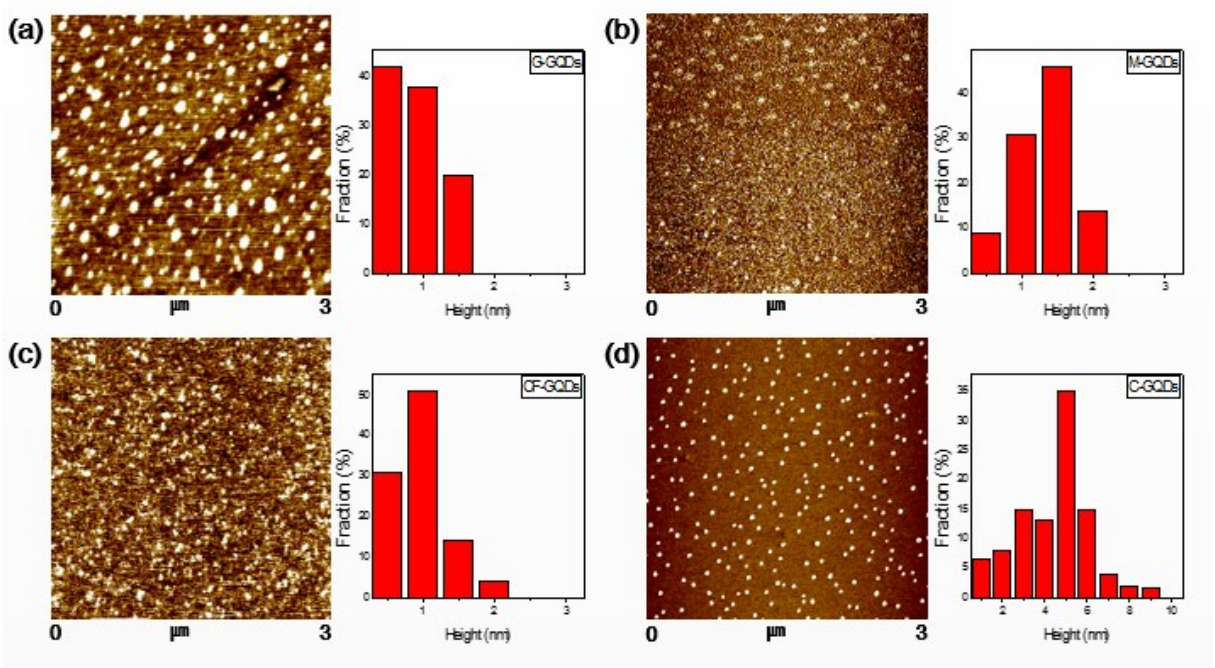

Figure S6. Typical AFM topographic images of GQDs with height distributions: (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs (scale: 3 x 3 ㎛).

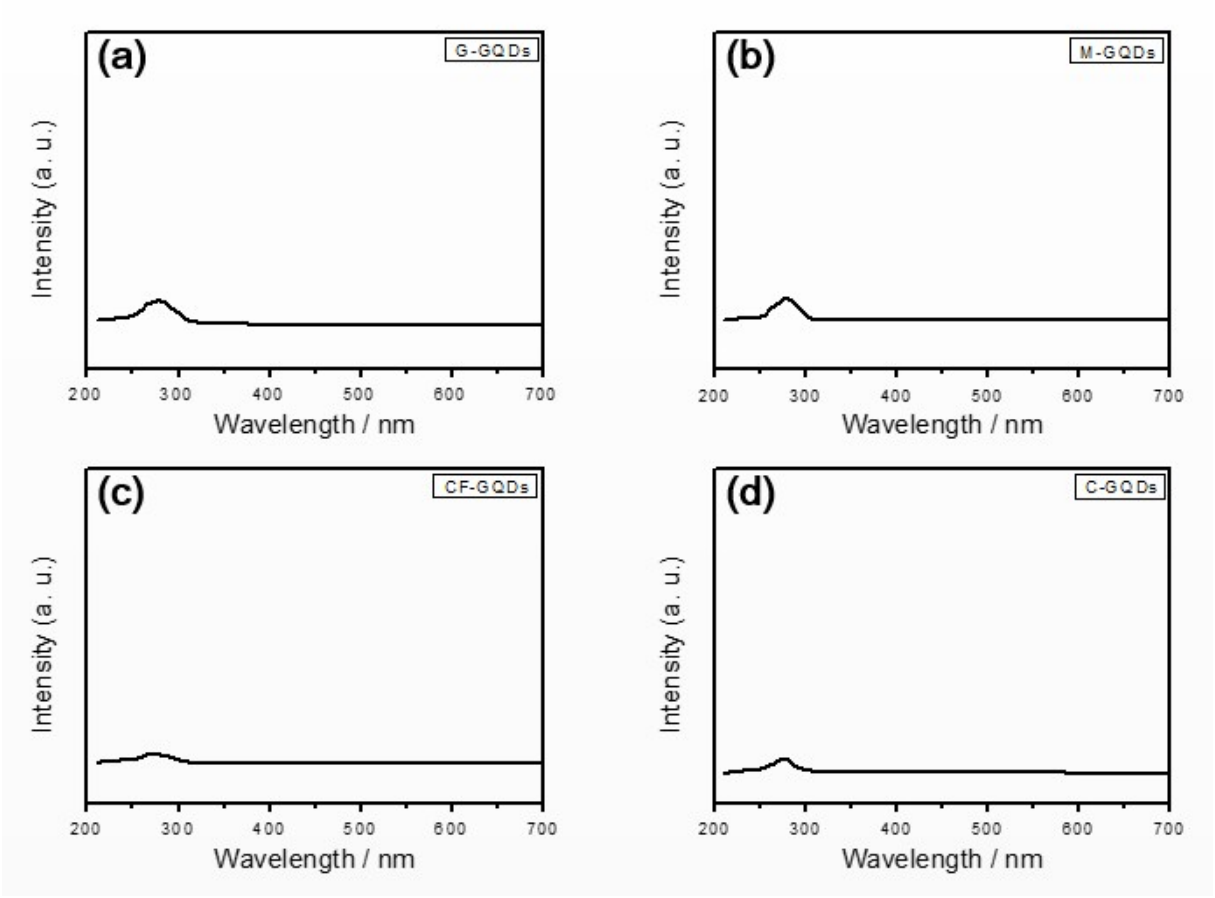

Figure S7. UV-vis absorption spectra of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs.

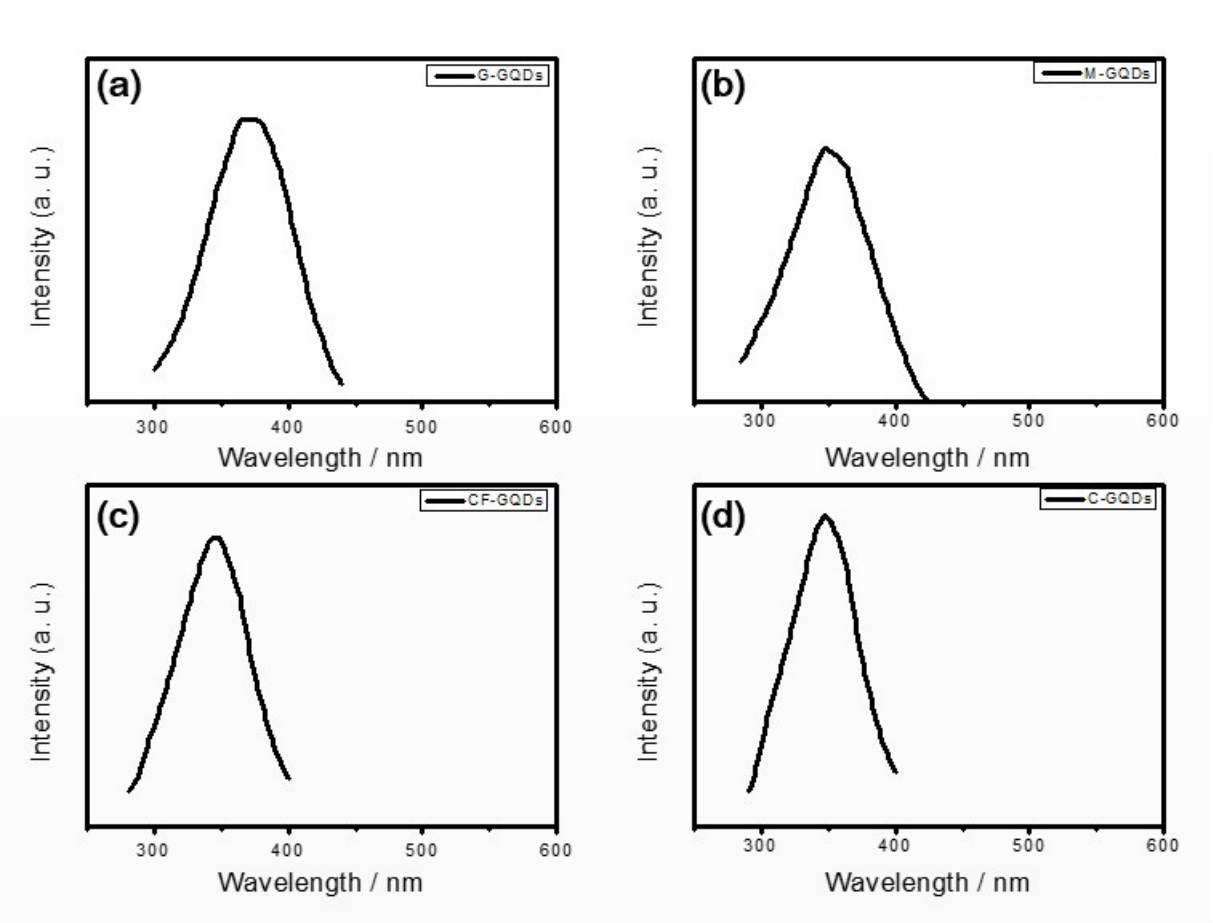

Figure S8. PLE spectra of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs and (d) C-GQDs

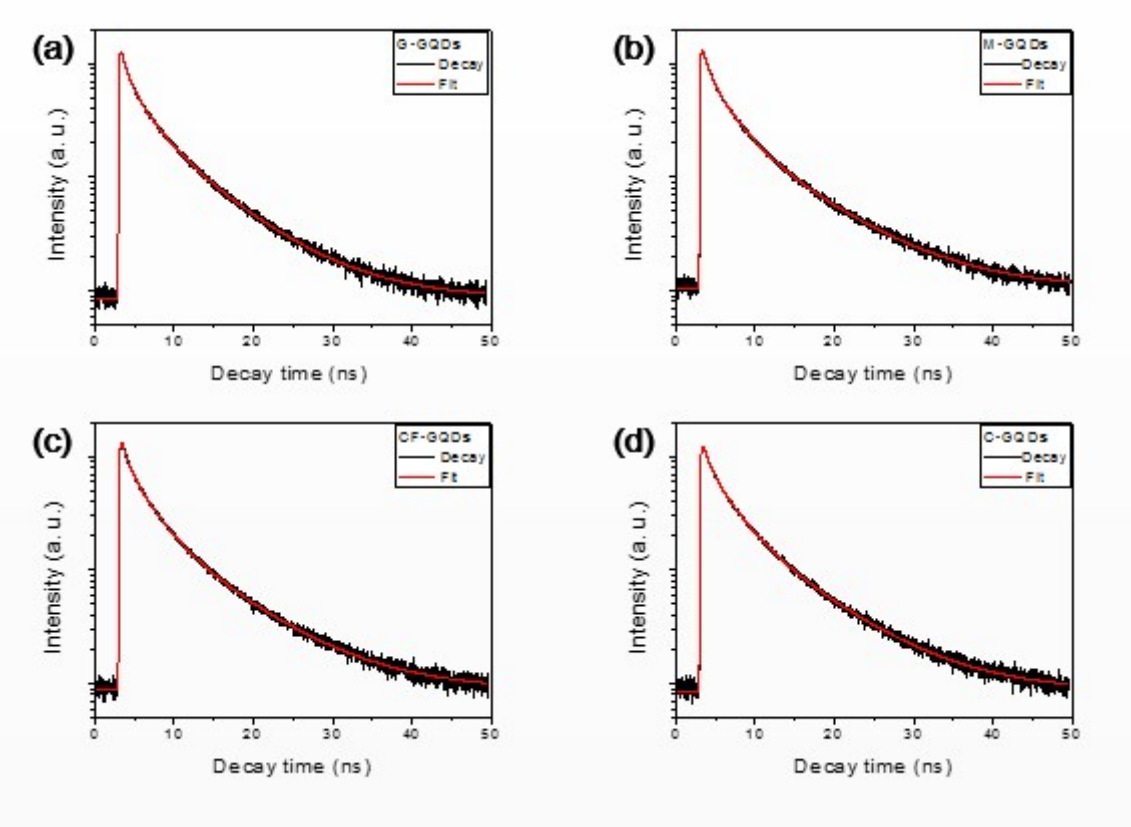

Figure S9. Time-resolved PL decay profiles of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs (probed at 375 nm).

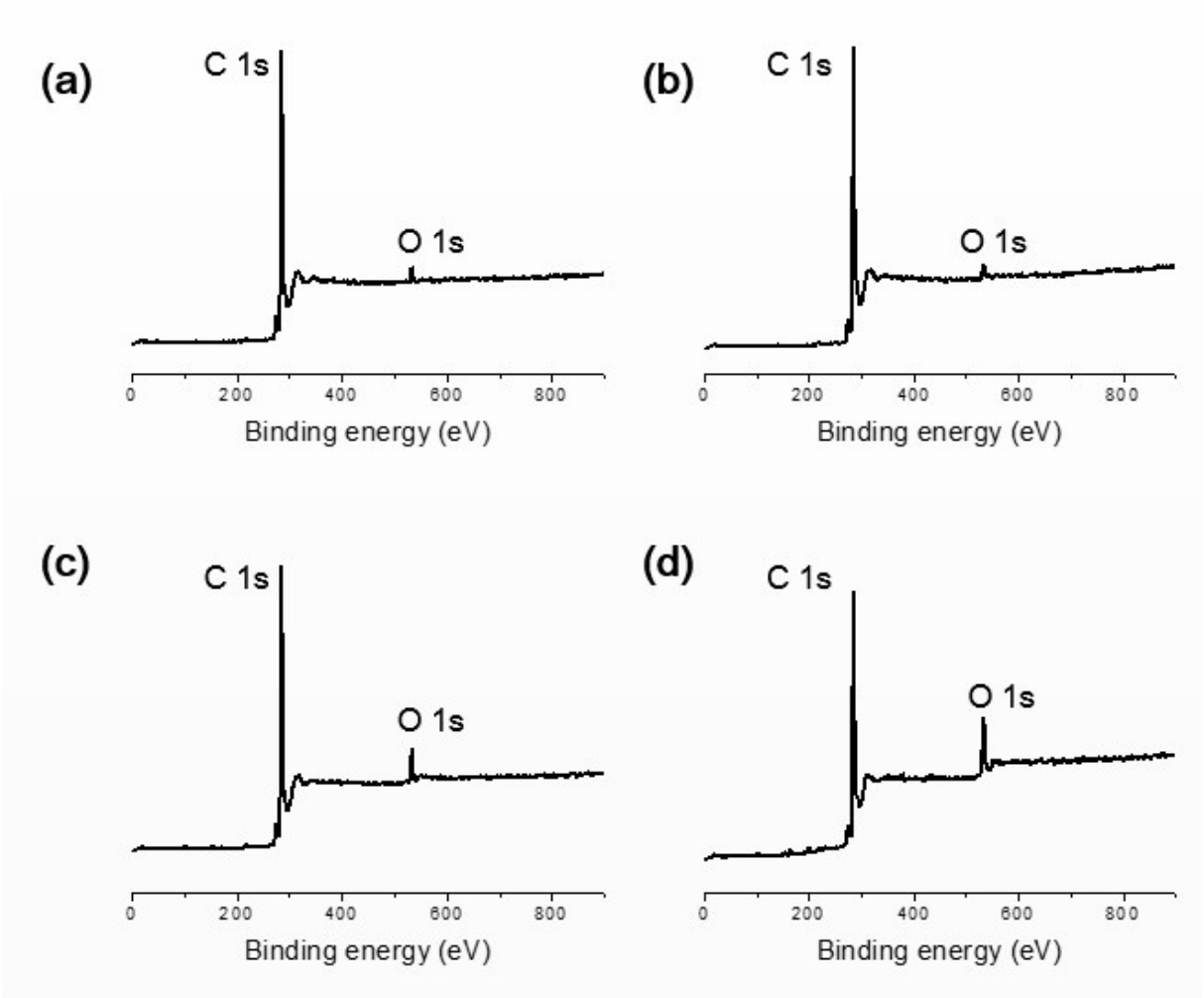

Figure S10. XPS spectra of starting materials including (a) graphite, (b) MWCNT, (c) carbon fiber, and (d) charcoal.

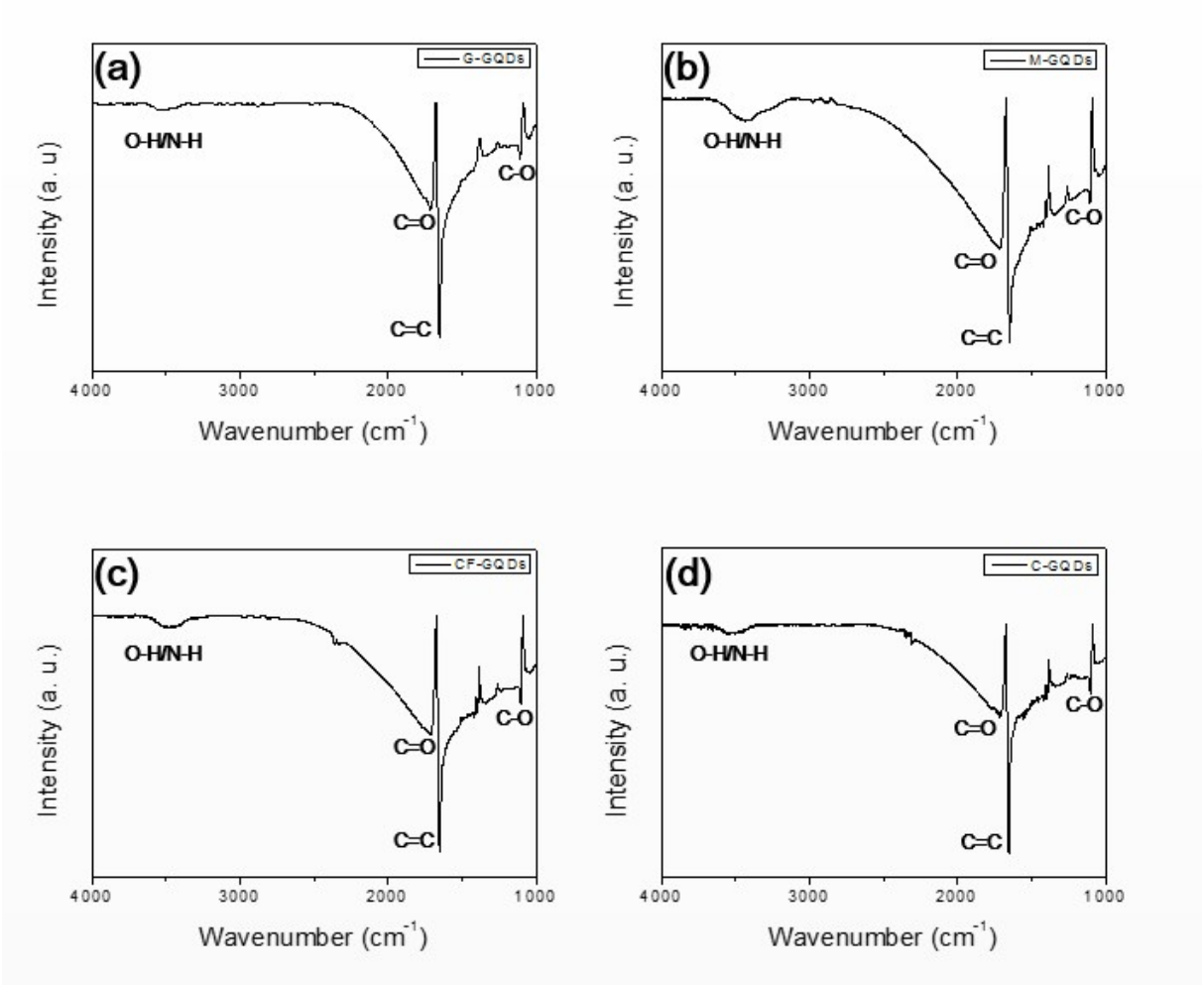

Figure S11. FT-IR spectra of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs.

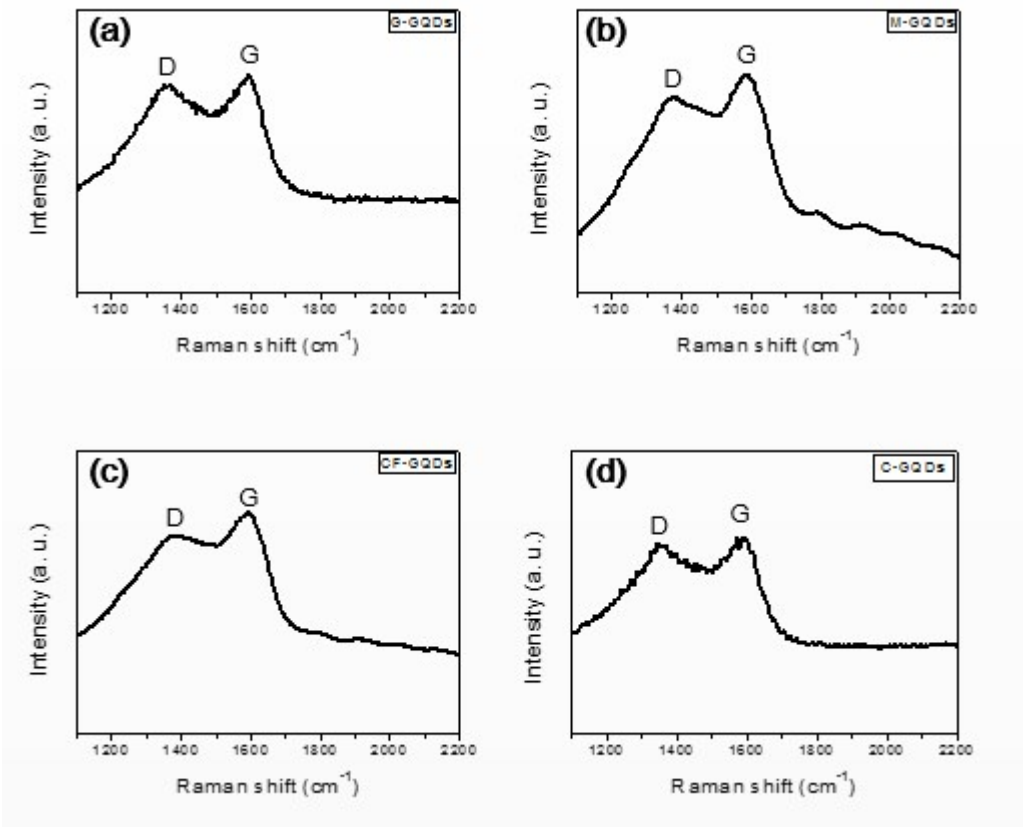

Figure S12. Raman spectra of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs and (d) C-GQDs.