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Supplementary Information

A new mild, clean and high-efficient method for preparation of graphene quantum dots without by-products

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Experimental Section

Materials

WCl_6 (98 %), EtOH (AR), H_2O_2 (30 %), TA (99.5 %), LiCl (99.5 %), NaCl (99.5 %), KCl (99.5 %), $AgNO_3$ (99.5 %), $MgCl_2$ (99.5 %), $CaCl_2$ (99.5 %), $SrCl_2$ (99.5 %), $BaCl_2$ (99.5 %), $ZnCl_2$ (99.5 %), $CdCl_2$ (99.5 %), $HgCl_2$ (99.5 %), $CuCl_2$ (99.5 %), $Pb(NO_3)_2$ (99.5 %), $FeCl_2$ (99.5 %), $FeCl_3$ (99.5 %), $AlCl_3$ (99.5 %), $SnCl_4$ (99.5 %), NaF (99.5 %), NaCl (99.5 %), NaBr (99.5 %), KI (99.5 %), $NaNO_2$ (99.5 %), $NaNO_3$ (99.5 %), Na_2CO_3 (99.5 %), Na_2SO_4 (99.5 %), Na_2SO_3 (99.5 %), Na_2HPO_4 (99.5 %) and NaHS (99.5 %) were purchased from Aladdin (Shanghai, China) and used as received without further purification. Graphene oxide were purchased from SIBAT (Shanghai, China) and used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Synthesis of $W_{18}O_{49}$ nanowire

Uniform hydrophilic $W_{18}O_{49}$ nanowire with a high aspect ratio, which was less than 15 nm in diameter and tens of microns in length was obtained by modified methods described previously. In a typical procedure, 150 mg WCl_6 was dispersed in 50 mL absolute alcohol, and then the resultant solution was transferred into a 100 mL Teflon®-lined autoclave and heated at 200 °C for 12 h. After the hydrothermal reaction, the autoclave was allowed to cool naturally to room temperature. The resulting product was collected by centrifugation and washed repeatedly with distilled water and absolute ethanol followed by vacuum drying at 60 °C overnight. The dispersion of nanowires in water was ivory coloured.

Synthesis of GQDs

Typically, 5.0 mL, 30 mg mL^{-1} GO aqueous solution was added into 5.0 mL, 2.0 M (6 wt. %) H_2O_2 aqueous solution. Then, 50 mg $W_{18}O_{49}$ nanowires was added into this mixture. The obtained mixture was transferred into a 15 mL Teflon®-lined autoclave and heated at 200 °C for 72 h. The pale yellow GQD aqueous solution (Figure 1) can be easily obtained after simple centrifugal separation (remove the catalyst). The obtaided GQD aqueous solution is 5.8 mg mL^{-1} and the yield is 77.3 % which is higher than most previous reports.

Characterization

TEM measurements were carried out on a spherical aberration-corrected TEM (FEI Titan 80-

300) at 80 kV. X-ray photoelectron spectra (XPS) were carried out on a PHI Quantera II system (Ulvac-PHI, INC, Japan). The UV-vis spectra were obtained on a UV5800 Spectrophotometer. PL and PLE spectra were recorded on a PerkinElmer LS55 luminescence spectrometer (PerkinElmer Instruments, U.K.) at room temperature in aqueous solution. The stability of these products was determined via contrast the fluorescent emission intensity of products aqueous solution under different conservative time at room temperature.

As the most direct and important index, the quantum yield (φ) of GQDs was calculated according to equation 1:[s1]

$$\varphi = \varphi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2} \qquad (1)$$

where I is the measured integrated emission intensity, η is the refractive index of the solvent, A is the optical density, and the subscript R refers to the reference standard with a known φ (RhB in ethanol solution, φ_R=0.68). In order to minimize reabsorption effects, absorbance was kept under 0.1 at 345 nm excitation wavelength in 10×10 mm fluorescence cuvette.

Cells experiments

The HELA cell line was obtained from the Cell Bank of Chinese Academy of Science and cultured in the standard medium at 37 °C in 5% CO_2. Cells were seeded in a 96-well plate for 24 h before GQDs treatment. Serial dilutions of GQDs with known concentrations were added into cells. After 24 h incubation, the relative viabilities of cell samples were determined by colorimetric 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) assays were performed to assess the metabolic activity of cells treated as described above. Cells were lysed with acidulated sodium dodecyl sulfate (SDS). Absorbance was measured at 570 nm using microplate reader (Bio-Rad 680, U.S.A.). All measure-ments were done in triplicate, and at least three independent experiments were carried out.

Supplementary figures

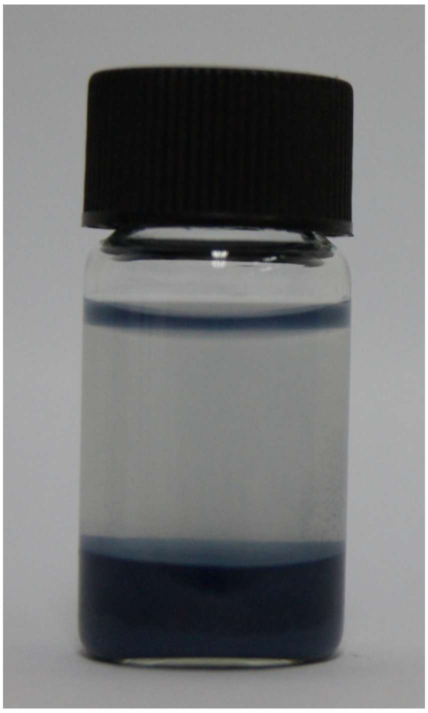

Fig. S1 Digital photo of $W_{18}O_{49}$ nanowire

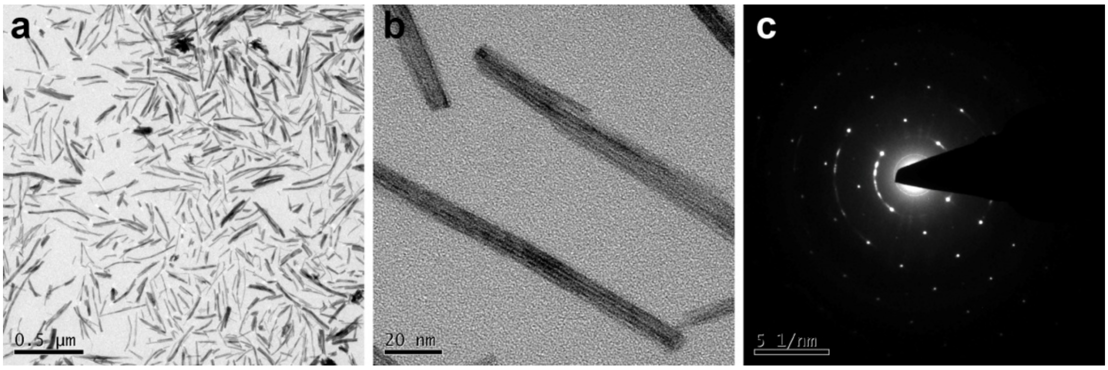

Fig. S2 (a) TEM image of $W_{18}O_{49}$ nanowire. (b) High resolution TEM image of $W_{18}O_{49}$ nanowire. (c) SAED pattern of a single$W_{18}O_{49}$ nanowire.

Fig. S3 Digital photo of the mixture after hydrothermal reaction.

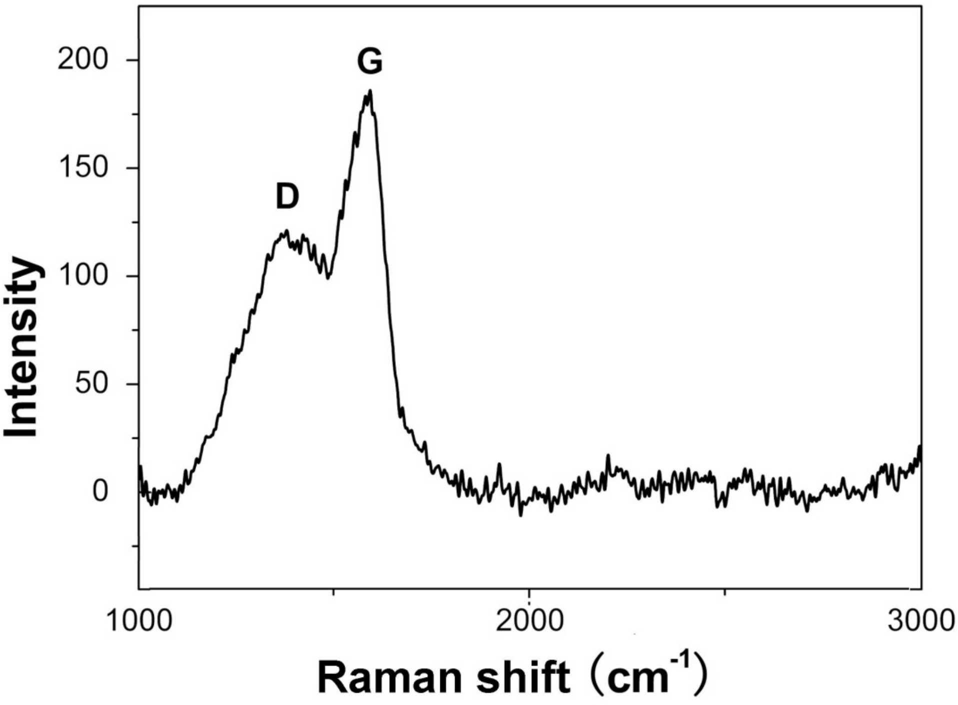

Fig. S4 Raman spectrum of GQDs.

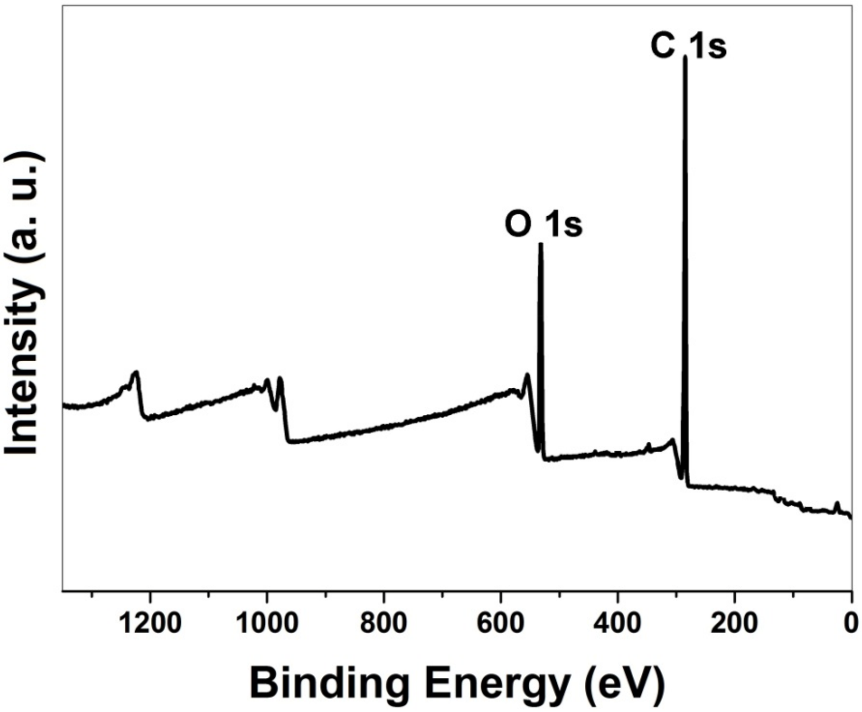

Fig. S5 XPS spectrum of GQDs.

Table S1 A brief summary of GQDs.

Size (nm)	λ_{ex} (nm)	λ_{em} (nm)	FWHM (nm)	φ	Ref.
3.4	345	408	70	0.69	This work
4	402	448	70	0.57	This work
6	421	476	80	0.56	This work
9	474	532	95	0.49	This work
15	498	557	120	0.47	This work
3	325	445	102	0.699	S2
2	530	530	130	0.981	S3
5	375	570	150	0.10	S4
3	370	452	90	0.365	S5
2	320	430	75	0.155	S6
3	305	413	80	0.345	S7
5	390	520	90	0.31	S8
4	320	405	120	0.164	S9
3	360	430	90	0.545	S10
3	340	440	80	0.78	S11

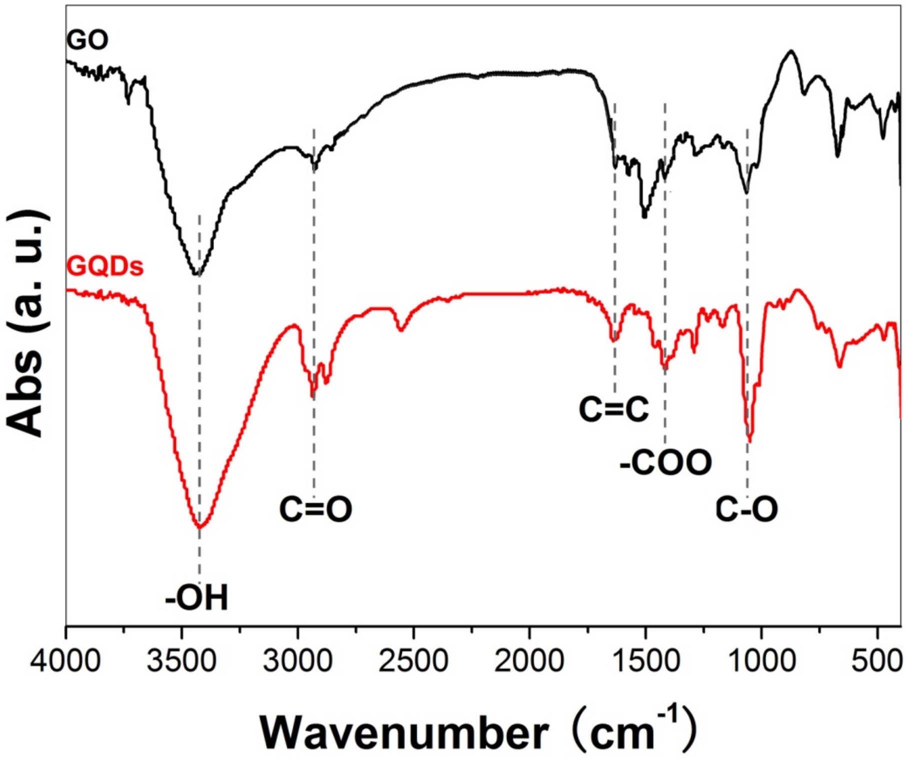

Fig. S6 FTIR spectra of GO (black curve) and GQDs (red curve).

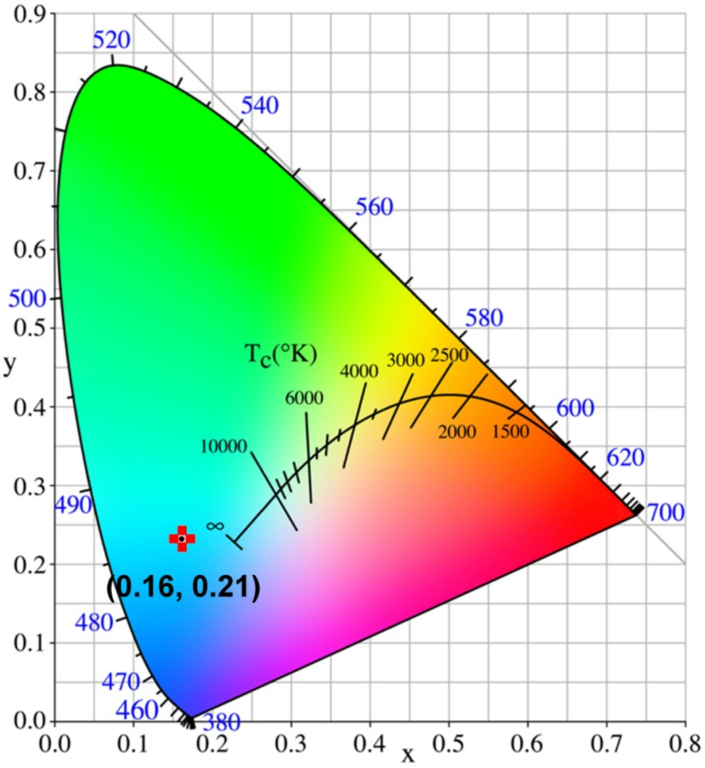

Fig. S7 The CIE chromaticity coordinates for GQDs aqueous solution in Figure 3b.

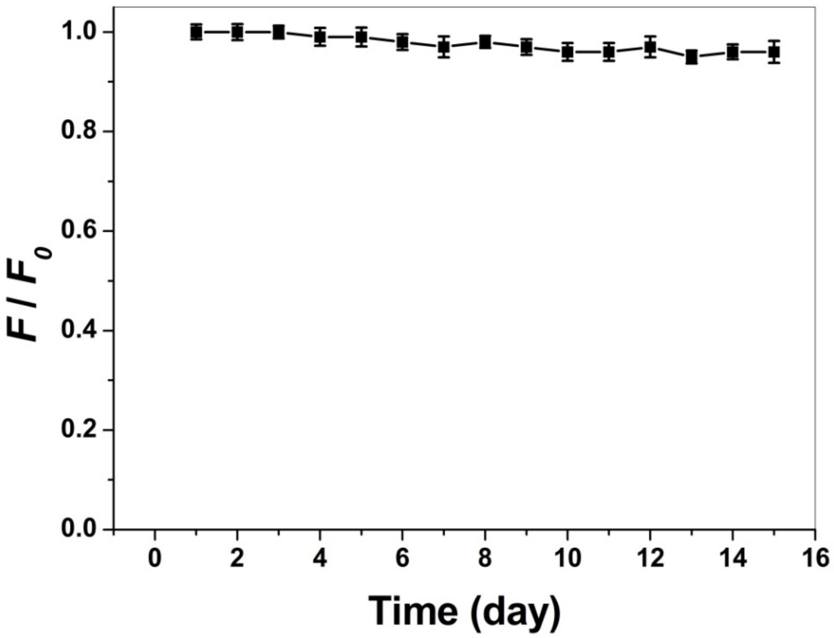

Fig. S8 Stability of GQDs under visible light. The concentration of GQDs is 0.1 mg/mL. F_0 is PL intensity of GQDs (0.1 mg/mL), F is PL intensitie of GQDs (0.1 mg/mL) under different time.

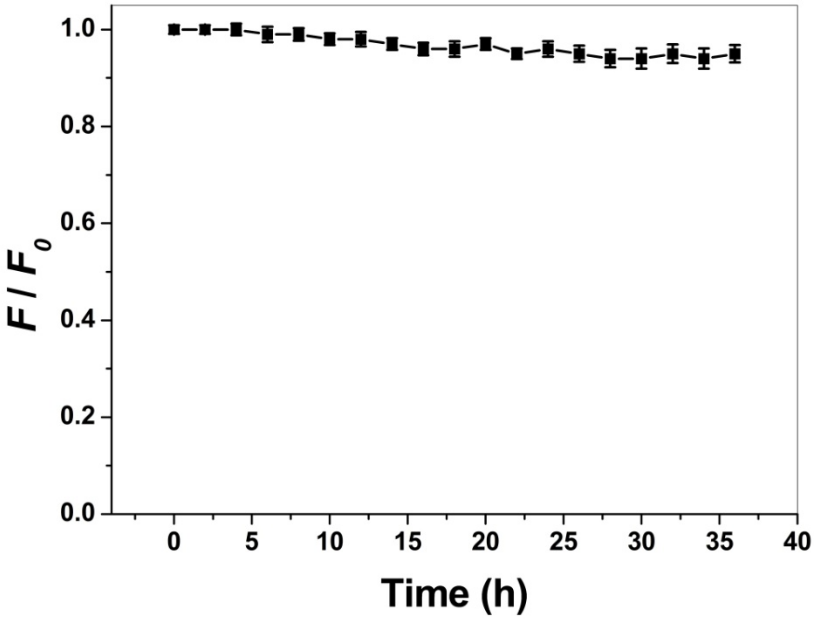

Fig. S9 Stability of GQDs refluxed in acid. The acid refluxing experiments are measured by refluxing GQDs in 0.1 M HCl aqueous solution at 100 °C. The concentration of GQDs is 0.1 mg/mL. F_0 is PL intensity of GQDs (0.1 mg/mL), F is PL intensitie of GQDs (0.1 mg/mL) under different refluxing time.

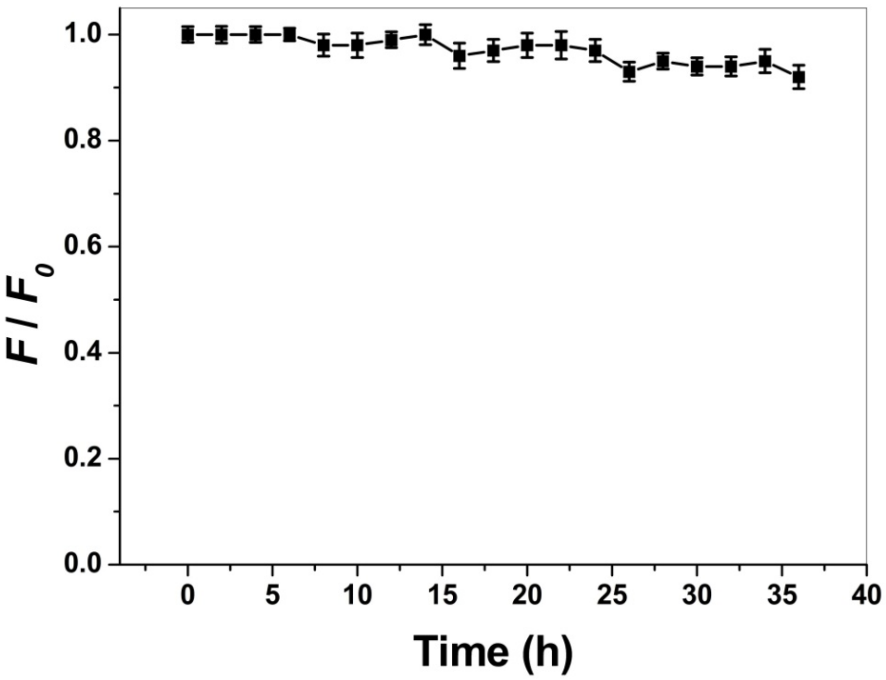

Fig. S10 Stability of GQDs be refluxed in base. The acid refluxing experiments are measured by refluxing GQDs in 0.1 M NaOH aqueous solution at 100 °C. The concentration of GQDs is 0.1 mg/mL. F_0 is PL intensity of GQDs (0.1 mg/mL), F is PL intensitie of GQDs (0.1 mg/mL) under different refluxing time.

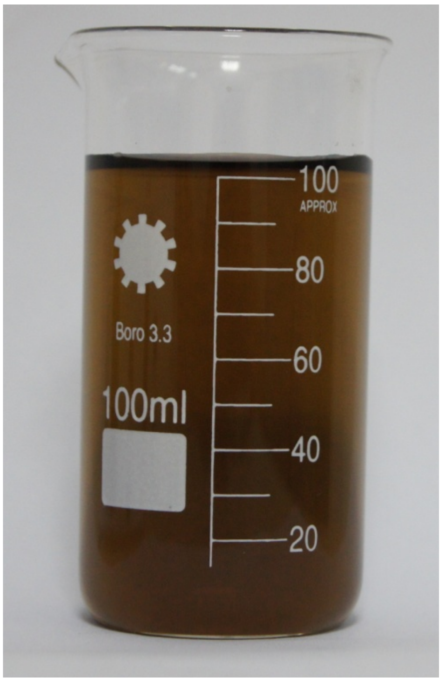

Fig. S11 Digital photo of reaction liquid without $W_{18}O_{49}$ nanowire after hydrothermal reaction.

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