Electronic Supplementary Information

Nearly Monodisperse Graphene Quantum Dots Fabricated by amine-assisted Cutting and Ultrafiltration

Qi Xue,He Huang, Liang Wang, Zhiwen Chen, Minghong Wu, Zhen Li,* and Dengyu Pan*

Experimental Part

Materials

Except natural graphite (CP, Sinopharm), all oxidizing and reducing agents(AR), including sulphuric acid, nitric acid, hydrochloric acid, potassium persulfate, phosphorus pentoxide, hydrogen peroxide, potassium permanganate, and 30% ammonia water, were obtained from Sinopharm.

Synthesis

In a typical procedure for synthesizing and sorting monolayer GQDs, graphene oxide sheets were first prepared by the modified Hummers method, and then converted into chemically derived graphene sheets as the precursor of the GQDs by thermal deoxidation in a nitrogen atmosphere at 200 °C with a heating rate of 10 °C min^{-1}. 100 mg of graphene sheets was re-oxidized in an ultrasonic bath with a mixed acid of HNO_3 (120 mL) and H_2SO_4 (60 mL) for 24h. The mixture was diluted with DI water and filtered with a 0.22 um microporous membrane to remove the acid. A 70 mL aqueous dispersion of the oxidized graphene sheets (1 $mg{\cdot}mL^{-1}$) was mixed with 0.1g of branched PEI solution (70000,30%w/v, Alfar Aesar) under magnetic stirring, and then transferred to a 100 mL poly (tetrafluoroethylene) (Teflon)-lined autoclave. After heated at 150 °C for 10h, the suspension was cooled naturally to room temperature. A light-yellow supernatant containing GQDs of 1-3 layers was initially isolated from the product by filtration through a 0.22 um microporous membrane. Further ultrafiltration was performed on a centrifugal filter device at a rotating speed of 4750 r/min with a 3K Da molecular weight cut-off membrane (Amicon Ultra-15, Millipore) to sort monolayer GQDs from the supernatant. The bilayer GQDs were also isolated from the supernatant using a 10k Da molecular weight cut-off membrane at the same rotating speed.

Cell imaging:

Gastric epithelial cell line (GES-1) was cultured in Dulbecco's Modified Eagle Medium (DMEM) with L-glutamine, pyridoxine hydrochloride (Hyclone, USA), 10% (v/v) fetal bovine serum (Hyclone, USA), 0.1 mg mL^{-1} penicillin G sodium, and 0.1 mg mL^{-1} streptomycin sulfate (Amresco, USA). Approximately 2×10^5 GES-1cells were seeded in culture dishes (diameter: 40 mm) and cultured using the same culture medium (2 mL per dish) at 37 °C under 5% CO2/95% air. All cells were incubated for at least 24 h until approximately 80% confluence was reached. Then, an aqueous

solution of monolayer GQDs was introduced to the cells with a final concentration of ~ 0.02 mg mL^{-1} in the culture medium. After incubation for 1 h, the cells were washed twice with 1 mL D-Hanks solution and kept in D-Hanks solution (1 mL) for the confocal microscopy (Olympus FM 1000) analysis using a laser of 405 nm and detection in the 420~520 nm range.

Characterization Part

Samples were characterized by AFM using a SPM-9600 atomic force microscope, TEM on a JEOL JEM-2010F electron microscope operating at 200 kV, X-ray powder diffraction (XRD) with a Rigaku D/max-2500 using Cu Ka radiation, FT-IR spectroscopy recorded on a Bio-Rad FTIR spectrometer FTS165, and Raman spectroscopy on a Renishaw in plus laser Raman spectrometer with 514 nm. Absorption and fluorescence spectra were recorded at room temperature on a Hitachi 3100 spectrophotometer and a Hitachi 7000 fluorescence spectrophotometer, respectively. X-ray photoelectron spectroscopy (XPS) data were obtained with an AMICUS electron spectrometer from SHIMADZU using 300W Al K_{α} radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Curve fitting of the C 1s and N 1s spectra was performed with a Gaussian-Lorentzian peak shape. Zeta potential analysis of PEI-GQDs was performed with a Zetasizer Nano ZS90 zeta potential analyzer (MALVERN INSTRUMENTS LTD, England).

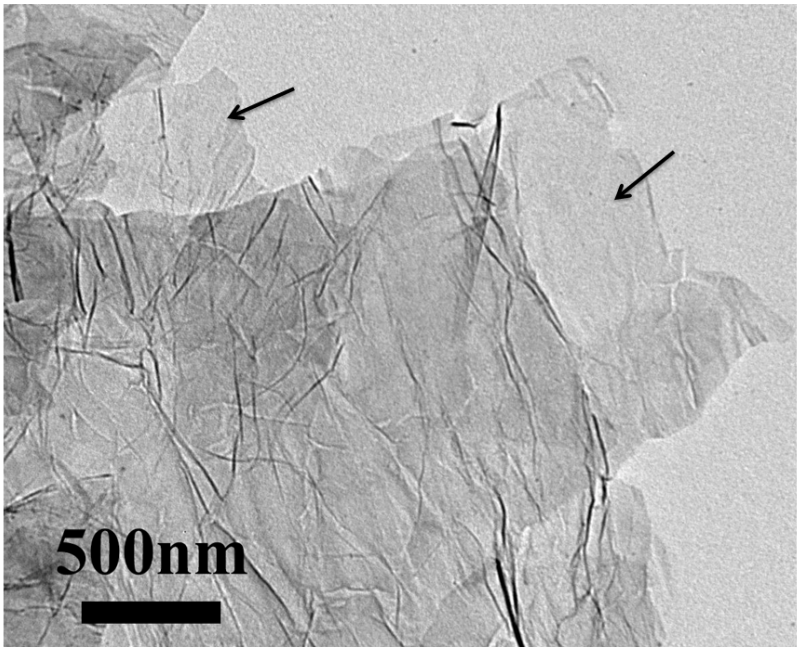

Figure S1. TEM image of thermally reduced graphene sheets (rGSs). Arrows point at single-layer rGSs.

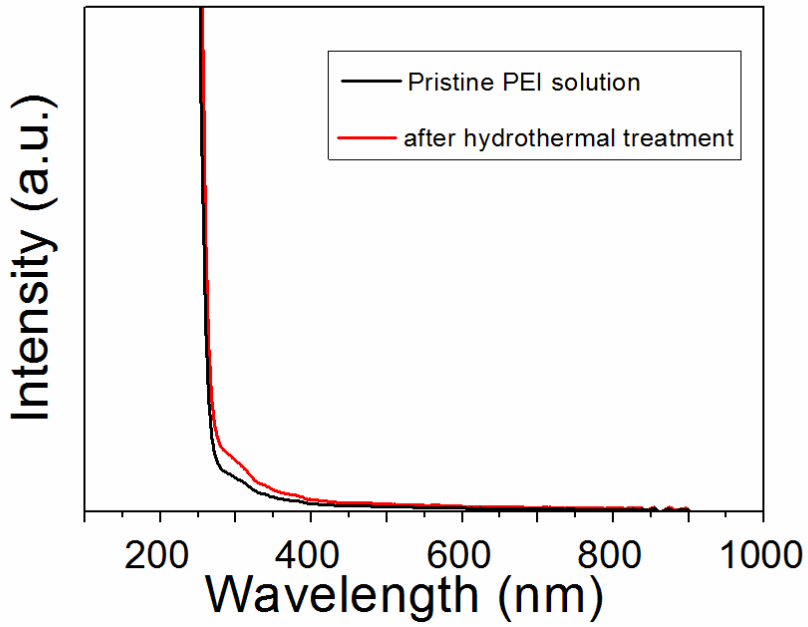

Figure S2. UV-vis absorption spectra of pristine PEI aqueous solution (black) and PEI solution after hydrothermal treatment for 10h at 150 ^{o}C (red). Their similar absorption spectra indicate that PEI molecules remain stable at 150 ^{o}C.

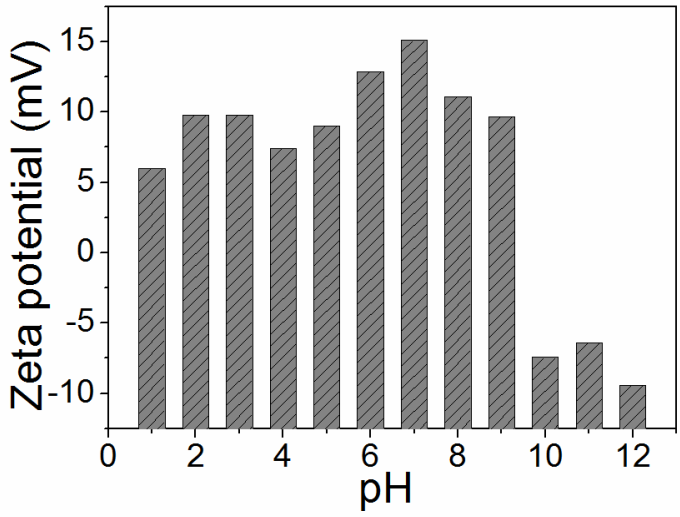

Figure S3. Effect of solution pH on the zeta potentials of PEI-GQDs.

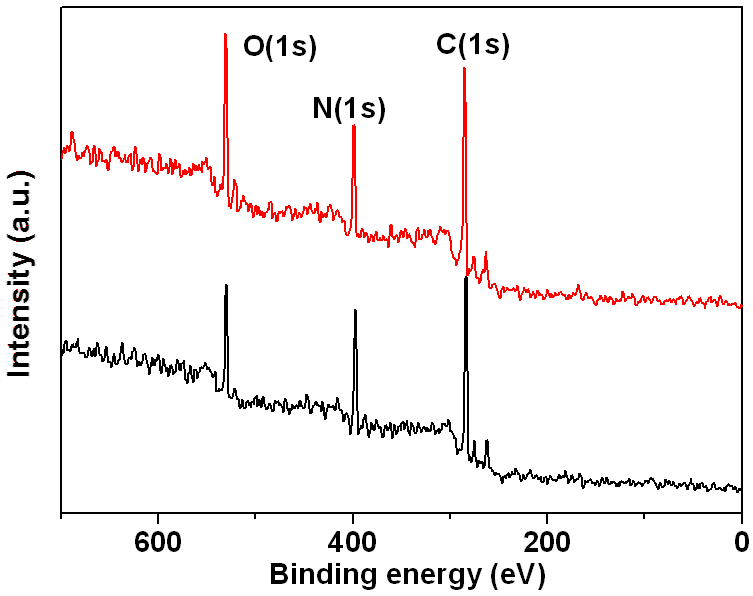

Figure S4. Survey XPS spectra of monolayer GQDs (red) and bilayer GQDs (black).

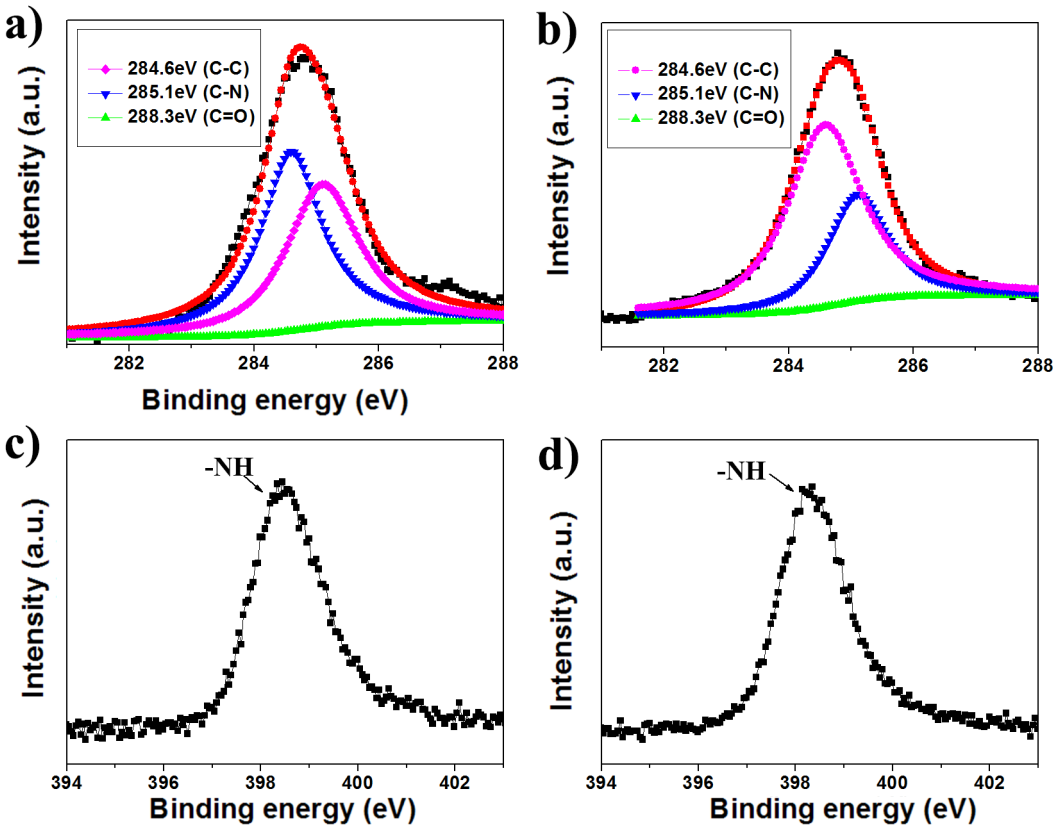

Figure S5. a) High-resolution C 1s spectrum of monolayer GQDs. a) High-resolution C 1s spectrum of bilayer GQDs c) High-resolution N 1s spectrum of monolayer GQDs. d) High-resolution O 1s spectrum of bilayer GQDs.

.

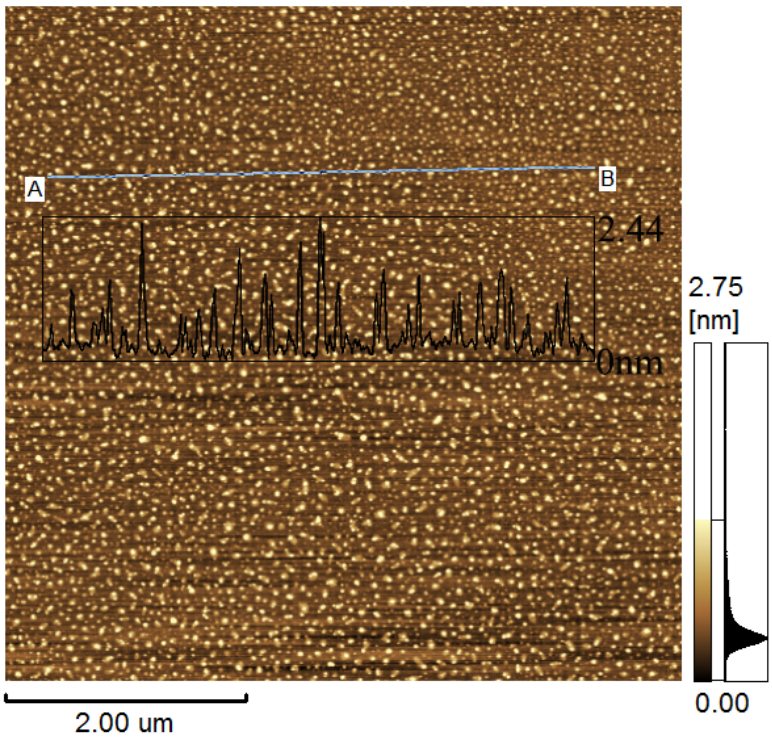

Figure S6. AFM image of the pristine PEI-GQDs on a mica substrate.

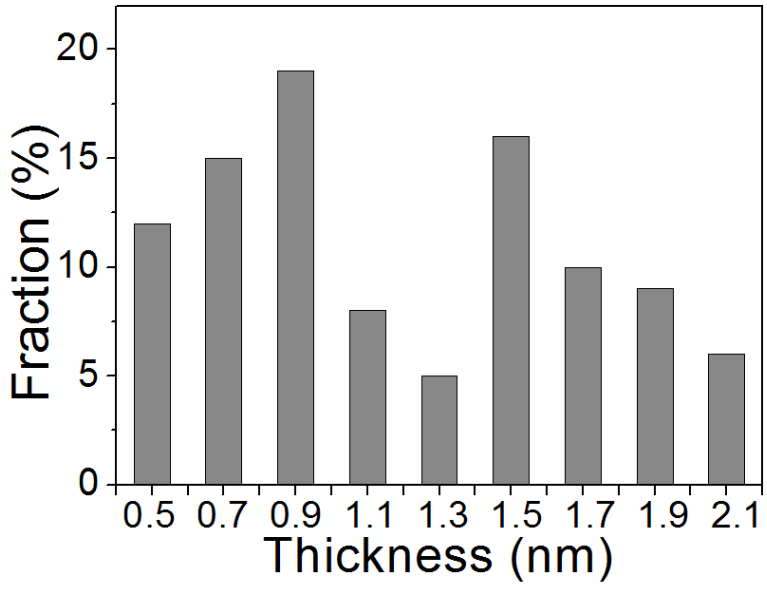

Figure S7. Height distribution of the pristine PEI-GQDs from the AFM analysis (Figure S2).

Table S1. PL quantum yields of PEI-GQDs using quinine sulfate as a reference according to the formula QYs=QYr (Is/Ir) (Ar/As) (ns/nr) 2, where 's' denotes the sample, and 'r' the reference.

Sample	Integrated emission intensity (I)	Abs.at 340 nm(A)	Refractive index of solvent (n)	Quantum yield (QY)
Quinine sulfate	76898	0.015	1.33	54%
Monolayer GQDs	80336	0.040	1.33	21%
Bilayer GQDs	29762	0.031	1.33	10%