Supporting Information

Electrochemical synthesis of small-sized red fluorescent graphene quantum dots as a bioimaging platform

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Experimental Section

Preparation of RF-GQDs. High purity graphite rods were purchased from Shanghai Carbon Co., Ltd. All solvents and reagents were purchased from J&K and used without further purification. The electrolysis of the graphite rod was performed on CHI 705 with a current intensity in the range of 80–200 mA cm^{-2} (potential: 5V) in 7 mL 0.01 M $K_2S_2O_8$ aqueous solution (pH = 7). Based on the previous work, [1] the O and OH radicals produced by anodic oxidation of water can serve as electrochemical "scissors" to cut graphene sheets from the graphite. Then the top solution was decanted carefully and centrifuged at 10000 rpm for 10 min to remove the insoluble residual. In order to get a pure GQD solution of pH = 7 for culturing with living cells, the obtained solution was dialyzed over deionized water in a dialysis bag (retain molecular weight 3500 Da) for one day.

Quantum Yield Calculation. The quantum yield (Φ) of RF-GQDs was calculated using rhodamine B as reference. The quantum yield was calculated using the below equation:

$$\Phi_X = \Phi_{ST} (m_X / m_{ST}) (\eta_X^2 / \eta_{ST}^2)$$

Where Φ is the quantum yield, m is slope, η is the refractive index od the solvent, ST is the standard and X is the sample. The quantum yield for RF-GQDs is 1.8%.

MTT assays. The MTT assays were performed to evaluate the toxicity of RF-GQDs and were detected by Victor3 V Multilabel reader (PerkinElmer, U.S.A). Mean absorbance for drug dose was expressed as a percentage of the control untreated well absorbance and plotted vs. drug concentration. Inhibition of different cell lines obtained after 24 h regular treatment of GQDs by MTT assay is shown in Figure 4c. No significant loss of cell viability was observed with the concentration of incubated RF-GQDs 1000 μg mL^{-1}.

Characterizations. Transmission electron microscopy (TEM) was taken on JEOL JEM 2100. Sample solution was drop-cast from solution onto a carbon-coated TEM grid and the solvent was evaporated at room temperature. X-ray diffraction (XRD) patterns were obtained by using Cu Ka radiation (XRD, PANalytical X'Pert Pr MPD). The FT-IR spectra were measured using a Nicolet 380 spectrograph. Fourier transform X-ray photoelectron spectroscopy (XPS) were carried out by an ESCAlab 250Xi electro spectrometer from Thermo Scientific using 300WAl Ka radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The UV–vis absorption and the PL spectra were measured with a UV-2450 spectrometer and a Cary Eclipse fluorimeter, respectively. An Olympus fluorescence microscope was used to obtain fluorescence microscopy images, with excitation wavelengths at 488 nm. The Raman spectra were taken with Laser Confocal Micro-Raman Spectroscopy (Lab- RAM Aramis). The atomic force microscope (AFM) images were obtained by MultiMode V SPM (VEECO).

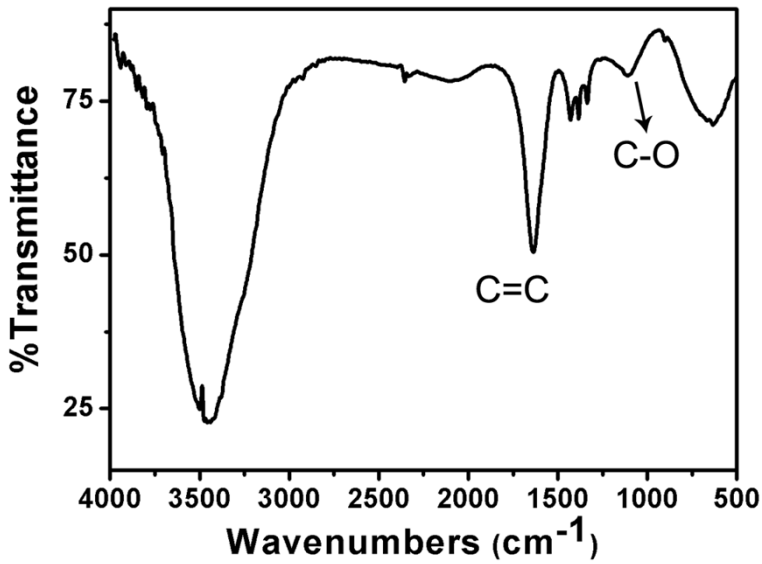

Figure S1 FT-IR spectrum of RF-GQDs. The peak at ~1125 cm-1 indicates C-O stretching vibrations and peak at ~1683 cm-1 is due to C=C stretching vibrations.

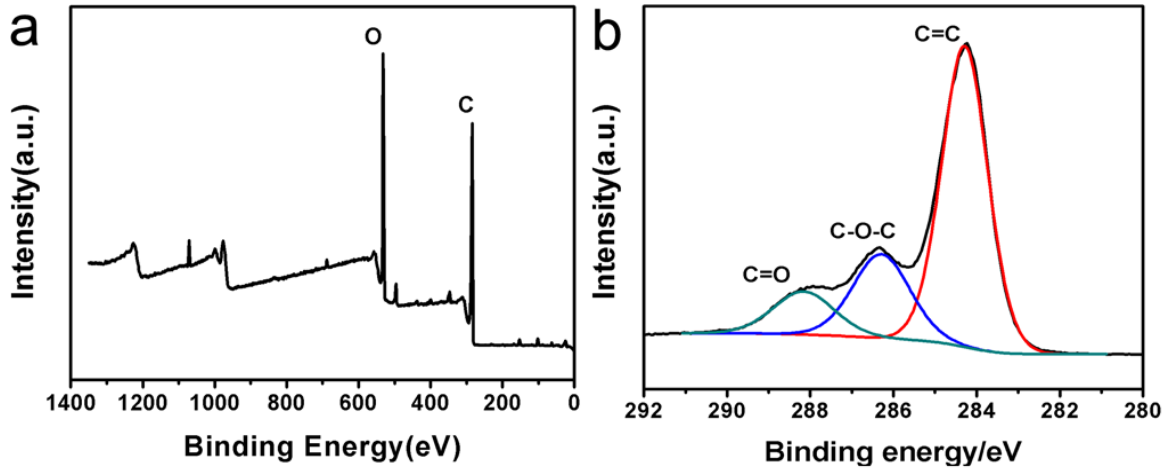

Figure S2 Survey XPS analysis (a) and high-resolution C1s XPS spectra (b) of RF-GQDs. Deconvoluted C1s indicates three components assigned as C=C at ~284.3eV, C-O-C at ~286.5eV and C=O at ~288.3eV.

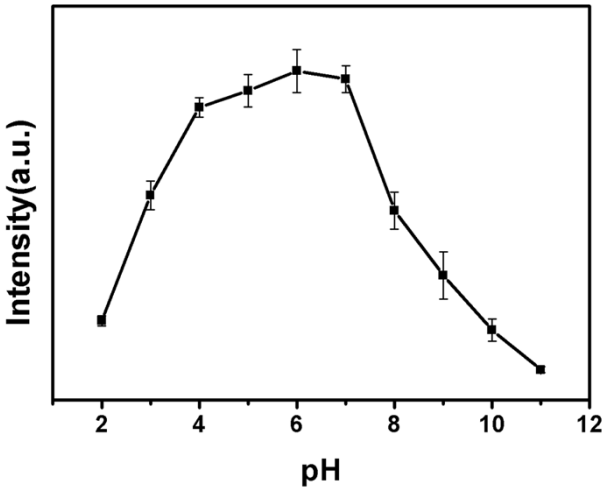

Figure S3 The influence of pH value of the solution on the fluorescence intensity of RF-GQDs (5 μg/mL)

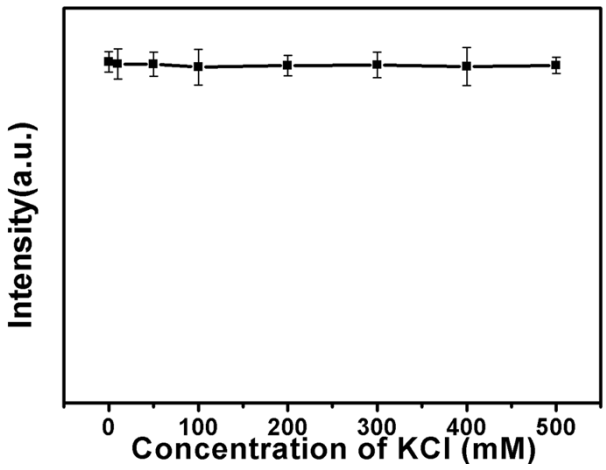

Figure S4 The influence of KCl concentration (0, 10, 50, 100, 200, 300, 400, 500 mM) on the fluorescence intensity of RF-GQDs (5 μg/mL)

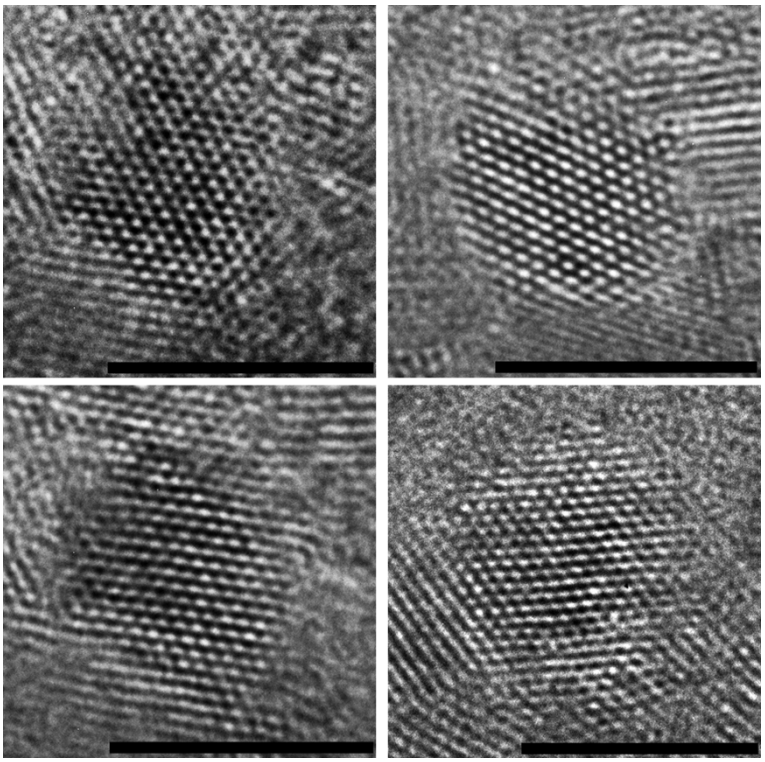

Figure S5 HRTEM image of RF-GQDs prepared from different batches (scale bar: 5 nm)

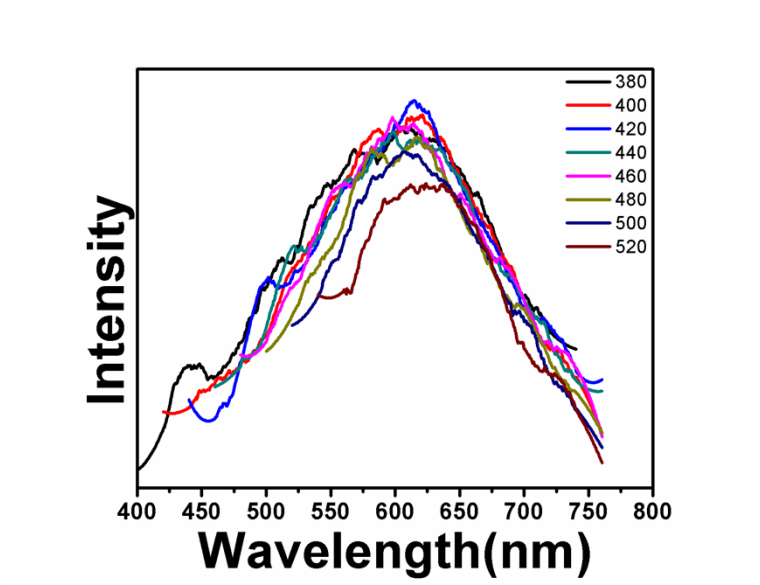

Figure S6 PL spectra of GQDs by electrolysis graphite in 7 mL 0.1 M Na_2SO_4 aqueous solution

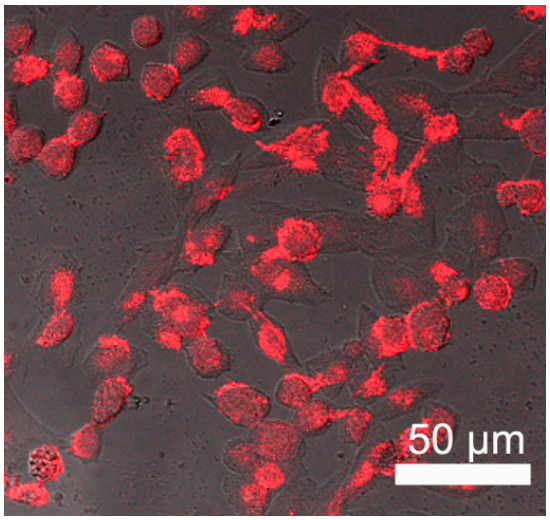

Figure S7 Merged fluorescent and bright-field image

Notes and references

1 M. Zhang, L. Bai, W. Shang, W. Xie, H. Ma, D. Fang, H. Sun, L. Fan, L.; Han, M.; Liu, C.; Yang, S., *J. Mater. Chem.* 2012, **22**, 7461.