

Electronic Supplementary Information

Highly Efficient Photoluminescent Graphene Oxide with Tunable Surface Properties

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Experimental

Procedures for graphene oxide functionalization: The starting graphene oxide powder was prepared from natural graphite flakes by a modified Hummers method.^{S1,S2} The dried graphene oxide (20 mg) and *N,N*-dimethylformamide (2 mL) were refluxed in dichlorosulfoxide (20 mL) at 80°C for 48 h. After centrifugation, the supernatant was decanted and the remaining solid was washed with anhydrous tetrahydrofuran two times followed by drying in vacuum at room temperature. A mixture of the activated GO acyl chloride (GO-COCl) and *n*-butylamine (1 mL) was heated under nitrogen at 60°C for 72 hours. The reaction mixture was cooled down to room temperature and then dispersed in DI water (20 mL). A light green supernatant was obtained after the mixture was centrifuged at 8000 rpm for 10 min. The supernatant was then dried by rotary evaporation. The alkylamine modified GO powder was readily re-dispersed in DI water (20 mL) to get light green suspension with a concentration of about 1.8 mg/mL. The same procedure was used to prepare other alkylamine functionalized graphene oxides as for *n*-butylamine except for the temperatures. Specifically, the temperature is 80°C for 1,6-hexylenediamine, octylamine, and dodecylamine, while 120°C for PEG_{1500N}. The resulting products were dispersed in water, ethanol, and other organic solvents respectively according to their solubility.

Photoluminescence quantum yield measurements: Quinine sulfate in 0.1 M H₂SO₄ (quantum yield 0.54 at 350 nm) was chosen as a standard for the fluorescence quantum yield measurement.^{S3} The values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

$$(1) \quad QY_{sample} = QY_q \cdot \frac{A_{sample}}{A_q} \cdot \frac{F_q}{F_{sample}} \cdot \frac{\eta_{sample}^2}{\eta_q^2} \quad (2) \quad F = 1 - 10^{-D}$$

where QY is the quantum yield, A is the measured integrated emission intensity, and F which is calculated by equation 2 is the fraction of light absorbed. D is the absorbance at the excitation wavelength, and η is the refractive index. The subscript “ q ” refers to the reference fluorophore quinine sulfate of known quantum yield. The calculation details are presented in Fig. S1 and Table S1.

Instrumentation and characterization: UV-vis absorption and fluorescence spectra were recorded at room temperature on a Shimadzu UV-2550 spectrometer and Perkin-Elmer LS-45 luminescence spectrometer, respectively. FTIR spectra were recorded with a Thermo-Fisher Nicolet iS10 FTIR spectrometer. Photographs were taken with a canon 350D digital camera. AFM images were taken using a Atomic Force Microscope Nano First-3100. The XPS measurements were carried out with an Thermo ESCALAB 250 high performance electron spectrometer with an Al K α (1486.6 eV) radiation.

References

- S1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, **80**, 1339.
S2. V. C. Tung, M. J. Allen, Y. Yang, R. B. Kaner, *Nature Nanotech.* 2009, **4**, 25.
S3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd Ed., Kluwer Academic/Plenum Publishers, New York, 1999.

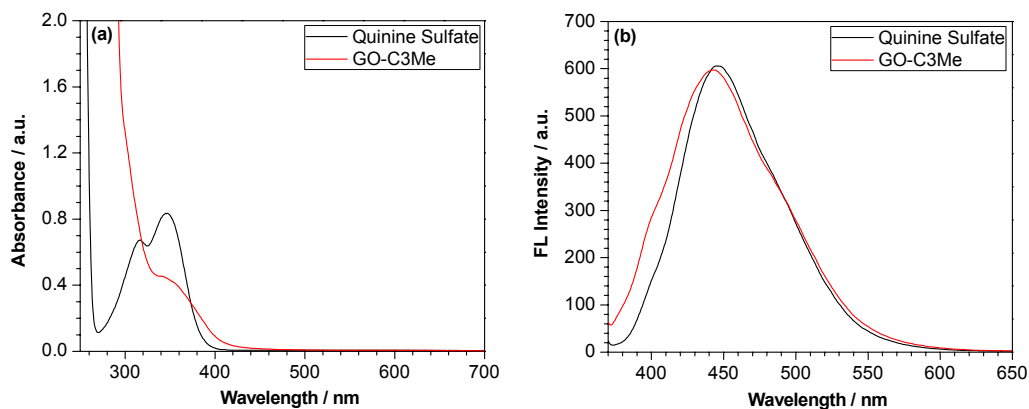


Figure S1. (a) UV-vis absorption of 0.1 mg/ml quinine sulfate in 0.1M H₂SO₄ and 3 mg/ml GO-C3Me in water. (b) Fluorescence spectra of 0.05 μg/ml quinine sulfate in 0.1M H₂SO₄ and 25 μg/ml GO-C3Me in water.

Table S1. Example for the fluorescence quantum yield calculation of GO-C3Me in water based on the standard.

Sample	A	F _{350nm}	η	Φ (%)
Quinine Sulfate	50480	1.89×10 ⁻³	1.33	54.0
GO-C3Me	50967	8.08×10 ⁻³	1.33	12.8

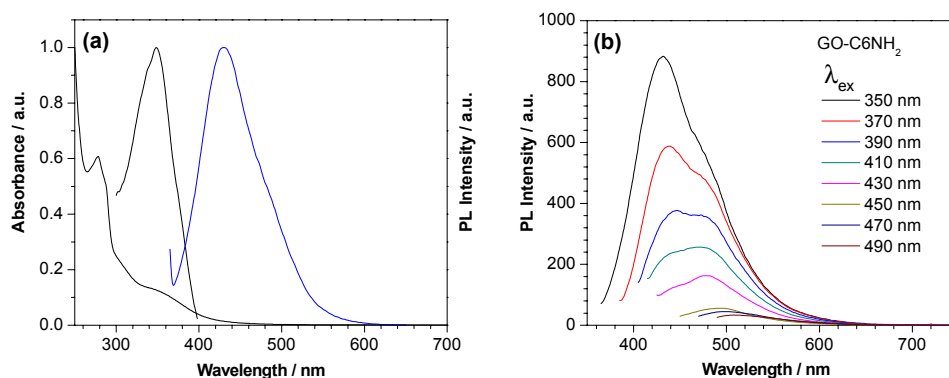


Figure S2. (a) UV-vis absorption and fluorescence spectra of GO-C6NH₂ in aqueous solution. The emission spectrum was obtained under excitation at 350 nm and the excitation spectrum was obtained at the maximum emission wavelength of 430 nm. (b) Fluorescence spectra of GO-C6NH₂ in water are recorded for progressively longer excitation wavelengths from 350 to 490 nm in 20 nm increments.

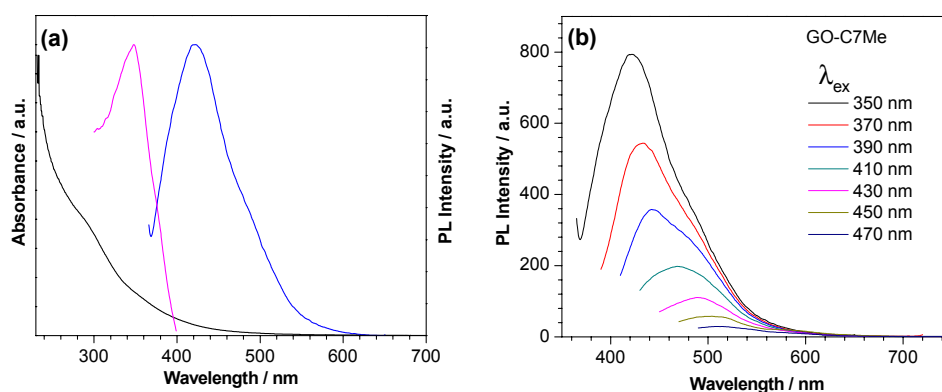


Figure S3. (a) UV-vis absorption and fluorescence spectra of GO-C7Me in ethanol. The emission spectrum was obtained under excitation at 350 nm and the excitation spectrum was obtained at the maximum emission wavelength of 420 nm. (b) Fluorescence spectra of GO-C7Me in ethanol are recorded for progressively longer excitation wavelengths from 350 to 510 nm in 20 nm increments.

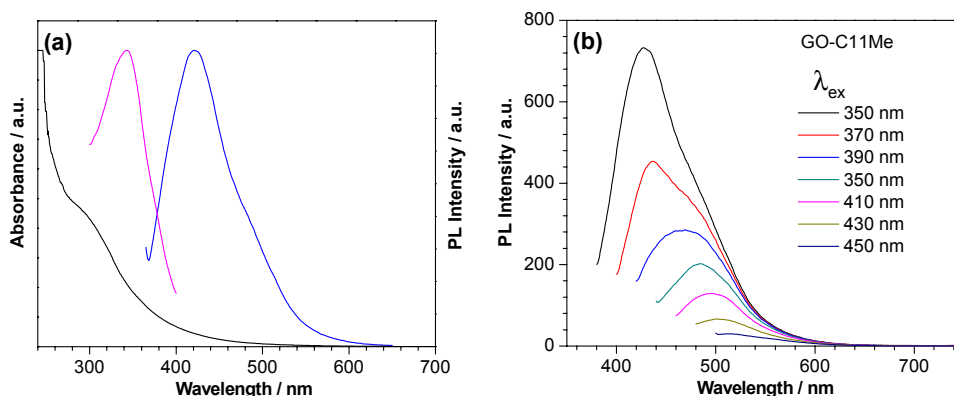


Figure S4. (a) UV-vis absorption and fluorescence spectra of GO-C11Me in ethanol. The emission spectrum was obtained under excitation at 350 nm and the excitation spectrum was obtained at the maximum emission wavelength of 420 nm. (b) Fluorescence spectra of GO-C11Me in ethanol are recorded for progressively longer excitation wavelengths from 350 to 490 nm in 20 nm increments.

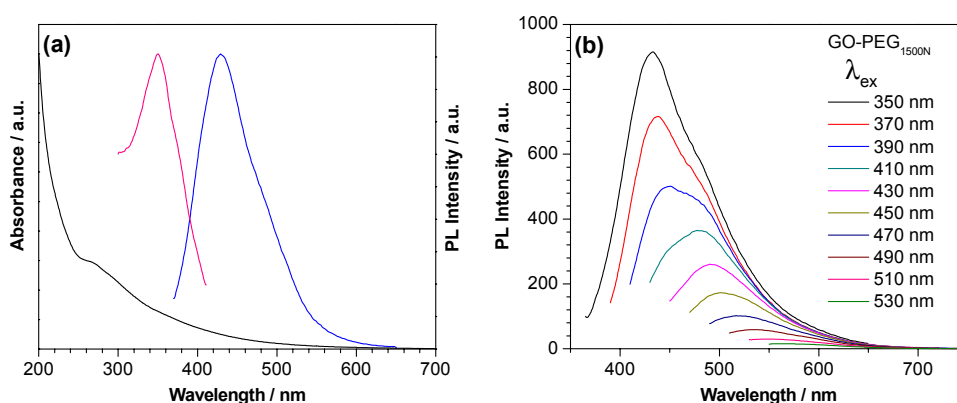


Figure S5. (a) UV-vis absorption and fluorescence spectra of GO-PEG_{1500N} in water. The emission spectrum was obtained under excitation at 350 nm and the excitation spectrum was obtained at the maximum emission wavelength of 430 nm. (b) Fluorescence spectra of GO-PEG_{1500N} in water are recorded for progressively longer excitation wavelengths from 350 to 530 nm in 20 nm increments.

Table S2. Surface charges of different alkylamine functionalized GO dispersed in water at three pH values. The surface charges of GO-C11Me and GO-C7Me are not measured because they are insoluble in water.

pH	5.0	7.4	10.0
GO	-30.2 mv	-37.2 mv	-42.0 mv
GO-C3Me	-15.5 mv	-23.4 mv	-28.0 mv
GO-C6NH ₂	-3.9 mv	-8.1 mv	-14.6 mv
GO-PEG ₁₅₀₀ N	-17.0 mv	-23.3 mv	-25.6 mv

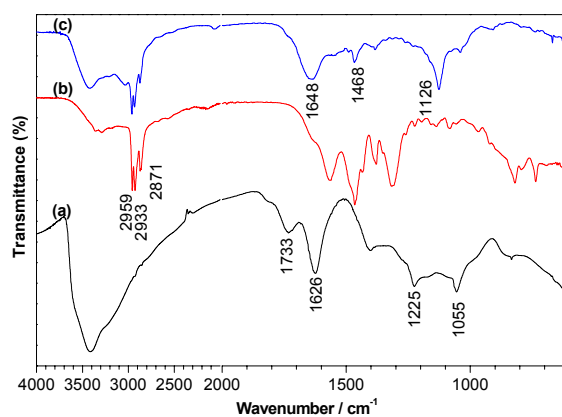


Figure S6. FT-IR spectra of (a) un-modified GO, (b) *n*-butylamine, and (c) *n*-butylamine modified GO (GO-C3Me).

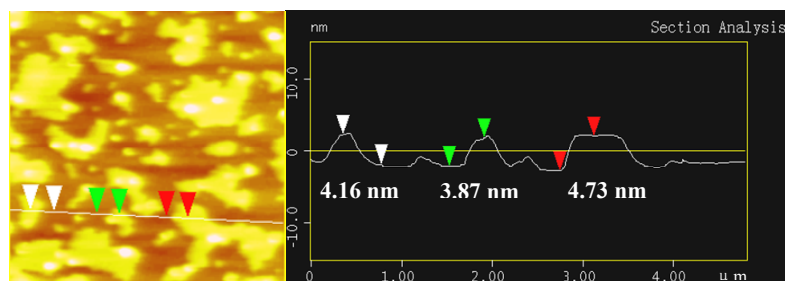


Figure S7. AFM image and cross-section analysis of GO-C3Me deposited on freshly cleaved mica substrate by spin coating of the aqueous solution. The thickness is about 4 nm.