Electronic Supporting Information (ESI)

Enhancement Fluorescence of Carbon Dots by Graphene and Highly Sensitive Detection of Tetracycline Hydrochloride

Wei He, Xiangying Sun*, Wenting Weng, Bin Liu

College of Materials Science and Engineering, Huaqiao University, Key Laboratory of Molecular Designing and Green Conversions (Fujian University), 361021 Xiamen, China.

Correspondence:

E-mail: sunxy@hqu.edu.cn

Tel: +86592 6162225

Fax: +86592 6160088

Contents

1. Synthesis of PDDA functionalized graphene with different reduction degree

GO (1 mg/mL, 20 mL) was uniformly dispersed in water by ultrasonication for 3 h. PDDA solution (20%, 0.5 mL) was added to GO solution with vigorous stirring. After 3 h, hydrazine hydrate solution (0.5 mL) was added to the above solution and stirred for 5min. Next, the mixture was reacted under hydrothermal conditions at 100℃, room temperature and light (the distance between the control solution and the Xe lamp was 10 cm) for 3 h, respectively. Then, the resulting mixture was washed with ultrapure water, centrifuged several times to remove unreacted chemicals and freeze-dried at -40°C under vacuum. Finally, PDDA-G, PDDA-RG and PDDA-LG solid powder were obtained, respectively.

2. Calculation the energy levels of CDs

To demonstrate the quenching mechanism of CDs, the HOMO and LUMO levels of CDs were calculated according to the following equation:

$$E_{HOMO} = -e(E_{ox} + 4.4)\ (eV) \quad (1)$$

$$E_{LUMO} = -e(E_{red} + 4.4)\ (eV) \quad (2)$$

$$E_{HOMO} = E_{LUMO} - E_g \quad (3)$$

where E_{ox} and E_{red} are onset of oxidation and reduction potential for CDs respectively. The E_{red} was determined to be -0.475 eV. The corresponding LUMO level was -3.93 eV. However, the HOMO energy could not be obtained due to the irreversible of the oxidation behavior (data not shown). E_g was estimated to be 3.54 eV (E_g resulting from the absorption edge in the absorption spectrum). So, the E_{HOMO} was calculated to be -7.47 eV.

3. Figures

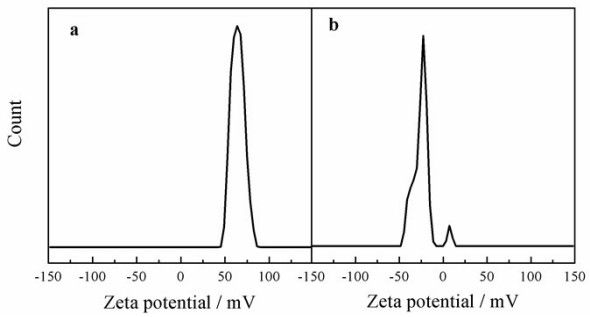

Fig. S1 Zeta potential of PDDA-G (a) and CDs (b).

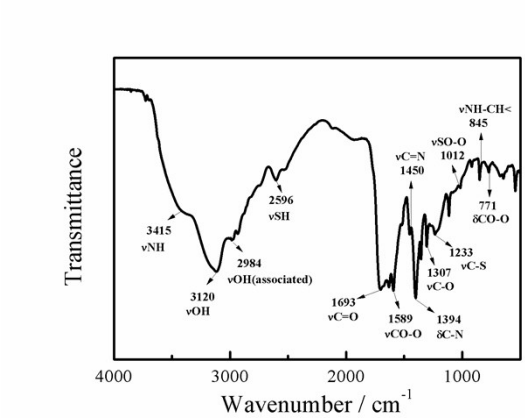

Fig. S2 FTIR spectra of CDs .

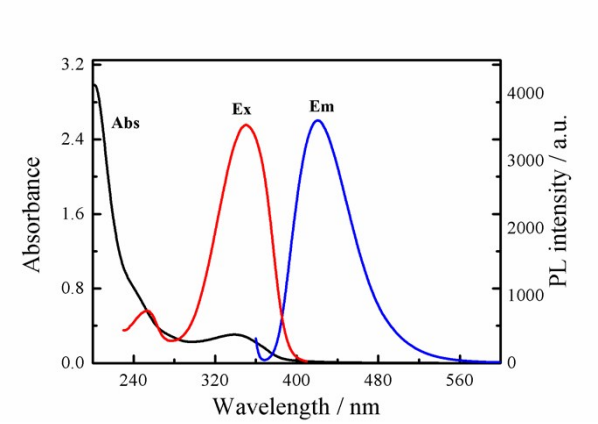

Fig. S3 UV-Vis absorption spectra, excitation and emission spectra of CDs

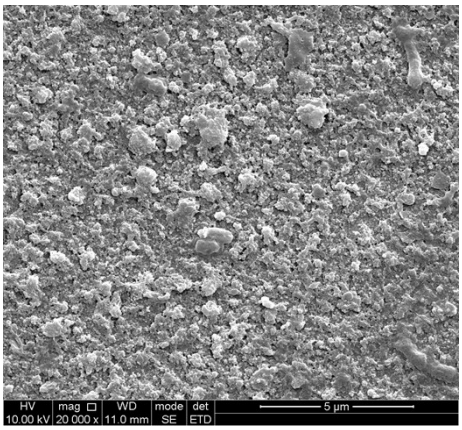

Fig. S4 SEM images of Quartz/PDDA-G/$(PSS/PDDA)_3$/CDs SAMs.

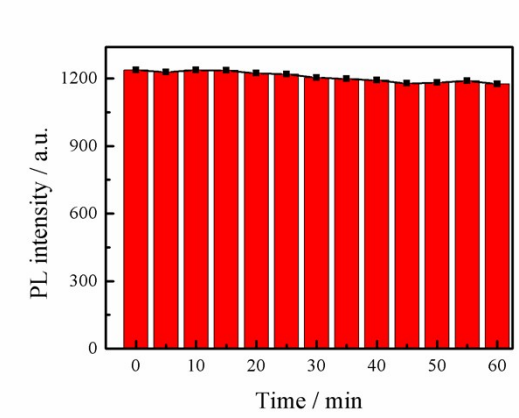

Fig. S5 Fluorescence intensity of Quartz/PDDA-G/$(PSS/PDDA)_3$/CDs SAMs for different irradiating time under UV lamp.

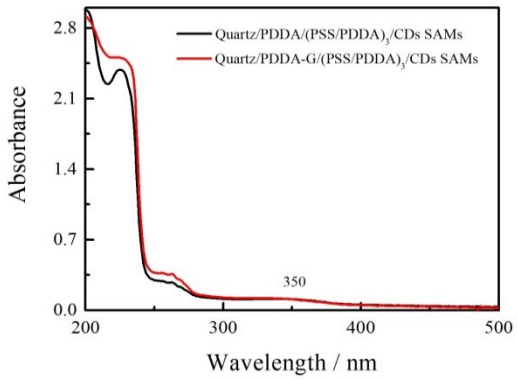

Fig. S6 UV-Vis absorption spectra of Quartz/PDDA-G/$(PSS/PDDA)_3$/CDs SAMs and Quartz/PDDA/$(PSS/PDDA)_3$/CDs SAMs.

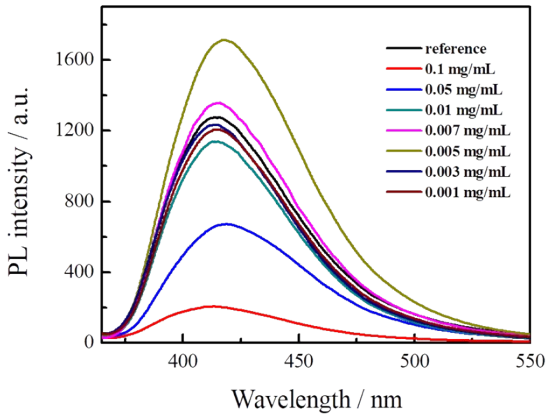

Fig.S7 Fluorescence spectra of Quartz/PDDA-G/$(PSS/PDDA)_3$/CDs SAMs with different PDDA-G concentration.

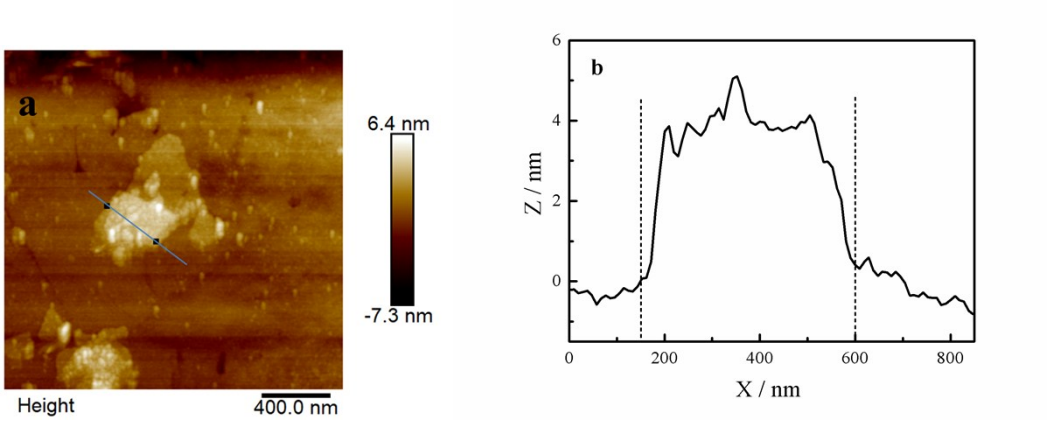

Fig.S8 (a) AFM images of Quartz/PDDA-G flim. (b) Corresponding thickness.

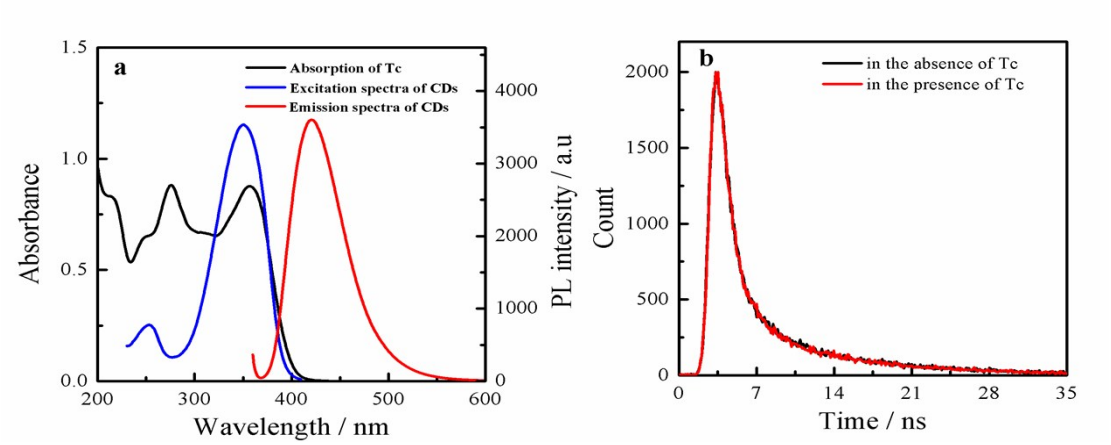

Fig. S9 (a) UV-Vis absorption spectra of Tc, fluorescence emission and excitation spectrum of CDs. (b) Fluorescence decay curves of Quartz/PDDA-G/$(PSS/PDDA)_3$/CDs SAMs in the absence or presence of 56.6 nM Tc.

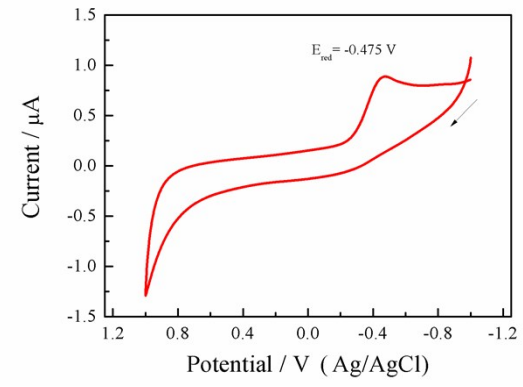

Fig. S10 The cyclic voltammetry curve of 0.1 mg/ mL CDs in 0.1 M pH=7 PBS with platinum sheet as the working electrode, a Pt-wire counter electrode and an Ag/AgCl reference electrode.

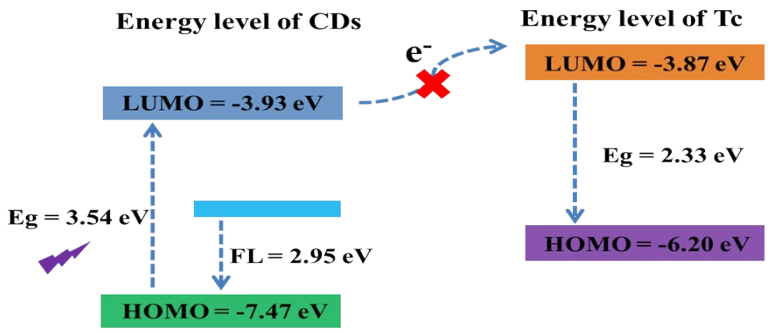

Fig. S11 Energy levels of the LUOM and HOMO of CDs and Tc.

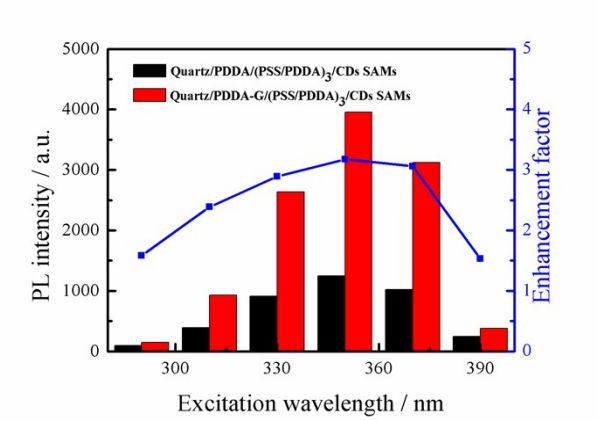

Fig. S12 Fluorescence spectra of Quartz/PDDA/(PSS/PDDA)$_3$/CDs SAMs and Quartz/PDDA-G/(PSS/PDDA)$_3$/CDs SAMs and enhancement factor with different excitation wavelength.

4. Tables

Table S1 Comparison of CDs SAMs with different methods for the detection of Tc

Analytical method	Sensor	Linear range(μM)	LOD(nM)	Ref.
Fluorescence	Eu^{3+}-AgNPs	0.0001-10	4	1
Fluorescence	CDs	2-150	520	2
Fluorescence	MQDs	0.01-0.7	1.2	3
Fluorescence	CDs@MIPs	0.02–14	5.5	4
Capillary electrophoresis	-	0.1125–0.5625	3.29	5
High performance liquid chromatography	-	0.027–1.362	5.355	6
Electrochemistry	Aptasensor	0.01125–11.25	2.25	7
Fluorescence	CDs SAMs	0.004762-0.09091	0.9284	This work

Table S2 Effect of interfering components on the detection of Tc

Coexiting substance	Concentration (M)	Change of fluorescence intensity (%)	Coexiting substance	Concentration (M)	Change of fluorescence intensity (%)
Trimethoprim	1×10^{-6}	-2.79	$CoSO_4$	1×10^{-6}	-1.99
1,3,5-Triazine	1×10^{-6}	-3.32	$MgSO_4$	6×10^{-6}	-1.84

Cefotaxime sodium	1×10^{-6}	-7.50	$ZnSO_4$	5×10^{-6}	-5.85
Clindamycin hydrochloride	1×10^{-6}	+6.67	$CaCl_2$	1×10^{-6}	+4.97
Procaine hydrochloride	1×10^{-6}	-3.61	KCl	8×10^{-6}	-2.84
Aspartic acid	5×10^{-6}	-8.83	NaCl	8×10^{-6}	-3.22
Lysine	1×10^{-6}	+4.15	$Fe(NO_3)_3$	1×10^{-6}	-4.35
Glucose	5×10^{-6}	-3.41	$Hg(AC)_2$	2×10^{-6}	-2.78

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