Electronic supplementary information

A fluorescence and scattering dual-mode probe based on carbon dots@cerium-guanosine monophosphate coordination polymer network for tetracycline detection

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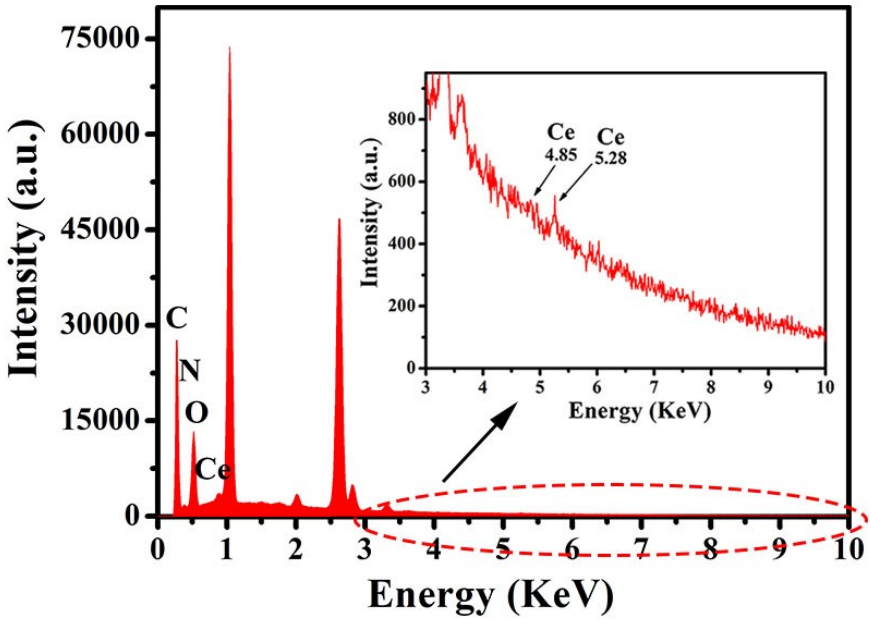

Fig. S1 EDS spectrum of the CDs@GMP-Ce. Inset is an amplified EDS spectrum image of the energy from 3 to 10 KeV.

Table S1 Element content of the CDs@GMP-Ce by EDS analysis.

Element	Weight (%)	Atomic (%)	Error (%)
C	42.19	49.37	4.99
N	10.65	10.68	11.39
O	45.27	39.76	9.16
Ce	**1.89**	**0.19**	**39.57**

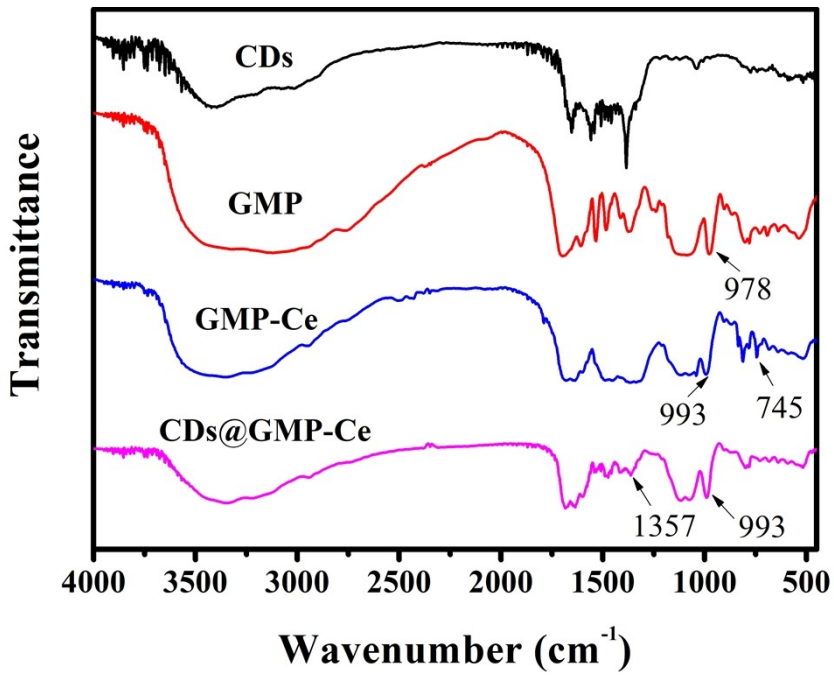

Fig. S2 FT-IR spectra of CDs, GMP, GMP-Ce, and CDs@GMP-Ce.

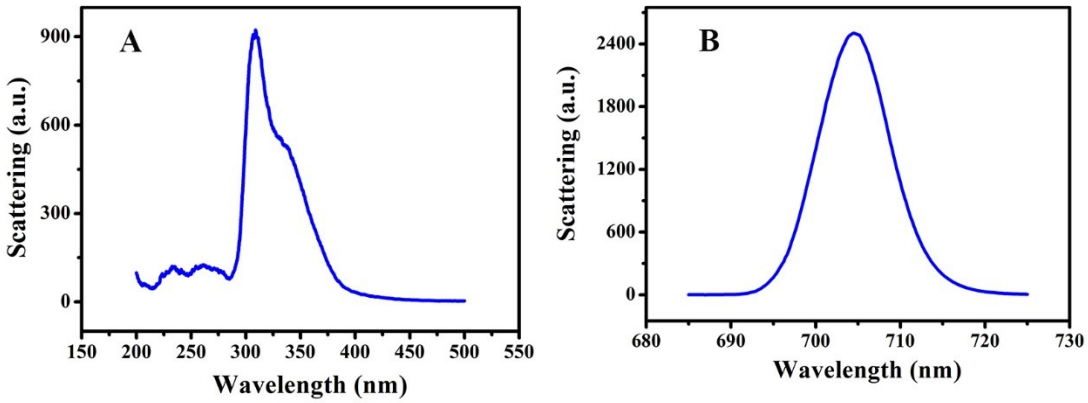

Fig. S3 (A) Synchronous Rayleigh scattering spectrum (synchronous scanning with $\lambda_{ex} = \lambda_{em}$, 200-500 nm) and (B) second-order Rayleigh scattering spectrum (excitation, 350 nm) of the CDs@GMP-Ce.

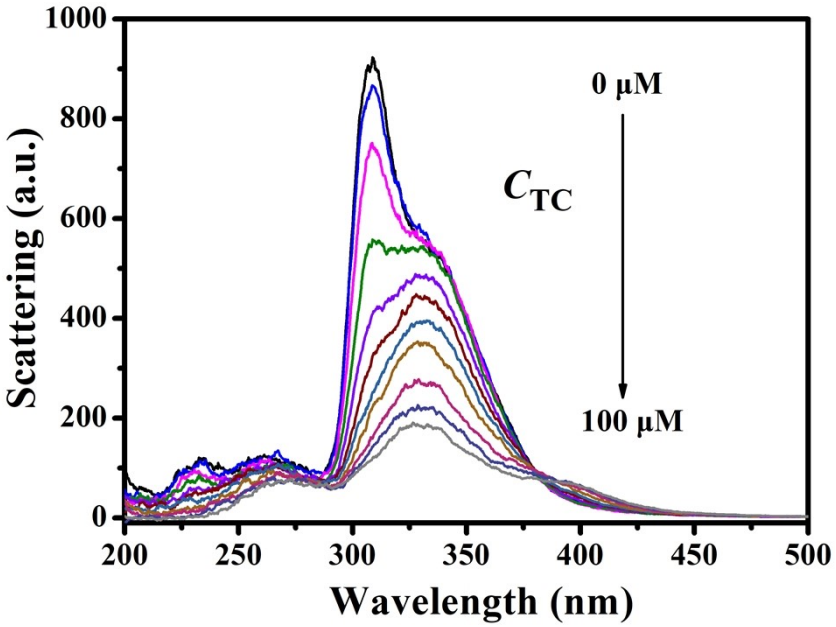

Fig. S4 Synchronous scattering spectra of the CDs@GMP-Ce solution with the addition of different TC concentrations from 0 to 100 μM. Condition: CDs@GMP-Ce, 84 mg mL^{-1}; PBS buffer, pH 7.2, 10 mM.

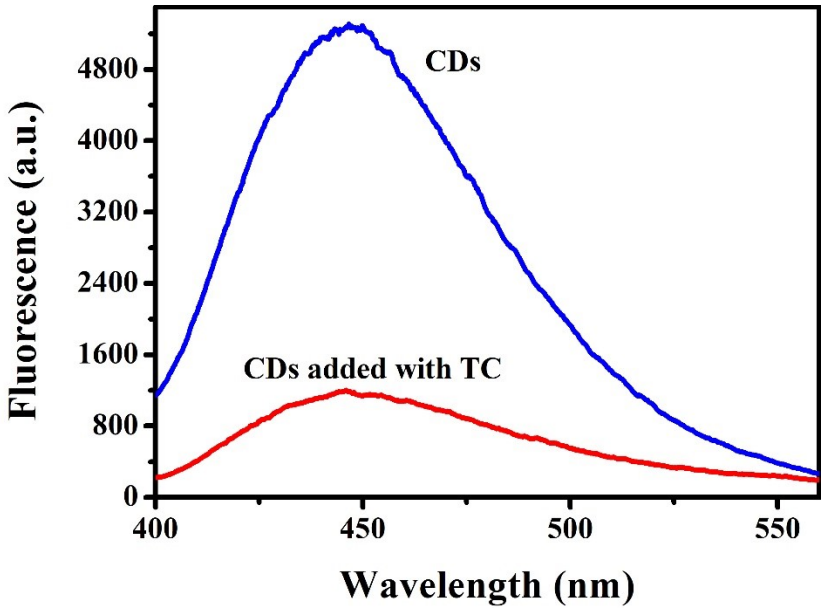

Fig. S5 Fluorescence spectra of CDs and CDs added with TC. Condition: CDs, 0.64 mg mL^{-1}; TC, 100 μM; PBS buffer, pH 7.2, 10 mM.

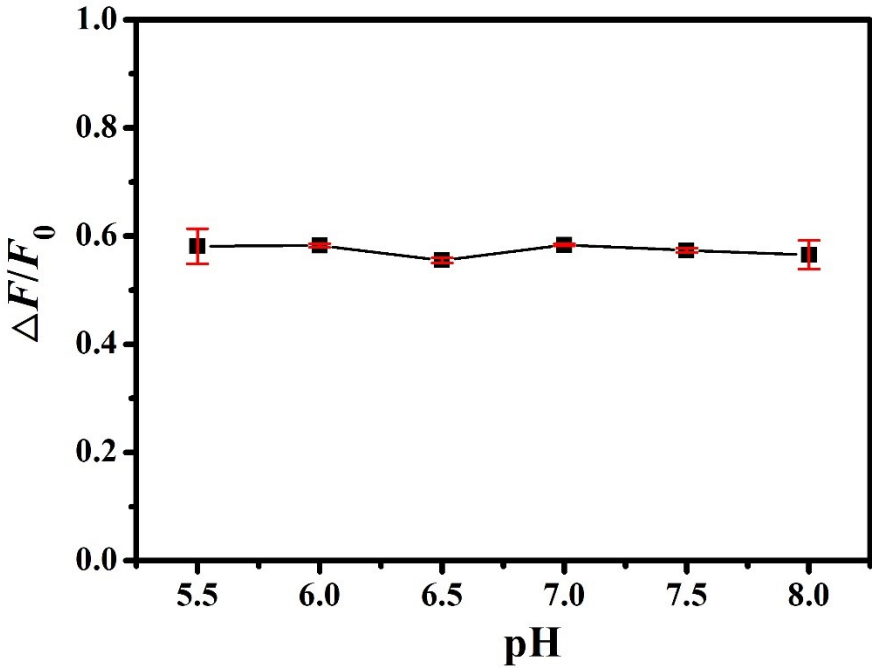

Fig. S6 Effect of pH on TC detection. Conditions: CDs@GMP-Ce, 84 mg mL^{-1}; PBS buffer, 10 mM; incubation time, 5 min; excitation/emission, 350/445 nm.

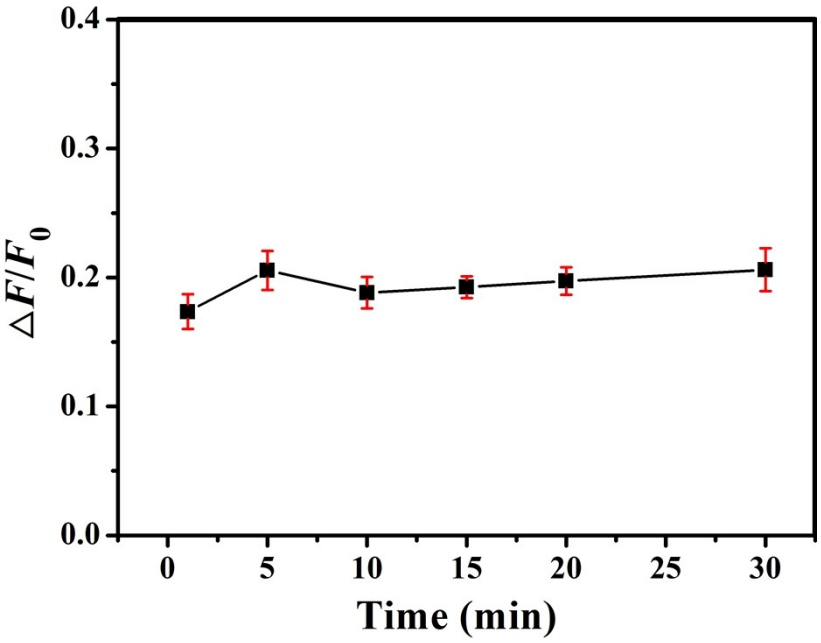

Fig. S7 Effect of incubation time on TC detection. Conditions: CDs@GMP-Ce, 84 mg mL^{-1}; PBS buffer, pH 7.2, 10 mM; excitation/emission, 350/445 nm.

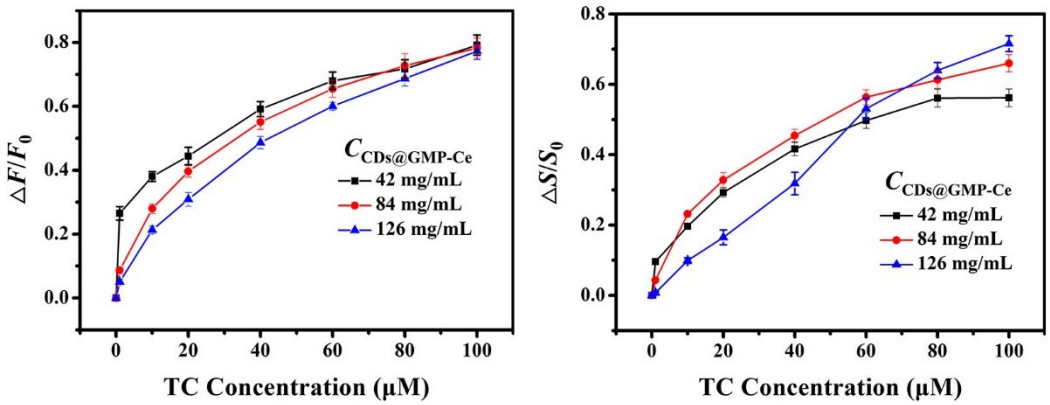

Fig. S8 The changes of fluorescence quenching efficiency ($\Delta F/F_0$) and scattering quenching efficiency ($\Delta S/S_0$) under different probe (CDs@GMP-Ce) concentrations (42, 84, and 126 mg/mL).

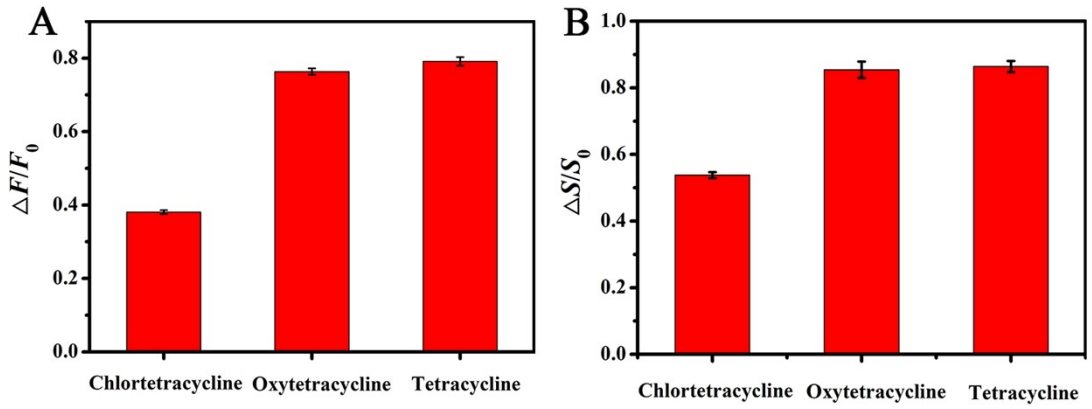

Fig. S9 Fluorescence (A) and second-order scattering (B) responses of the sensor to chlortetracycline, oxytetracycline, and tetracycline. The concentrations of all the three antibiotics are 100 μM. Sensing system: CDs@GMP-Ce, 84 mg mL^{-1}; PBS buffer, pH 7.2, 10 mM.

Table S2 Comparison of some reported sensors for TC detection in analytical performance.

Material	Sensing mode		Detection of TC		Ref.
	Mode	Signal	Linear range (μM)	Detection limit (μM)	
Au nanoclusters	Single-mode	Colorimetry	1 – 16	0.046	S1
Fe_3O_4 nanoparticles	Single-mode	Colorimetry	0.1 – 1	0.045	S2
Carbon-doped WO_3	Single-mode	Electrochemistry	0.1×10^{-3} – 100×10^{-3}	4.8×10^{-5}	S3
MCS@UiO-66-NH_2[a]	Single-mode	Electrochemistry	1 – 60	0.894	S4
BCDs-Eu/CMP-Cit[b]	Single-mode	Fluorescence	0.05 – 30	0.008	S5
Al-MOFs[c]	Single-mode	Fluorescence	0 – 73	0.026	S6
r-CDs[d]	Dual-mode, two instruments	Fluorescence	0 – 150	0.00173	S7
		Colorimetry	0 – 150	0.46	
CNQD@AgNPs[e]	Dual-mode, two instruments	Fluorescence	$0.1 – 10\times10^3$	0.015	S8
		Electrochemistry	0.001 – 100	0.00026	
Monooxygenase	Dual-mode, two instruments	Colorimetry	0.1 – 7	0.06	S9
		Electrochemistry	0.1 – 0.8	0.04	
CDs@GMP-Ce	**Dual-mode, one instrument**	**Fluorescence**	**0.1 – 80**	**0.043**	**This work**
		Scattering	**0.1 – 40**	**0.077**	

Note: MCS@UiO-66-NH_2[a], mesoporous carbon sphere@UiO-66-NH_2; BCDs-Eu/CMP-Cit[b], carbon quantum dots-cytidine monophosphate/europium coordination polymer nanoparticle; Al-MOF[c], Al-based metal−organic frameworks; r-CDs [d], reduced state carbon dots; CNQD@AgNPs[e], carbon nitride quantum dots@silver nanoparticles.

Table S3 Detection of TC in real samples using the proposed dual-mode probe and a commercial ELISA kit (n = 3).

Sample	Method	Concentration		Recovery (%)	RSD (%)
		Added (μM)	Found (μM)		
Milk	Proposed method (fluorescence)	0	N.D.[a]	/	/
		10	10.96	109.6	0.1
		20	20.26	101.3	0.1
		40	36.86	92.2	1.0
	Proposed method (scattering)	0	N.D.	/	/
		10	12.18	121.8	1.0
		20	23.80	119.0	0.3
		40	35.64	89.1	0.6
	Commercial kit	0	N.D.	/	/
		10	9.26	92.6	3.2
		20	21.38	106.9	2.8
		40	42.22	105.6	2.3
Tap water	Proposed method (fluorescence)	0	N.D.	/	/
		10	9.58	95.8	0.3
		20	17.42	87.1	0.3
		40	44.20	110.5	0.1
	Proposed method (scattering)	0	N.D.	/	/
		10	1.15	114.7	0.7
		20	18.84	94.2	0.2
		40	37.12	92.8	1.7
	Commercial kit	0	N.D.	/	/
		10	10.48	104.8	1.2
		20	19.20	96.0	0.8
		40	38.96	97.4	1.3

Note: N.D.[a], not detected.

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