

**Visual and fluorescent detection of pyrogallol
based on a ratiometric fluorescence-enzyme system**

Hanbing Rao, Yongcheng Dai, Hongwei Ge, Xin Liu, Bingyao Chen, Ping Zou,
Xianxiang Wang, Yanying Wang*

College of Science, Sichuan Agricultural University, Ya'an 625014, P.R.China

*Corresponding author: College of Science, Sichuan Agricultural University, Ya'an
625014, P.R.China.*

E-mail addresses: wyy@sicau.edu.cn

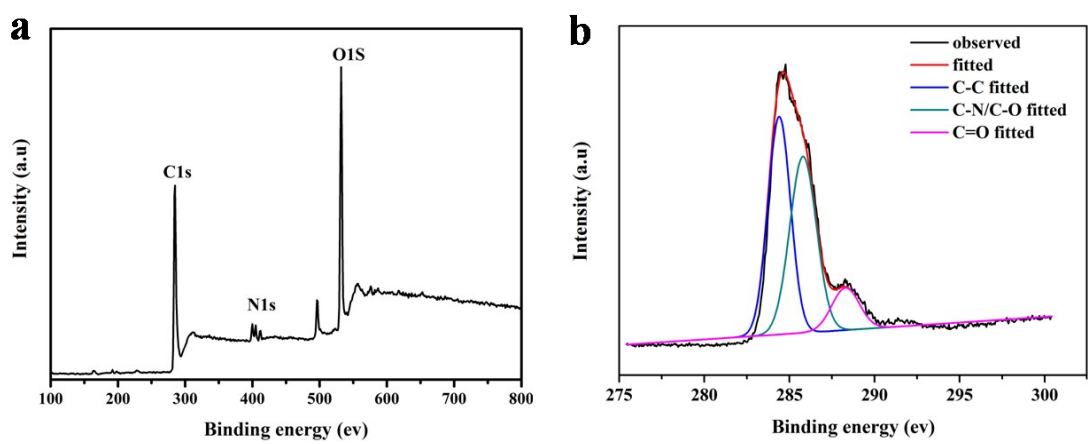


Fig. S1 (a) XPS survey spectrum of CQDs, (b) the high-resolution C1s peaks and the fitting curves.

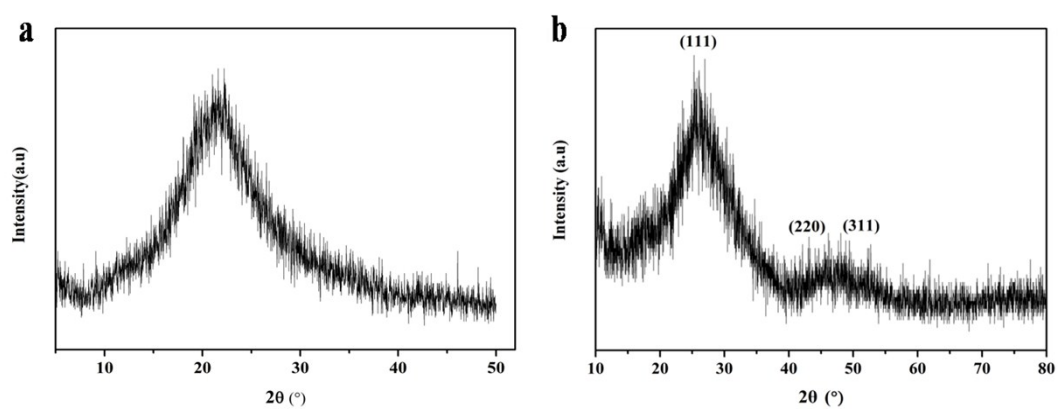


Fig. S2. XRD pattern of CQDs (a) and GSH-CdTe QDs (b).

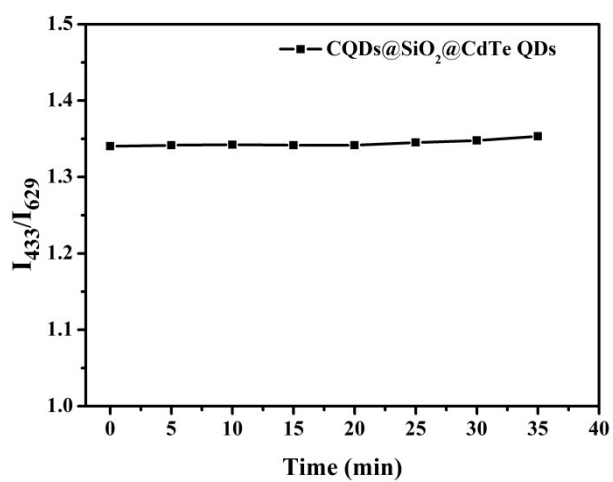


Fig. S3 Fluorescence stability of CQDs@SiO₂@CdTe QDs under UV illumination

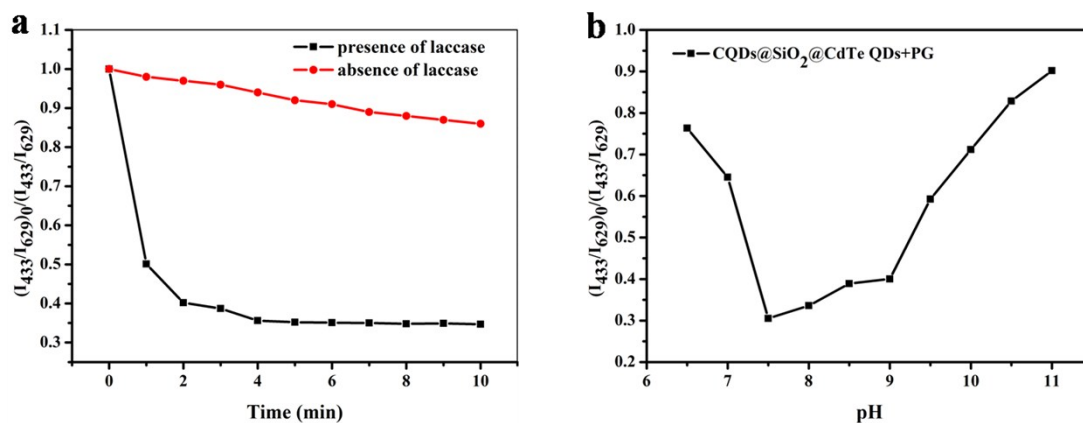


Fig. S4 (a) Kinetic study of fluorescence quenching by PG in the absence/presence of laccase, (b) effect of pH on the fluorescence intensity ratio $(I_{433}/I_{629})_0/(I_{433}/I_{629})$ of the CQDs@SiO₂@CdTe QDs-PG

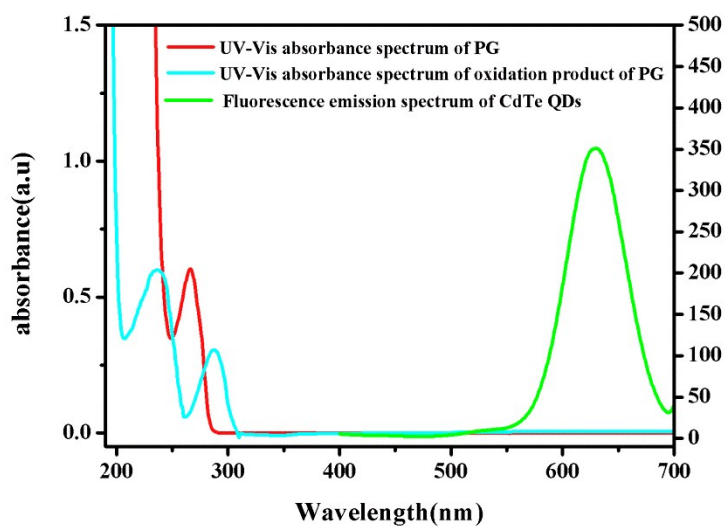


Fig. S5 Fluorescence emission spectrum of the CdTe QDs and the UV-Vis absorption spectrum of PG and oxidation product of PG.

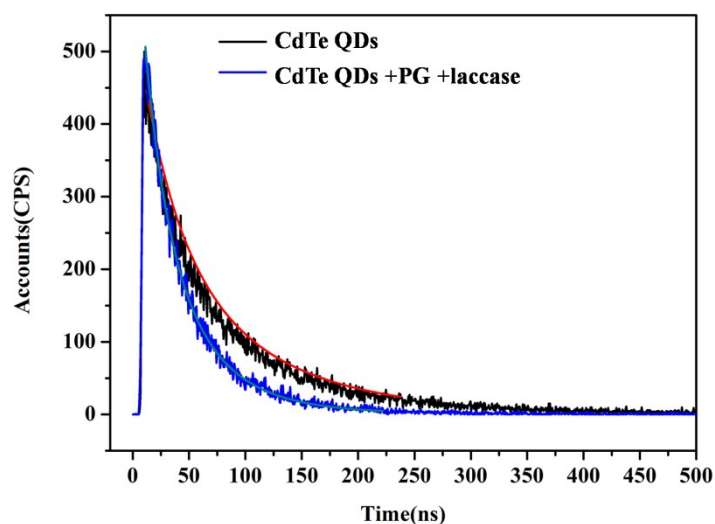


Fig. S6 Fluorescence decays of CdTe QDs and CdTe+PG+laccase

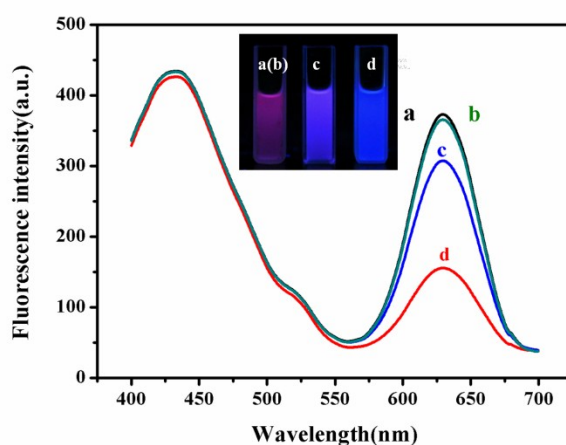


Fig. S7 The fluorescence spectrum of (a) CQDs@SiO₂@CdTe QDs; (b) CQDs@SiO₂@CdTe QDs with 50 μ L of a 0.2 mg/mL laccase solution; (c) CQDs@SiO₂@CdTe QDs with 50 μ L of a 0.2 mg/mL laccase solution and 1.5 μ M PG; (d) CQDs@SiO₂@CdTe QDs with 50 μ L of a 0.2 mg/mL laccase solution, 1.5 μ M PG and 5 μ M AA. The inset is the optical photo of the above solutions taken under sunlight and 365 nm UV light.

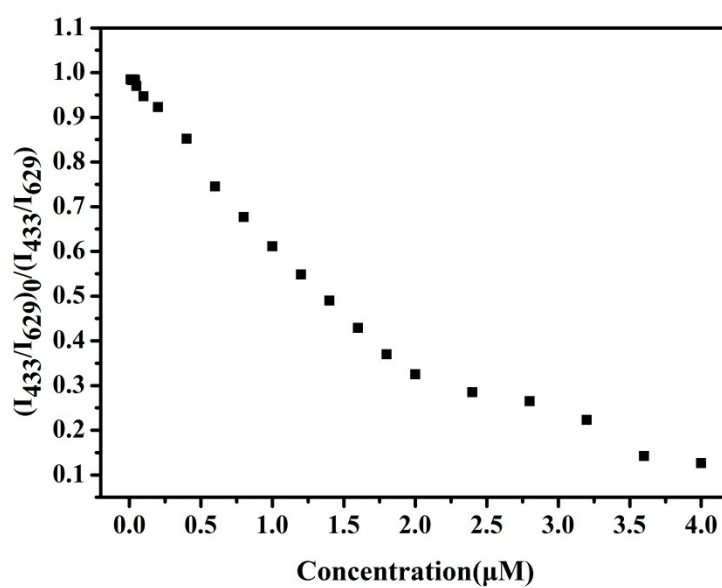


Fig. S8 The relationship between the fluorescence intensity of CQDs@SiO₂@CdTe QDs and the concentration of PG.

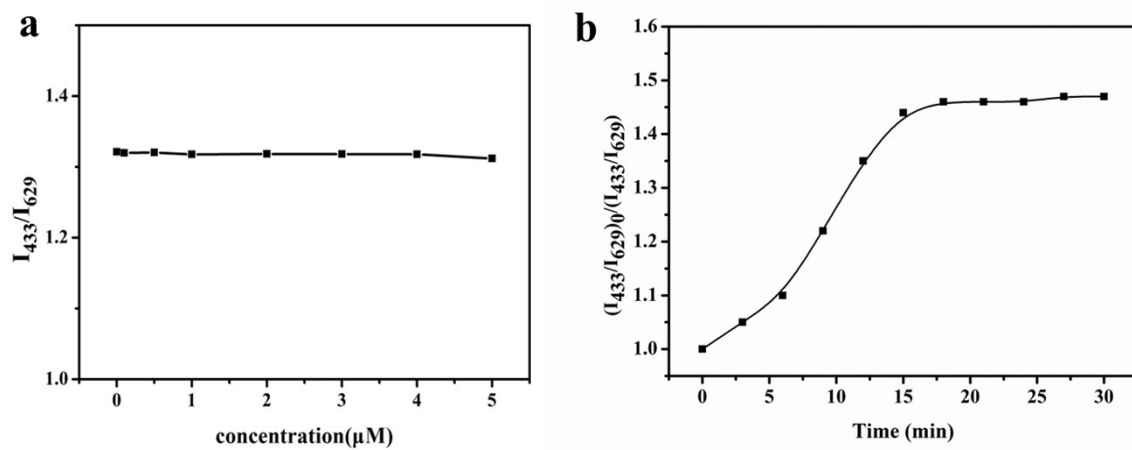


Fig. S9 (a) The fluorescence intensity ratio (I_{433}/I_{629}) of CQDs@SiO₂@CdTe QDs in the presence of different concentration of AA. (b) The kinetics of fluorescence restoration by AA.

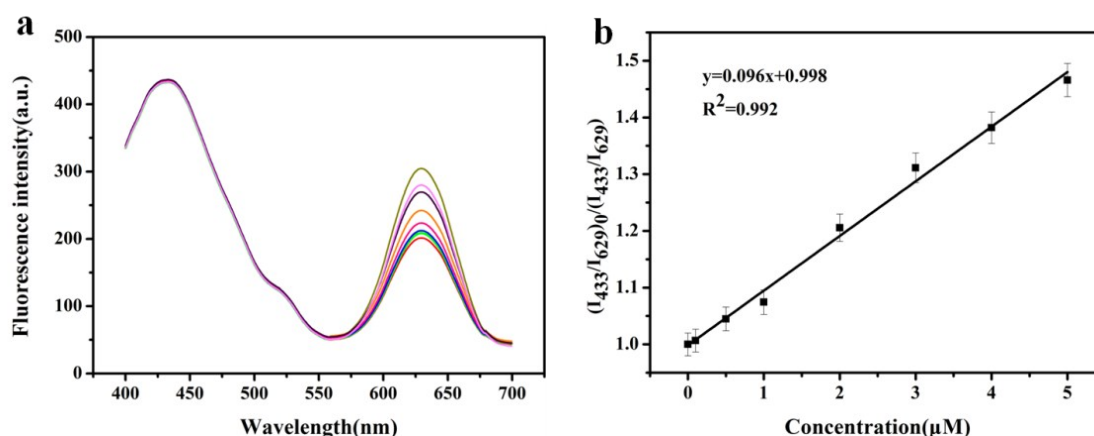


Fig. S10 (a) Fluorescence spectra of CQDs@SiO₂@CdTe QDs-PG system with different concentrations of AA. The concentrations of AA were 0, 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 μM, respectively. (b) Plot of the fluorescence intensity ratio $(I_{433}/I_{629})_0/(I_{433}/I_{629})$ versus the concentration of AA. $(I_{433}/I_{629})_0$ and (I_{433}/I_{629}) are the fluorescence intensity ratios of the CQDs @SiO₂@ CdTe QDs-PG system in the absence and presence of AA, respectively.

Table. S1 Nanosecond time-resolved luminescence transients of CdTe QDs in different systems..

system	τ_1 (ns)	Rel %	τ_2 (ns)	Rel %	τ (ns)
CdTe QDs	24.8397	18.02	85.5643	81.98	74.62172
CdTe QDs+PG+laccase	19.5617	24.45	47.5954	75.55	40.7412

Table. S2 Comparison of PG the determination methods.

Method	Linear detection range	Detection limit	Reference
Langmuir–Blodgett films	up to 400 μM	4.87×10^{-8} M	1
Chemiluminescence	1.0×10^{-7} – 1.0×10^{-4} M	4.6×10^{-8} M	2
Electrochemical methods	1.0×10^{-6} – 1.0×10^{-3} M	6.3×10^{-7} M	3
Kinetic determination	1.5×10^{-6} – 1.0×10^{-4} M	-	4
Ratiometric fluorescence detection	5.0×10^{-8} – 2.0×10^{-6} M	4.2×10^{-8} M	this work

References

1. F. J. Pavinatto, E. G. R. Fernandes, P. Alessio, C. J. L. Constantino, J. A. de Saja, V. Zucolotto, C. Apetrei, O. N. Oliveira Jr and M. L. Rodriguez-Mendez, *Journal of Materials Chemistry*, 2011, **21**, 4995.
2. S. N. Shah, H. Li and J. M. Lin, *Talanta*, 2016, **153**, 23-30.
3. C.-H. Hung, W.-T. Chang, W.-Y. Su and S.-H. Cheng, *Electroanalysis*, 2014, **26**, 2237-2243.
4. G. Hu, P. Chen, W. Wang, L. Hu, J. Song, L. Qiu and J. Song, *Electrochimica Acta*, 2007, **52**, 7996-8002.