

Supporting information

**Highly Efficient Electrochemiluminescence of Ruthenium
Complex-Functionalized CdS Quantum Dots and Its
Analytical Application**

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Experimental section

Synthesis of Ru-NH₂-functionalized CdS QDs.

CdS-Ru nanoparticles were prepared as following process. First, diazonium Ru(bpy)₂(N₂⁺-phen)[PF₆]₂ (Ru-N₂⁺) was synthesized using a reported procedure.¹ Briefly, add 5 mL of 0.14 mg/mL NaNO₂ into 5 mL of 0.5 M HCl solution containing 9.0 mg Ru-NH₂ and stay in complete darkness for 10 min in an ice bath. Then, 0.4 mg NaBH₄ were added drop-wise into the above mixture and stirred for 1 h at room temperature.² Finally, 0.144 mL of 1.0 mg/mL CdS QDs solution was added into the above mixture and the reaction mixture was stirred at room temperature for 2 h. The initial solution was centrifuged at 4000 rpm for 20 min and then the supernatant was continually centrifuged at 10000 rpm for 20 min. Finally, the obtained CdS-Ru nanoparticles on the bottom were homogeneously dispersed in 1 mL of aqueous solution and stored in 4 °C.

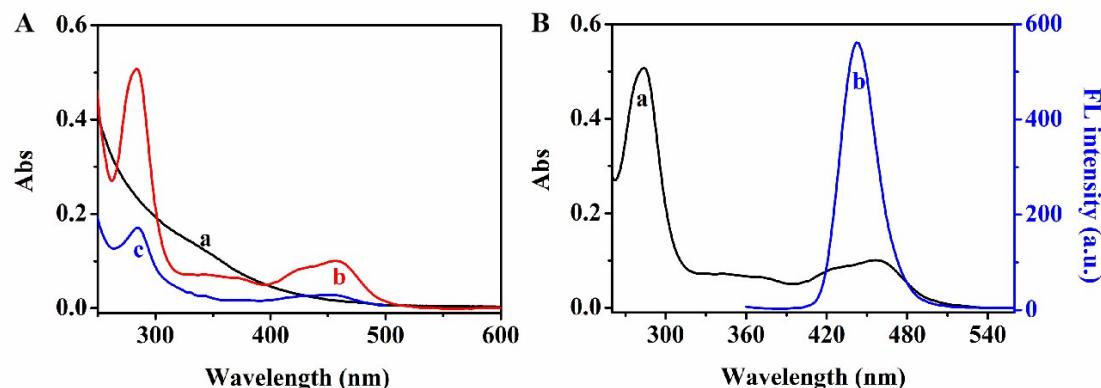


Figure S1. (A) UV-Vis of (a) 0.02 mg/mL CdS QDs; (b) 0.2 mg/mL Ru-NH₂; (c) 0.06 mg/mL Ru-NH₂ nanoparticles. (B) UV-Vis absorption spectrum of (a) 0.2 mg/mL Ru-NH₂ and fluorescence spectrum of (b) 0.02 mg/mL CdS QDs.

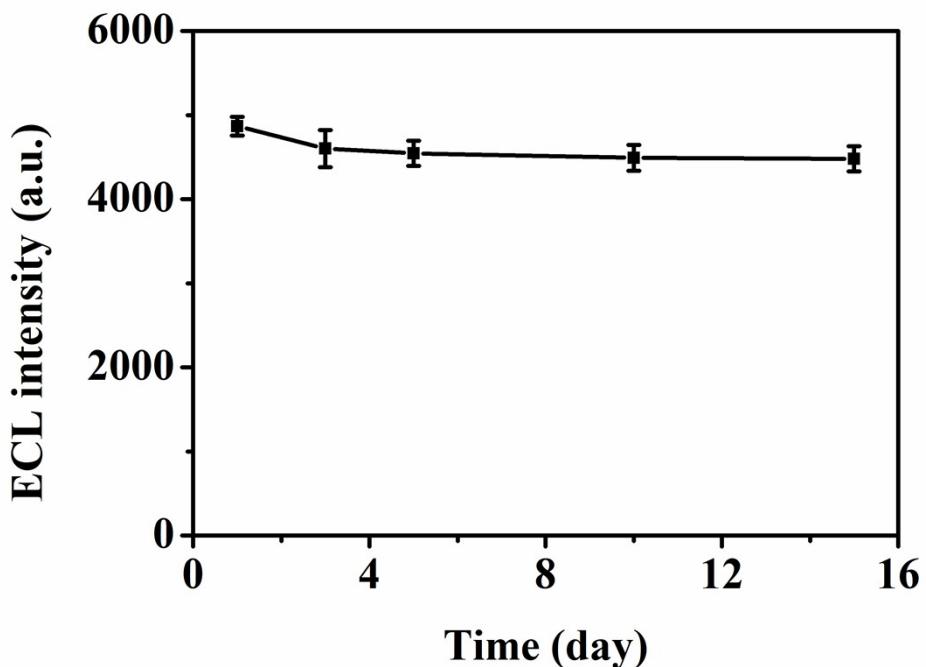


Figure S2. ECL responses of 0.06 mg/mL CdS-Ru nanoparticles after the storage of 1, 3, 5, 10 and 15 days in a refrigerator at 4 °C. ECL measurement conditions: 0.1 M PBS (pH 7.4) containing 45 mM TPA, scan rate, 0.1 V/s. PMT= -500 V.

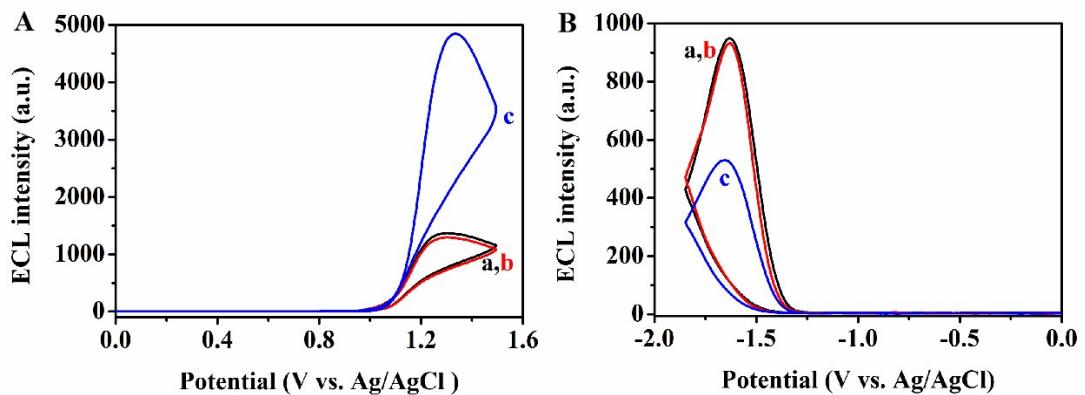


Figure S3. (A) ECL intensity *vs.* potential profiles of (a) 0.06 mg/mL Ru-NH₂, (b) the mixture of 0.02 mg/mL CdS QDs and 0.06 mg/mL Ru-NH₂ and (c) 0.06 mg/mL CdS-Ru nanoparticles in 0.1 M PBS containing 45 mM TPA. (B) ECL intensity *vs.* potential profiles of (a) 0.02 mg/mL CdS QDs, (b) the mixture of 0.02 mg/mL CdS QDs and 0.06 mg/mL Ru-NH₂ and (c) 0.06 mg/mL CdS-Ru nanoparticles in 0.1 M PBS containing 45 mM K₂S₂O₈. PMT= -500 V, scan rate, 0.1 V/s.

Table S1. Results for the determination of thrombin.

Method	Materials used	Linear range	Detection limit	Ref
Graphene				
Colorimetry	oxide/gold/platinum nanoparticles	0.30-100 nM	0.15 nM	3
Chemiluminescence	Graphene oxide	0.25-1 nM	83 pM	4
Fluorescence	silica nanoparticles	0.6-100 nM	0.20 nM	5
Electrochemistry	Graphene-porphyrin nanocomposite	5-1500 nM	0.2 nM	6
	Gold-streptavidin nanoparticles and			
Electrochemistry	silver reduction	0.1-100 pM	0.3 pM	7
	enhancement			
	Ag nanoparticles			
Electrochemistry	decorated graphene oxide	0.05-5 nM	0.03 nM	8
ECL	Streptavidin modified QDs	27.2-545 nM	2.72 nM	9
ECL	graphene oxide	0.9-226 pM	0.4 pM	10
ECL	CdS-Ru nanoparticles	1-100 pM	0.6 pM	This work
ECL	CdS-Ru nanoparticles	1-500 pM	0.7 pM	This work

Table S2. Analytical results for thrombin in human serum.

Sample number	Added in the serum (pM)	Found results (pM)	Recovery (%)
1	10.0	10.73±0.02	107.3
2	20.0	20.56±0.02	102.8
3	50.0	45.52±0.01	91.04

References

1. H. L. Qi, M. Li, R. Zhang, M. M. Dong and C. Ling, Double electrochemical covalent coupling method based on click chemistry and diazonium chemistry for the fabrication of sensitive amperometric immunosensor, *Anal. Chim. Acta*, 2013, **792**, 28-34.
2. S. Krishnakumar and K. R. Gopidas, Covalent functionalization of organic nanoparticles using aryl diazonium chemistry and their solvent-dependent self-assembly, *Langmuir*, 2017, **33**, 1162-1170.
3. L. Wang, W. Yang, T. F. Li, D. Li, Z. M. Cui, Y. Wang, S. L. Ji, Q. X. Song, C. Shu and L. Ding, Colorimetric determination of thrombin by exploiting a triple enzyme-mimetic activity and dual-aptamer strategy, *Microchim. Acta*, 2017, **184**, 3145-3151.
4. Y. N. Lin, J. B. Li, Y. H. Wang, Y. L. Sun, C. F. Ding, W. Y. Sun and C. N. Luo, A chemiluminescence biosensor for the detection of thrombin based on the aptamer composites, *Spectrochim. Acta A*, 2018, **192**, 153-158.
5. Q. L. Yue, T. F. Shen, L. Wang, S. L. Xu, H. B. Li, Q. W. Xue, Y. F. Zhang, X. H. Gu, S. Q. Zhang and J. F. Liu, A convenient sandwich assay of thrombin in biological media using nanoparticle-enhanced fluorescence polarization, *Biosen. Bioelectron.*, 2014, **56**, 231-236.
6. H. F. Zhang, S. M. Shuang, L. L. Sun, A. J. Chen, Y. Qin and C. Dong, Label-free aptasensor for thrombin using a glassy carbon electrode modified with a graphene-porphyrin composite, *Microchim. Acta*, 2014, **181**, 189-196.
7. C. Ocaña and M. D. Valle, Signal amplification for thrombin impedimetric aptasensor: Sandwich protocol and use of gold-streptavidin nanoparticles, *Biosens. Bioelectron.*, 2014, **54**, 408-414.
8. B. Qin and K. Yang, Voltammetric aptasensor for thrombin by using a gold microelectrode modified with graphene oxide decorated with silver nanoparticles, *Microchim. Acta*, 2018, **185**, 407.
9. H. P. Huang, J.-J. Zhu, DNA aptamer-based QDs electrochemiluminescence biosensor for the detection of thrombin, *Biosens. Bioelectron.*, 2009, **25**, 927-930.

10. X.-Y. Wang, A. Gao, C.-C. Lu, X.-W. He and X.-B. Yin, An electrochemiluminescence aptasensor for thrombin using graphene oxide to immobilize the aptamer and the intercalated Ru(phen)₃²⁺ probe, *Biosens. Bioelectron.*, 2013, **48**, 120-125.