Supplementary Information

Sensitive and selective "signal-off" electrochemiluminescence sensing for prostate-specific antigen based on aptamer and molecularly imprinted polymer

Yuanyuan Wang^{a, b}, Xianwen Kan^{a*}

^a College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China; The Key Laboratory of Functional Molecular Solids, Ministry of Education; Anhui Laboratory of Molecule-Based Materials, Anhui Key Laboratory of Chemo-Biosensing ^b Scholl of Basic Courses, Bengbu Medical College, Bengbu 233030, PR China

Fig. S1 CV response of (A) GCE and (B) AuNPs/ GCE with scan rates from 20 mV/s to 200 mV/s in 5.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution containing 0.1 M KCl. Linear relationship between the peak current and half power of scan rate corresponding with (C) GCE and (D) AuNPs/GCE.

Fig. S2 ECL-potential curves of each modification step of the MIP sensor prepared by method 1 (A) and method 2 (B): (a) before and (b) after the removal of PSA, and (c) after the rebinding of PSA. The ECL measurements were performed under the same conditions to the aptamer-MIP and aptamer sensor.

In method 1, the constructed procedure was the same to the aptamer-MIP sensor except that no aptamer was immobilized onto the AuNPs/GCE. PSA cannot be anchored on the AuNPs/GCE due to no interaction between the PSA and the electrode, resulting in no PSA molecules can be entrapped in the polymer matrix. In method 2, 1 μg/mL of PSA was placed into the polymerization solution with the successive polymerization of MIP on the AuNPs/GCE under the same condition of the aptamer-MIP sensor. There is also no imprinted effect, which was probably due to the unsuitable conditions for MIP synthesis. In addition, the reported results only showed the preparation and performances comparison between of the aptamer-MIP based sensors and the aptamer based sensors or aptamer-NIP based sensor for biomacromolecules detection.^{1, 2} The main reason may be the difficulty of immobilization of template on the electrode. Therefore, there's no way to compare the performances between MIP sensor and aptamer-MIP sensor in the present work. Also, the electrochemical properties of MIP sensor would be unable to conduct.

Fig. S3 ECL response of the MIP (a, b) and NIP (c, d) modified sensor before (a, c) and after (b, d) the incubation of PSA in the experimental optimization section "Concentration of dopamine". (A) 4 mM, (B) 5 mM, (C) 6 mM, (D) 7mM, (E) 8 mM.

Fig. S4 ECL spectra of the selectivity study of (A) aptamer-MIP sensor, (B) NIP sensor, and (C) aptamer sensor (insert in A and C: the enlarged image of the area marked by the blue dash line).

Fig. S5 (A) ECL intensity-time curve under continuous scanning for 10 cycles, (B) Stability under different storage time of the aptamer sensor after rebinding of 1 ng/mL PSA. Error bars represent standard deviations of three parallel measurements.

Fig. S6 ECL spectra detected by aptamer-MIP sensor in blank electrolyte (a), human serum (b), and human serum with the addition of 5 ng/mL PSA (c).

Modified Electrode	Method	linear range	LOD	Ref.
		(ng/mL)	(pg/mL)	
f-MWCNTs/ITO	ECL	$2.6 - 12$	880	3
MOF/Au/G-quadruplex/GCE	ECL	$0.5 - 500$	58	4
$ox-GCMs/GC$	ECL	$5 - 1000$	270	5
GR/CHIT/GCE	ECL	$0.01 - 8$	8	6
AuNPs/rGO/GCE	ECL	$0.0001 - 10$	0.038	7
DpAu/GCE	ECL	$0.0005 - 5$	0.17	8
GCE/ABA-	ECL	$0.00005 - 1$	0.01	9
$Ab1$ <antigen>$Ab2/AGIS$</antigen>				
CdS-Au nanorod arrays	ECL	$1 - 12$	600	10
$SA-AuNPs/AE$	ECL	$0.00001 - 30$	0.01	11
Lu-Pt@GS/GCE	ECL	$0.001 - 10$	0.3	12
MIP/Aptamer/AuNPs/GCE	ECL	$0.005 - 50$	3.0	This
				work

Table S1 Comparison of analytical performances between our work and other reported sensors for the detection of PSA.

References

- 1. W. Li, Q. Zhang, Y.-J. Wang, Y.-Y. Ma, Z.-C. Guo, and Z. Liu, *Anal. Chem.*, 2019, **91**, 4831–4837.
- 2. P. Jolly, V. Tamboli, R.L. Harniman, P. Estrela, C.J. Allender, and J.L. Bowen, *Biosens. Bioelectron.*, 2016, **75**, 188–195.
- 3. A. Juzgado, A. Solda, A. Ostric, A. Criado, G. Valenti, S. Rapino, G. Conti, G. Fracasso, F. Paolucci and M. Prato, *J Mater. Chem. B.*, 2017, **5**, 6681.
- 4. K. Shao, B.-R. Wang, A.-X. Nie, S.-Y. Ye, J. Ma, Z. Li, Z.-C. Lv and H.-Y. Han, *Biosens. Bioelectron.*, 2018, **118**, 160-166.
- 5. R.-N. Wang, Y. Huang, Y.-P. Chen and Y.-W. Chi, *ACS Appl. Bio Mater.,* 2020, **3**, 6358–6367.
- 6. S.-J. Xu, Y. Liu, T.-H. Wang, J.-H. Li, *Anal. Chem.,* 2011, **83**, 3817-3823.
- 7. [Q.-C.](https://www.sciencedirect.com/science/article/pii/S001346861930252X#!) Fang, Z.-H. Lin, [F.-S.](https://www.sciencedirect.com/science/article/pii/S001346861930252X#!) Lu, Y.-W. Chen, X.-C. Huang and W.-H. Gao, *Electrochim. Acta,* 2019, **302**, 207-215.
- 8. J.-T. Cao, J.-J. Yang, L.-Z. Zhao, Y.-L. Wang, H. Wang, Y.-M. Liu and S.-H. Ma, *Biosens. Bioelectron.,* 2018*,* **99**, 92-98.
- 9. L. Fu, K.-N. Fu, X.-W. Gao, S.-T. Dong, B. Zhang, S.-J. Fu, H.-Y. Hsu and G.-Z. Zou, *Anal. Chem*., 2021, 93, **4**, 2160–2165.
- 10. X.-L. Huo, H. Yang, M.-X. Li, W. Zhao, J.-J. Xu, Y. Wang, X.-L. Luo and H.-Y. Chen, *Nanoscale*, 2018, **10**, 19224-19230.
- 11. Y.-C. Zhang, Z. Zhang, S.-Z. Rong, H.-W. Yu, H.-M. Gao, Q. Sha, P. Ding, H.-Z. Pan and D. Chang, *Anal. Chim. Acta*, 2020, **1109**, 98-106.
- 12. M. SaddamKhan, W.-J. Zhu, A. Ali, S.M. Ahmad, X.-J. Li, L. Yang, Y.-G. Wang, H. Wang and Q. Wei, *Anal. Biochem.*, 2019, **566**, 50-57.