Prussian blue-Au nanocomposites actuated hemin/G-quadruplexes catalysis for amplified detection of DNA, Hg^{2+} and adenosine triphosphate

Guangfeng Wang,[a,b]* Ling Chen[a,b], Yanhong Zhu[a,b], Xiuping He[a,b], Gang Xu[a,b] and Xiaojun Zhang[a,b]*

a Key Laboratory of Chem-Biosensing, Anhui province; Key Laboratory of Functional Molecular Solids, Anhui province; College of Chemistry and Materials Science, Center for Nano Science and Technology, Anhui Normal University, Wuhu 241000, PR China

b State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China

1. Table S1. DNA sequence

Name	**Sequence** (5'- 3')
S1 (capture probe)	HS-$(CH_2)_6$-GGC CTT TTT TTT T
S2 (target probe with G-rich)	GGT TGG GCG GGT TGG AAA AAA AAA
S2a (one base mismatch)	GGT TGG GCG GGT TGG AAA AAT AAA
S2b (two bases mismatch)	GGT TGG GCG GGT TGG AA TAA TAAA
S3(target probe with no G-rich)	AAA AAA AAA A
S4(for the formation of T-Hg^{2+}-T)	GGT TGG GCG GGT TGG TTT TTT TTT
S5(part of the aptamer of ATP)	HS-$(CH_2)_6$ -ATG CAC CTG GGG AGT AT
S6(part of aptamer of ATP with G-rich)	GGT TGG GCG GGT TGG TGC GGA GGA AGG TGC AT

2. Control experiments in CV Characterization

In a control experiment (Fig. S1), when we only used Au nanoparticles alone without PB to modify the GCE (curve b), the signal was also smaller than that of HRP-DNAzyme/S1/PB-Au/GCE (curve a), implying that PB played an important role in the catalytic cycle. Moreover, if S1/GE was hybridized with no G-rich sequence, S3, no HRP-DNAzyme formed in the system, the electrocatalytic signals was smaller (curve c) compared with that of HRP-DNAzyme/S1/PB-Au/GCE (curve a) which proved that HRP-DNAzyme was also very important to construct the electrochemical catalytic cycle with PB.

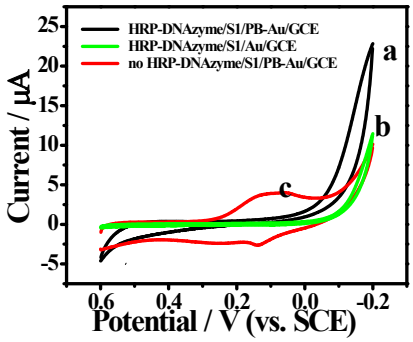

Fig. S1 CV of different modified eletrodes: HRP-DNAzyme/S1/PB-Au/GCE (a), HRP-DNAzyme/S1/Au/GCE (b), No HRP-DNAzyme/S1/PB-Au/GCE (c).

3. The Electrochemical Catalysis on H_2O_2

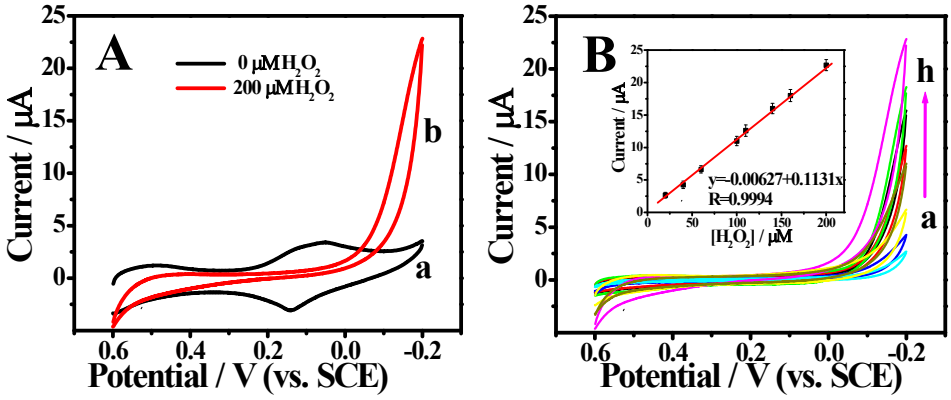

Fig. S2 (A) CV on the HRP-DNAzyme/S1/PB-Au/GCE in 0.05 M PBS (pH 7.4) with 0 (a) and 200 (b) μM H_2O_2; (B) CV of HRP-DNAzyme/S1/PB-Au/GCE in 0.05 M PBS (pH 7.4) with various concentrations of H_2O_2 (a–h): 20; 40; 60; 100; 110; 140; 160; 200 μM (inset: the corresponding calibration curve of current vs. the concentration of H_2O_2).

4. Optimization of External Conditions

In order to achieve high sensitivity, experimental conditions were optimized. The optimization of the variables of the system was shown in Fig. S3. Fig. S3A depicted the time-dependent voltammetric waves to form the composition of HRP-DNAzyme structure. As the interaction time of S2 and S1/PB-Au/GCE was prolonged, the currents increased. Upon incubation time was more than 10 hours, the signal of the current showed a level indicating that the reaction may complete in 10 hours. Therefore, 10 h was chosen as an optimized incubation time used in the experiments. From this result we can conclude that the electrochemical signal is closely relative to the S2 which showed the possibility to detect it. Furthermore, Fig. S3B depicted the effect of varying pH value on the electrocatalytic currents of HRP-DNAzyme/S1/PB-Au/GCE. When the pH vale was over 7.4, the current responses declined, resulting that the highest sensitivity was obtained in pH 7.4. In addition, the effect of different temperatures on the response of HRP-DNAzyme/S1/PB-Au/GCE was also conducted, as shown in Fig. S3C. We could see that the obtained highest currents were at 35 ^oC, which was consensus with human body [S1, S2]. Ultimately, we chose hybridization time of 10 h, incubation temperature of 35 ^oC and pH 7.4, as the optional experimental conditions. In addition, we also investigated the optimization of experimental conditions in the process of electrodeposition, such as the electrodeposition pH value (Fig. S3D), scan cycles (Fig. S3E) and electrodeposition ratio ($[K_3Fe(CN)_6]$: $[AuCl_3 \cdot HCl \cdot 4H_2O]$) (Fig. S3F).

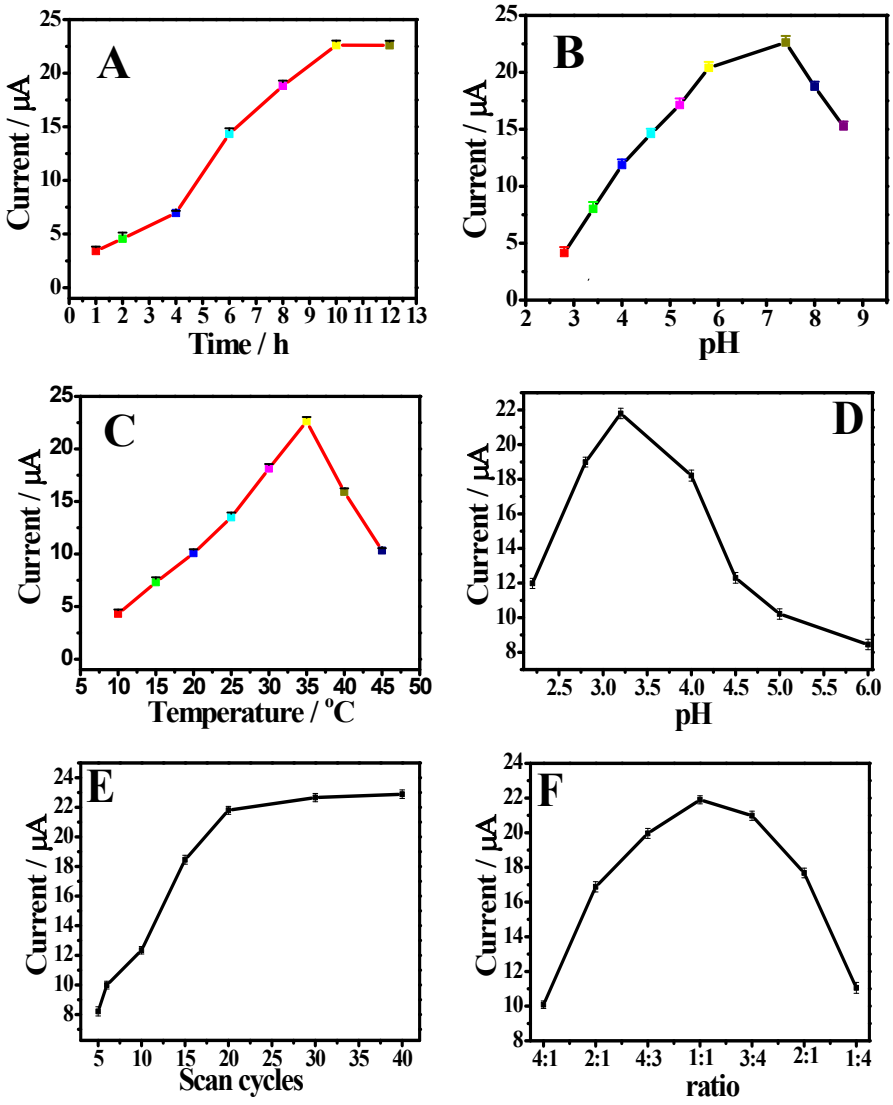

Fig. S3 Optimization of experimental conditions including hybridization time (A), hybridization pH value (B), incubation temperature (C), electrodeposition pH value (D), scan cycles (E) and electrodeposition ratio ($[K_3Fe(CN)_6]$: $[AuCl_3 \cdot HCl \cdot 4H_2O]$) (F) (CV were obtained on the HRP-DNAzyme/S1/PB-Au/GCE and error bars were deduced from N=6 experiments).

5. Table S2 Performance compared with other sensors for Hg^{2+} detection

Procedure	Linear range	Detection limit	References
Four steps	10-2000 nM	4.5 nM	Ref. S3
Five steps	0.5 nM to 2 μM	0.5 nM	Ref. S4
Five steps	--	10 nM	Ref. S5
Three steps	10 - 800 nM	10 nM	Ref. S6
Three steps	0.1 nM to 5 μM	0.06 nM	Ref. S7
Three steps	10^{-10}-10^{-2} M	30 pM	This paper

6.Table S3 Performance compared with other aptasensors for ATP detection

Procedure	Linear range	Detection limit	References
Three steps	10 nM - 6.4 μM	4.5 nM	Ref. S8
Five steps	0 - 0.2 mM	20 μM	Ref. S9
Three steps	1 μM - 3 mM	--	Ref. S10
One step	50-100 nM	10^{-8} M	Ref. S11
Six steps	0.1-100 nM	10^{-10} M	Ref. S12
Four steps	10^{-5}-5×10^{-3} M	10^{-6} M	Ref. S13
Three steps	10-8 -1 M	3 nM	This paper

Reference:

(S1) B. Y. Jiang, M. Wang, C. Li, J. Q. Xie, Biosens. Bioelectron., 2013, **43**, 289.

(S2) C. Sanson, J. F. Le Meins, C. Schatz, A. Soum, S. Lecommandoux, Soft Matter., 2010, **6**, 1722.

(S3) N. Lu, C. Shao, Z. Deng, Analyst, 2009, **134**, 1822.

(S4) R. Kong, X. Zhang, L. Zhang, X. Jin, S. Huan, G. Shen, R. Yu, Chem. Commun., 2009, **37**, 5633.

(S5) P. Miao, L. Liu, Y. Li, G. Li, Electrochem. Commun., 2009, **11**, 1904.

(S6) C. Yu, T. Cheng, W. Tseng, Biosens. Bioelectron., 2009, **25**, 204.

(S7) D. Wu, Q. Zhang, X. Chu, H. Wang, G. Shen, R. Yu, Biosens. Bioelectron., 2010, **25**, 1025.

(S8) L. Zhang, H. Wei, J. Li, T. Li, D. Li, Y. Li, E. Wang, Biosens. Bioelectron., 2010, **25**, 1897.

(S9) L. Cai, Z. Chen, X. Dong, H. Tang, D. Pang, Biosens. Bioelectron., 2011, **29**, 46.

(S10) L. Kashefi-Kheyrabadi, M. A. Mehrgardi, Biosens. Bioelectron., 2012, **37**, 94.

(S11) A. Kueng, C. Kranz, B. Mizaikof, Biosens. Bioelectron., 2004, **19**, 1301.

(S12) Y. Du, B. L. Lia, F. Wang, S. J. Dong, Biosens. Bioelectron., 2009, **24**, 1979.

(S13) K. Han, L. Chen, Z.S. Lin, G.X. Li, Electrochem. Commun., 2009, **11**, 157.