Supporting Information

An Efficient Electrochemical Self-Catalytic platform based on L-Cys-hemin/G-quadruplex and Its Application for Bioassay

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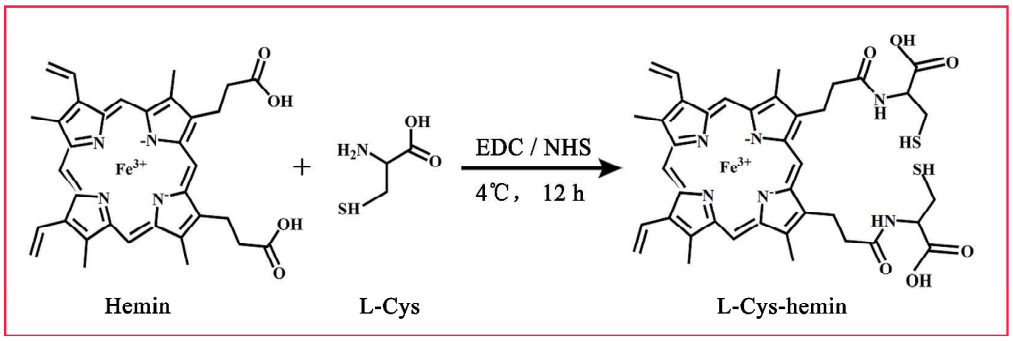

Fig. S1. The schematic diagram of the synthesis of L-Cys-hemin.

1. Preparation of hemin/branched G-DNAs/Fc-PHNs probe (probe A)

190 μL hemin (5 mM) was added into the branched G-DNAs decorated Fc-PHNs. After 2 h softly stirring, the hemin/branched G-DNAs/Fc-PHNs probe was centrifuged, washed and then dispersed in 1 mL deionized water and stored at 4 ºC for subsequent use.

2. Preparation of L-Cys-hemin/branched G-DNAs/Fc-PHNs probe (probe B)

L-Cys-hemin/branched G-DNAs/Fc-PHNs probe was prepared according to the method of the target probe (probe C), except that the probe finally stored in PBS rather than L-Cys solution when it not use.

3. The electrochemical characterization of the stepwise modified electrode

CV and EIS were applied to characterize the stepwise assembly of the aptasensor, where 5.0 mM $[Fe(CN)_6]^{3-/4-}$ was used as redox probe. As displayed in Fig. S1(A), pronounced redox peaks of $[Fe(CN)_6]^{3-/4-}$ were observed at bare GCE (curve a). When the electrode was deposited with Au NPs layer, the redox peak currents increased

(curve *b*) comparing to that of bare GCE, because the Au NPs provided a larger electrochemical surface area and facilitated the electron transfer. While the Au NPs layer modified electrode was incubated with TBA1, BSA and TB, respectively, the redox peak currents decreased in turn (curve *c*–*e*), because TBA1, BSA and TB were insulating, and thus perturbed electron transfer.

EIS was showed in Fig. S1(B). The bare GCE displayed a very small semicircle (curve a). When Au NPs were electrodeposited on the GCE, a sharp decrease of semicircle diameter was observed (curve b), which implied electron-transfer resistance at the electrode surface was decreased compared to bare GCE. When the non-conductive layers (TBA1, BSA, TB) were modified on the electrode successively, the EIS responses were increased in sequence (curve c-e), which were consistent with the fact that large biological molecules played the role of inert electron and mass transfer blocking layer.

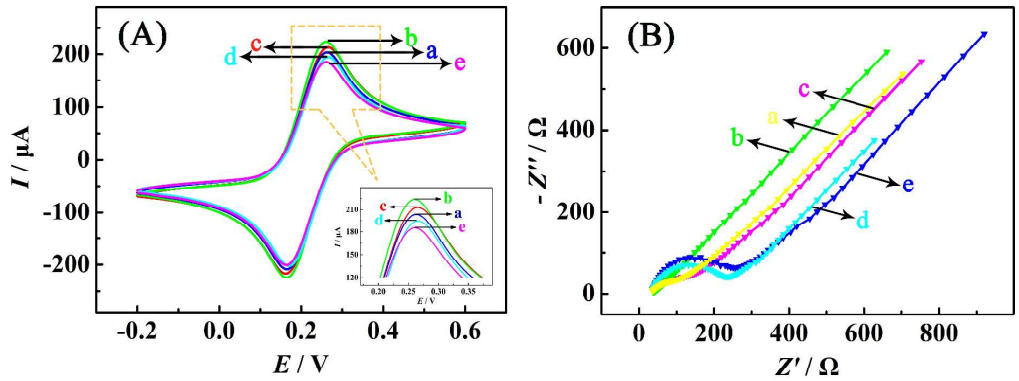

Fig. S1. The CV (A) and EIS (B) of different modified electrodes: (a) bare GCE, (b) Au NPs/GCE, (c) TBA1/Au NPs/GCE, (d)BSA/TBA1/Au NPs/GCE, (e) TB/BSA/TBA1/Au NPs/GCE in PBS (pH 7.4) containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$.

Table S1. Comparison of different methods for TB detection.

Analytical method	Linear range /(pM)	Detection limit /(fM)	References
Colorimetric	$1.3 \times 10^{2} \sim 1.3 \times 10^{2}$	1.7	[1]
Photoelectrochemical	$5.0 \times 10^{-1} \sim 1.0 \times 10^{3}$	1.67×10^{1}	[2]
Photoacoustic	$0 \sim 1.0 \times 10^{6}$	1.12×10^{6}	[3]
Photoelectrochemical	$2.0 \times 10^{-1} \sim 10$	20	[4]
Photoelectrochemical	$1.0 \times 10^{-3} \sim 10$	0.1	[5]
Raman	$1.0 \times 10^{-6} \sim 1.0 \times 10^{-4}$	0.057	[6]
Electrochemistry	$1.0 \times 10^{-4} \sim 80$	0.032	Our research

REFERENCES

(1) Li, J., Jiao, Y., Liu, Q., Chen, Z. *ACS Sustainable Chem. Eng.* 2018, 6, 6738-6745.

(2) Lan, F., Liang, L., Zhang, Y., Li, L., Ren, N., Yan, M., Yu, J. *ACS Appl. Mater. Interfaces* 2017, 9, 37839-37847.

(3) Zhang, J., Smaga, L. P., Satyavolu, N. S. R., Chan, J., Lu, Y. *J. Am. Chem. Soc.*2017, 139, 17225-17228.

(4) Li, C., Lu, W., Zhu, M.,Tang, B. *Anal. Chem.* 2017, *89*, 11098–11106.

(5) Xu, F., Zhu, Y. C., Ma, Z. Y., Zhao, W. W., Xu, J. J., Chen, H. Y. *Chem. Commun.* 2016, 52, 3034-3037.

(6) Hao, T., Wu, X., Xu, L., Liu, L., Ma, W., Kuang, H., Xu, C. *Small* 2017,13, 1603944.