Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information:

Sub-picomolar assay for protein by using cubic Cu_2O nanocages loaded with Au nanoparticles as robust redox probe and efficient nonenzymatic electrocatalysts

Jianmin Zhao, Ting Zheng, Jiaxi Gao, Shijing Guo, Xingxing Zhou and Wenju Xu*

Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, School of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, PR China

Optimization of the experimental conditions

The sensitivity and analytical performance of the developed aptasensor are influenced by the tested experimental conditions. Herein, the effect of the concentration of incubated SH-TBA, the incubation time of target TB, and the concentration of H_2O_2 on the electrochemical response was investigated in 0.1 $mol \cdot L^{-1}$ PBS containing 5 $mmol \cdot L^{-1}$ $[Fe(CN)_6]^{3-/4-}$, and the results are shown in Fig. S1. From Fig. S1A and S1B, the resulting oxidative peak current in CV decreased with the increasing of SH-TBA concentration in the range of 0.5 $\mu mol \cdot L^{-1}$ to 3.0 $\mu mol \cdot L^{-1}$, and levelled off at 2.5 $\mu mol \cdot L^{-1}$. Moreover, as shown in Fig. S1C and S1D, the extending of the incubation time of TB from 10 min to 50 min resulting in the gradual decrease of CV response, and reached to the maximum change at 40 min, which indicated the saturation of the specific bound between SH-TBA and TB. From the optimization results in Fig. S1E

and S1F, increasing of H_2O_2 concentration in tested solution resulted in gradual rising of DPV response of the proposed aptasensor, until 2.22 mmol·L^{-1} of H_2O_2. This suggested that AuNPs@Cu_2O-NCs as robust nonenzymatic electrocatalysts can efficiently catalyze the decomposition of H_2O_2, resulting in the significant enhancement of response signal. All the above observations demonstrated that the optimal measuring conditions were involved in 2.5 μmol·L^{-1} SH-TBA, 40 min TB binding time, and 2.22 mmol·L^{-1} H_2O_2 for the proposed aptasensor, respectively, which were all selected for the total experiments.

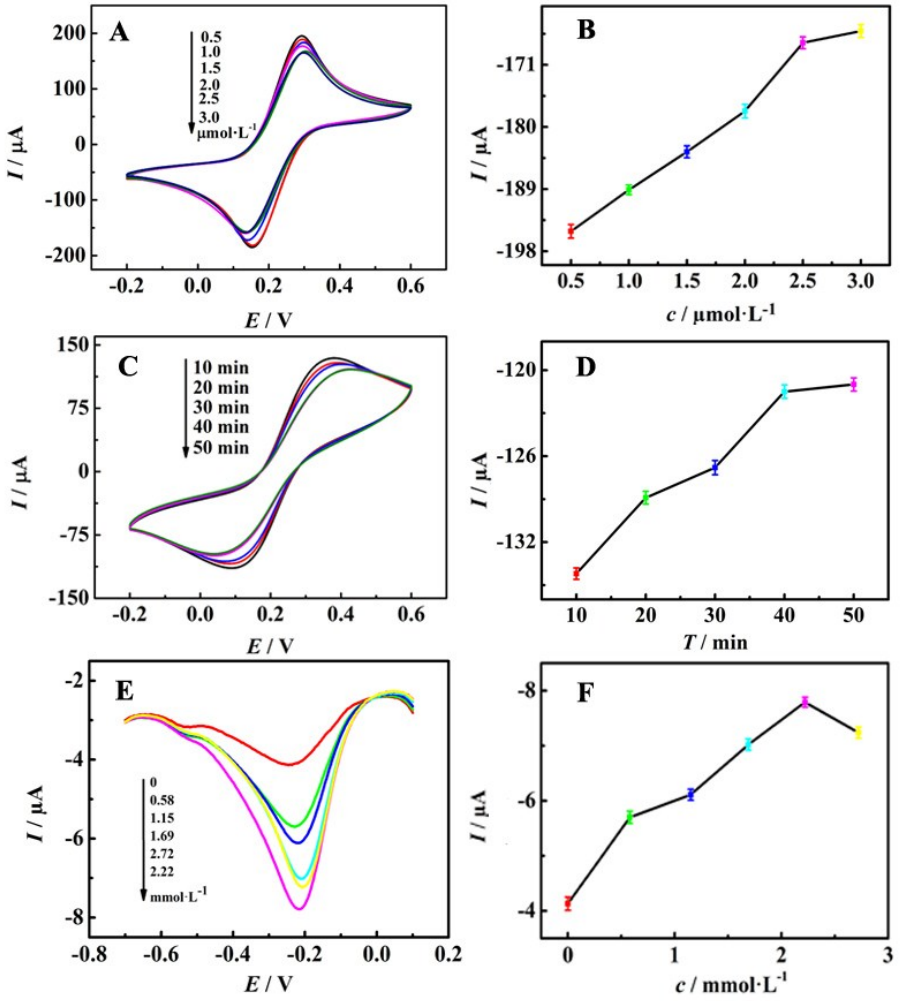

Fig. S1 The effect of SH-TBA concentration (A and B), TB incubation time (C and D) and H_2O_2 concentration (E and F) on the electrochemical response of the proposed

aptasensor. CV was measured in 5 mmol·L^{-1} $[Fe(CN)_6]^{3-/4-}$, and DPV was measured in PBS containing certain concentration of H_2O_2. Error bars: SD, n=3.

Table S1 Caparison of the analytical performance for different methodologies for TB

Methods[a]	Strategies	Dynamic linear range (pmol·L^{-1})	LOD (pmol·L^{-1})	Ref.
SERRS	Single-step target binding to TBA	1×10^2 – 1×10^3	100	3
FRET	Noncovalent π-π stacking of dye labeled TBA on graphene	62.5 – 187.5	31.3	4
Colorimetry	AuNPs and aptamer-thrombin recognition	1×10^2 – 1.5×10^4	100	5
EIS	Self-assembly of AuNPs and anti-TBA as recognition element	1×10^2 – 3×10^4	13	6
CV	Multiple ion channels embedded in polymeric membrane	3×10^3 – 5×10^4	600	8
SWV	Target-induced conformational switching	0 – 2×10^6	16000	9
DPV	Sandwich-type, aptamer-functionalized magnetic beads	1×10^2 – 1×10^5	450	7
DPV	Alkaline phosphatase decorated ZnO/Pt nanoflowers	5 – 1.5×10^4	0.15	10
DPV	AuNPs@Cu_2O-NCs	0.1 – 1×10^4	0.066	This work

[a] SERRS: surface enhanced resonance Raman scattering; FRET: fluorescence resonance energy transfer; CV: cyclic voltammetry; SWV: square wave voltammetry.