Supporting Information:

Signal Amplification Strategy and Sensing Application Using Single Gold Nanoelectrodes

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Preparation of 1 pM TB solution

It is not easy to prepare TB solution with the concentration of 1 pM due to the adsorption and errors during dilution. In this work, four volumetric flasks were prepared with 1mM of TB, and then these four flasks were allowed to sit at room temperature in dark for 3h. After that, the solution in flasks were poured out, and another 1 mM solution of TB was placed in the flask and the flask was sit in dark for 3 h. After this saturation process for 3 times, the flasks were cleaned with ultrapure water for 6 times. For preparing 1 pM solution of TB, dilution was made by pipetting 10 μL of the initial solution of TB into 10 mL of the solvent inside an equilibrated flask and 1 pM solution of TB were achieved.

Table S1. Comparisons of the prepared nanosensor with other reported sensors for the detection of TB. AuNDE Radius: 387 nm

Detection method	**Signal-off/ Reporter**	**Linear range**	**LOD**	**Ref**
ECL	Signal-on/ $Ru(bpy)_2Cl_2$	0.01nM-10 nM	6.3pM	[1]
EC	signal-on/hermin	0.1 nM-200 nM	0.1 nM	[2]
FL	Signal-on/	0.5 nM-20 nM	0.18 nM	[3]
EC	Signal-on/MB	5 pM-1 nM	1.7 pM	[4]
EC	signal-off/guanine	0.1 nM-10 nM	0.07 nM	[5]
CL		1-100 ng/mL	0.1 ng/mL	[6]
EC	signal-off/$Ru(NH_3)_6^{3+}$	0.1 pM-5 nM	0.02 pM	This work

Table S2. The reproducibility of the aptasensor

Number of the RP	0.5 pM thrombin	5 pM thrombin	50 pM thrombin
1	-116.86	-91.19	-74.19
2	-114.93	-95.43	-73.32
3	-113.01	-89.45	-76.91

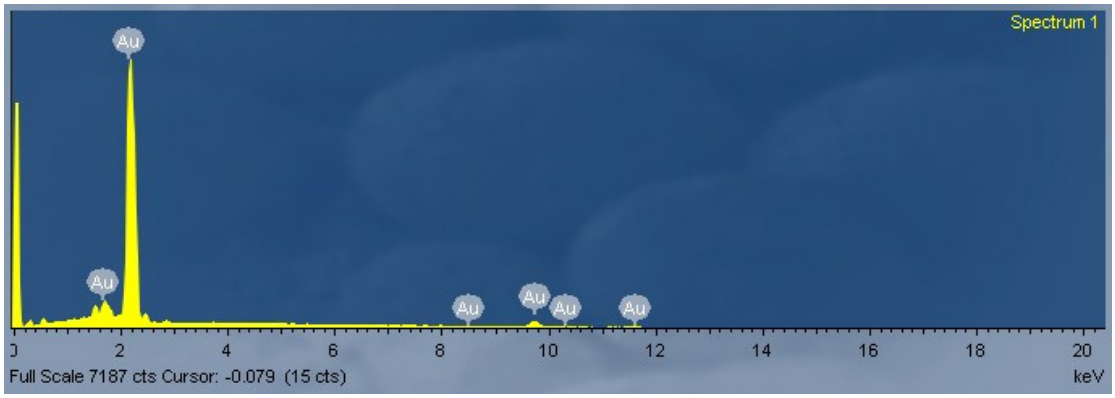

Figure S1. EDS of single gold nanoelectrode

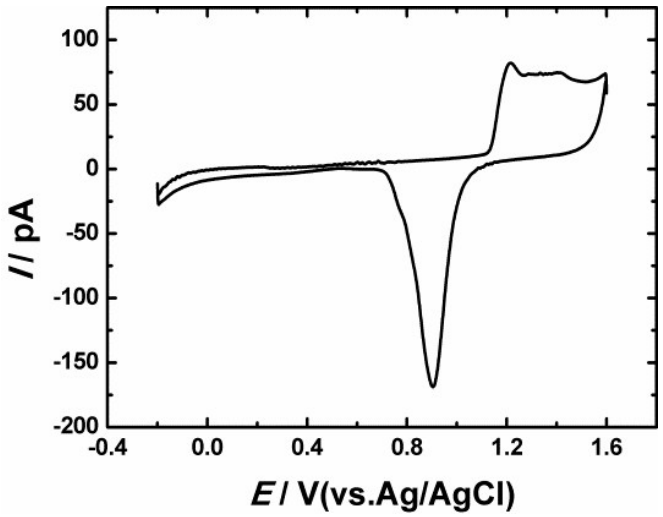

Figure S2. Cyclic voltammograms of a single Au nanodisk electrode in a 0.5 M H_2SO_4 solution. Radius, 256nm; scan rate, 20 mV/s.

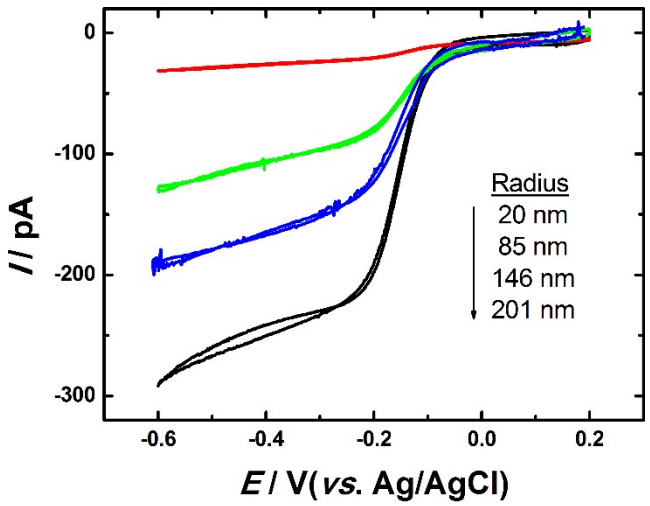

Figure S3. Cyclic voltammetric responses using single AuNDEs with different radius in an aqueous solution containing 5 mM $Ru(NH_3)_6^{3+}$ + 0.1 KCl. Scan rate, 20 mV/s.

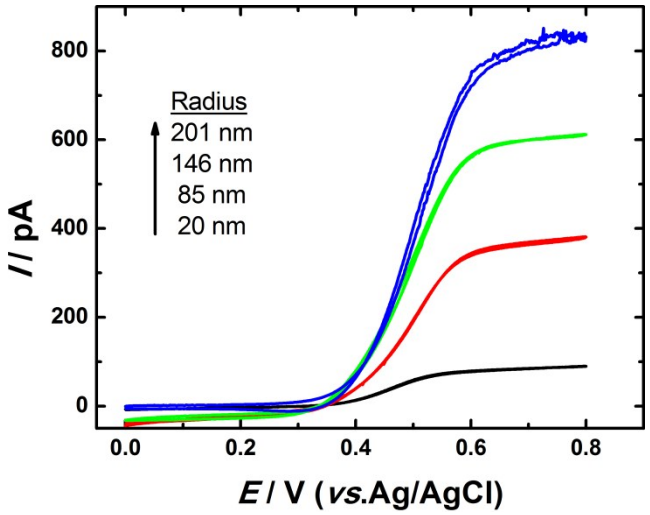

Figure S4. Cyclic voltammetric responses using single Au nanoelectrodes with different radius in a 5 mM Fc ACN solution in 0.1M KCl. Scan rate, 20 mV/s.

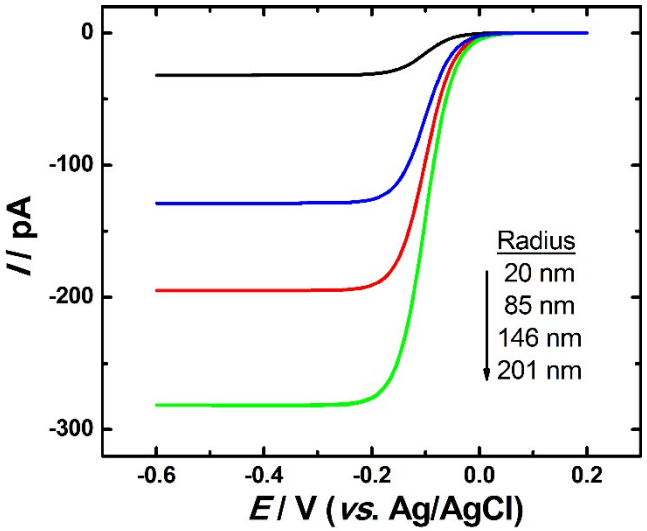

Figure S5. Simulated voltammetric responses of AuNDEs in an aqueous solution containing 5 mM $Ru(NH_3)_6^{3+}$ +0.1 M NaCl; scan rate, 20 mV/s.

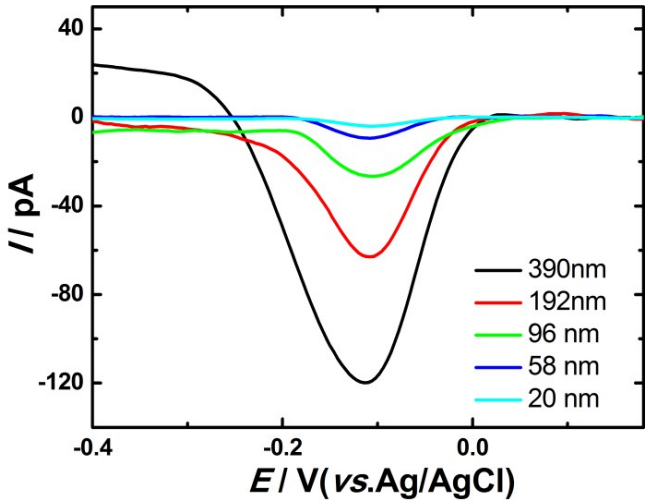

Figure S6. The effect of electrode size to the sensing performance in a 10 mM Tris-HCl buffer containing 400 μM $Ru(NH_3)_6^{3+}$.

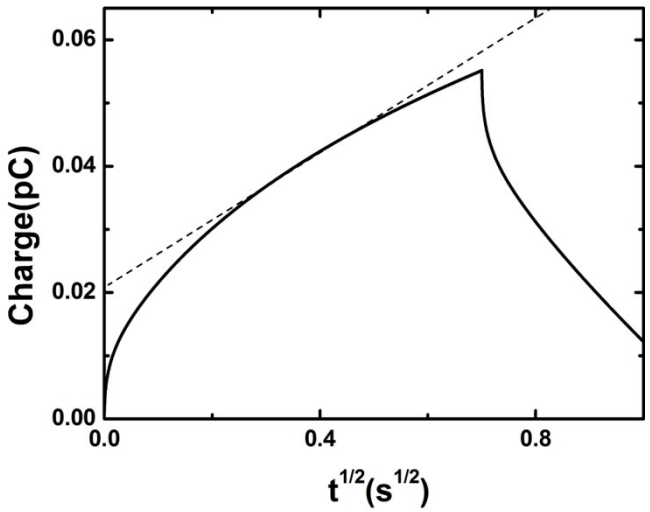

Figure S7. CC curves at the helper-DNA modified electrode in 10mM Tris-HCl buffer containing 10μM $Ru(NH_3)_6^{3+}$, AuNDE Radius: 400 nm

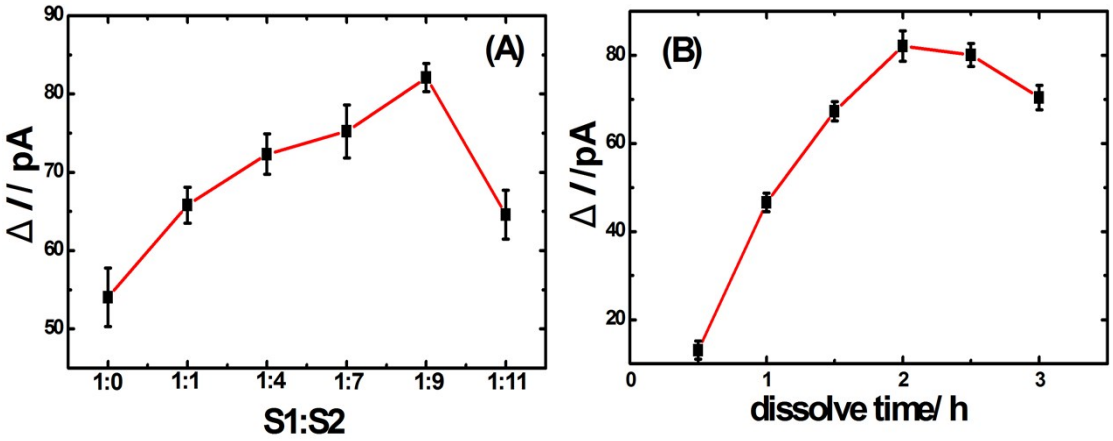

Figure S8. the optimization conditions. (**A**) the current change *via* the mole ratio of **S1/S2**, (**B**) the current change *via* the dissolving time of the sandwich DNA complexes. The error bars represent the standard deviation of four repetitive measurements. AuNDE Radius: 412 nm

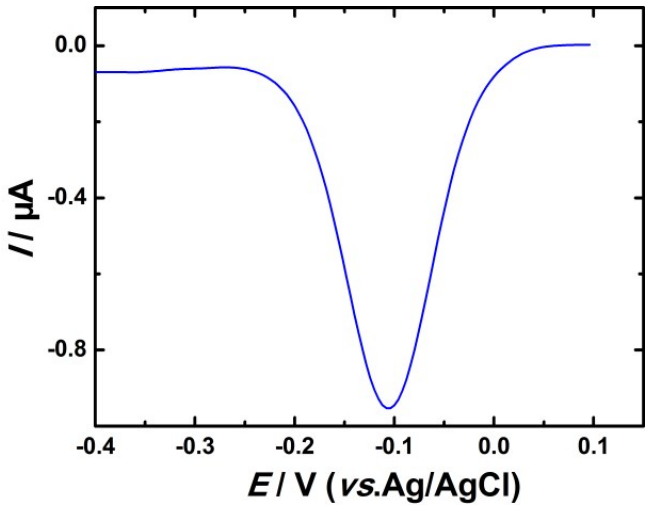

Figure S9. DPV response of the same sensor based on macroscale Au electrode in 10μM Tris-HCl containing 400μM $Ru(NH_3)_6^{3+}$.

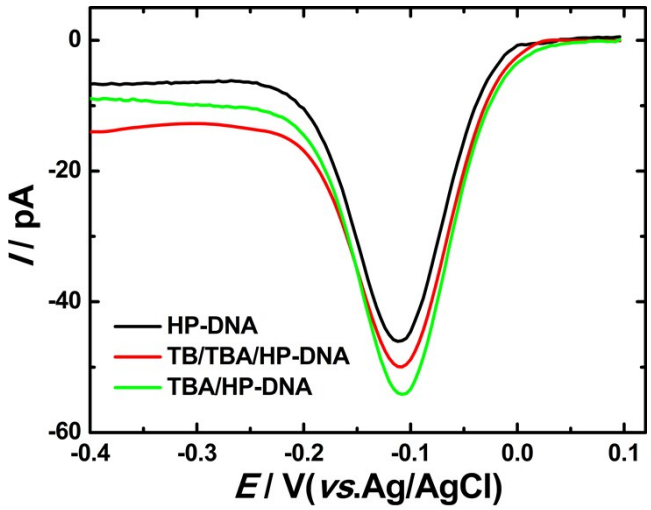

Figure S10. DPV responses of $Ru(NH_3)_6^{3+}$ solution using HP-DNA/MCH/AuNDE (black curve) and TBA/HP-DNA/MCH/AuNDE with (red curve) and without (green curve) incubation in a 500 pM thrombin solution for 2h.

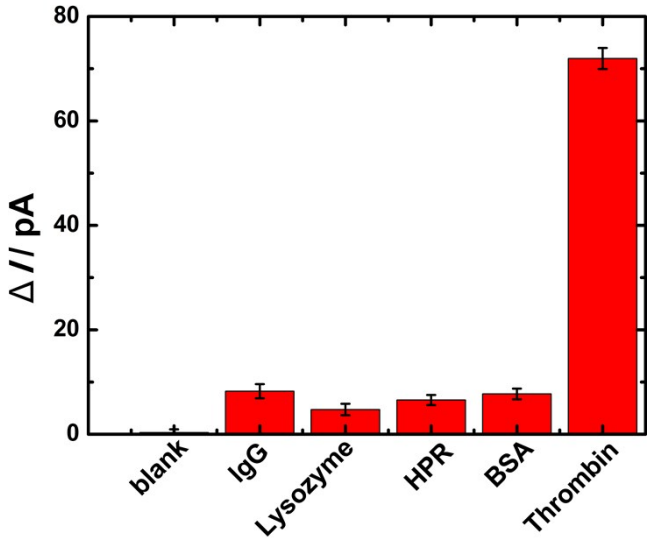

Figure S11. Selectivity of the aptasensor to thrombin. AuNDE Radius: 326 nm

References

1. Y. J. Li, Y. Q. Li, N. Xu, J. H. Pan, T. F. Chen, Y. W. Chen and W. H. Gao, *Sensors and Actuators B*, 2017, **240**, 742-748.
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