

## Supporting Information

### A label-free and ultrasensitive DNA impedimetric sensor with enzymatic and electrical dual-amplification

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#### Preparation of GO/rGO modified electrode

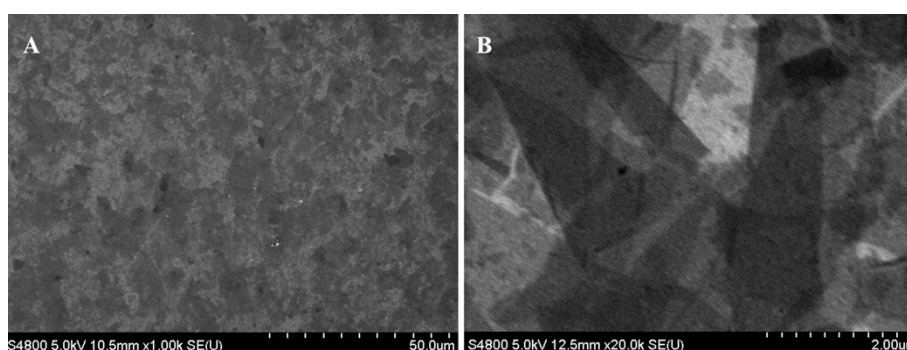


Figure S1. SEM images of the GO modified gold electrode with the amplification of 1k (A) and 20 k (B). It is illustrated that the electrode was covered by GO to a large extent, indicating the successful adsorption of GO.

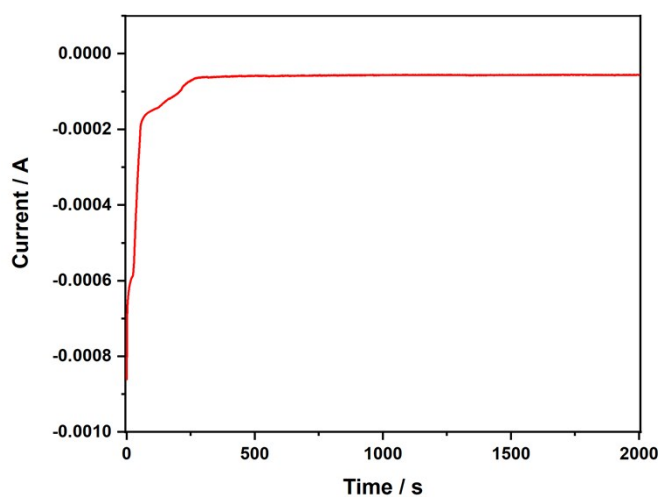


Figure S2. The *i-t* curve for the electrolysis of GO modified gold electrode at -0.9 v.

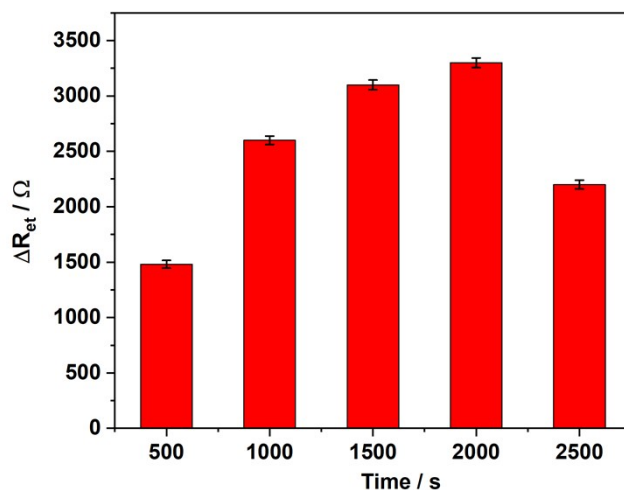


Figure S3. The changes of  $R_{et}$  ( $\Delta R_{et} = R_{et, DNA} - R_{et, electrolysis}$ , where  $R_{et, electrolysis}$  is the value of  $R_{et}$  after the electrolysis treatment, and  $R_{et, DNA}$  is the value of  $R_{et}$  after the adsorption of DNA probes) as a function of the time for the electrolysis treatment of GO modified gold electrode. The larger value of  $\Delta R_{et}$  indicates the possible larger responding in the detection. The gradually increased  $\Delta R_{et}$  before 2000 s can be explained by the continuously improved conductivity through electrochemical reduction of GO to enlarge the changes of  $R_{et}$  before and after adsorption of DNA probes. And the decreased  $\Delta R_{et}$  since 2500 s may be due to the possible exfoliation of rGO from the electrode or the declined adsorption ability after a long time electrolysis, indicating 2000 s would be an appropriate electrolysis time in the experiment.

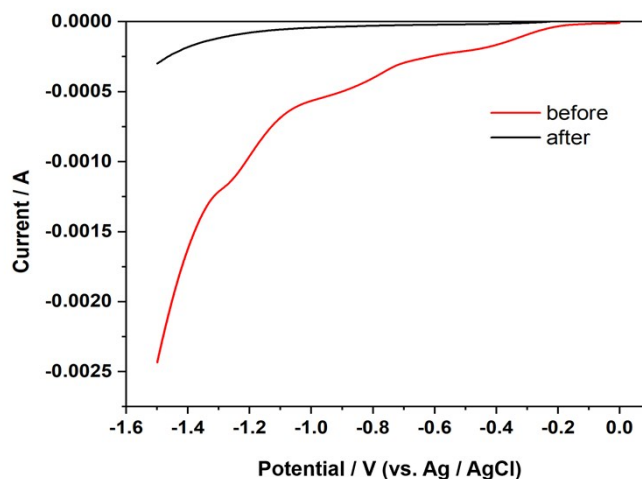


Figure S4. linear sweep voltammety of GO modified gold electrode before and after the treatment of applying negative potential. The obviously decreased current after electrochemical reduction can be explained by the efficient removal of oxygen functional groups on the surface.

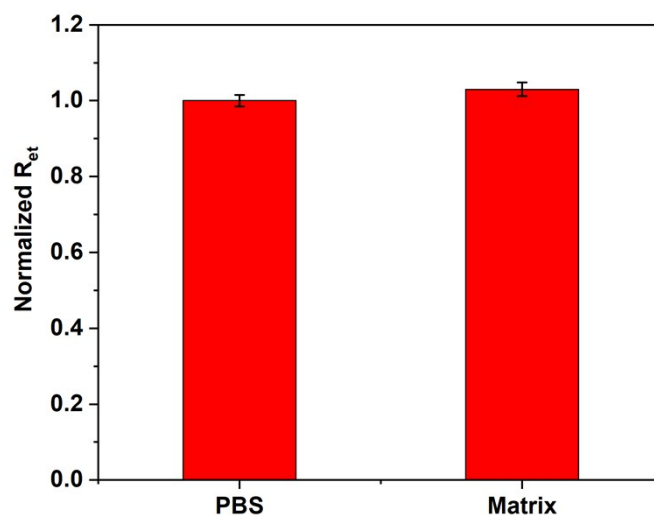


Figure S5. The normalized value of  $R_{et}$  for the BSA blocked sensor separately treated in PBS buffer and cell culture matrix. The not obvious changes in  $R_{et}$  indicate the non-specific adsorption has been effectively eliminated by BSA blocking.

Table S1 Comparison of sensors

Detection technique	Linear range (M)	Limit of detection (M)	Nanomaterials	Probe/target labeling	Reference
fluorescence	$2.0 \times 10^{-12}$ $-1.0 \times 10^{-9}$	$5.0 \times 10^{-13}$	graphene oxide	fluorophores labeled probe	1
mass spectroscopy	not mentioned	$1.0 \times 10^{-15}$	graphene oxide	none labeling	2
EIS	$5.0 \times 10^{-14}$ $-5.0 \times 10^{-9}$	$1.0 \times 10^{-14}$	graphene/Au nanocomposites	thiol labeled probe	3
EIS	$1.0 \times 10^{-13}$ $-1.0 \times 10^{-10}$	$2.3 \times 10^{-14}$	graphene-Nafion composite	none labeling	4
EIS	$1.0 \times 10^{-12}$ $-1.0 \times 10^{-7}$	$5.2 \times 10^{-13}$	tryptamine functionalized rGO	amino modified probe	5

DPV	$1.0 \times 10^{-16}$ $-1.0 \times 10^{-7}$	$3.0 \times 10^{-17}$	graphene stabilized gold nanoclusters	MB modified probe	6
EIS	$5.0 \times 10^{-17}$ $-1.0 \times 10^{-9}$	$1.0 \times 10^{-17}$	electrochemically reduced GO	none labeling	this work

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DPV: differential pulse voltammetry

### References

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