Supporting Information

A reagentless signal-on architecture for electronic, real-time copper sensors based on self-cleavage of DNAzymes

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Materials and methods

DNA sequences

DNA oligonucleotides were obtained from Takara Inc. (Dalian) The sequences of employed oligonucleotides are as follows.

DNA(1)

5'-GAATTCTAATACGACTCACTATAGG AAGAG ATGGC GACTG TTTAG AAGCA GGCTC TTTCT TATGC GTCTG GGCCT CTTTT TAAGA AC

DNA(2)

5' (Fc) -$(CH_2)_6$-GAATA TAGTG AGCTA CGCTA GAATT C-$(CH_2)_6$-SH 3'

Electrode preparation, DNA immobilization and copper detection

Gold electrodes (2 mm in diameter, CH Instruments Inc.) were first polished on microcloth (Buehler) with Gamma micropolish deagglomerated alumina suspension (0.05 μm) for 5 min. These electrodes were then sonicated in ethanol and Milli-Q water for 5 min, respectively. Finally, the electrodes were then electrochemically cleaned to remove any remaining impurities.

DNA duplexes (dsDNA) were prepared as follows: The mixture of DNA(1) and DNA(2) (1 μM each) in 1M $NaClO_4$ containing 1 mM TCEP (tris-(2-carboxyethyl))(TCEP was employed to cleave disulfides) was heated to 90℃ and then slowly cooled to room temperature. Then the DNA duplex was ready for immobilization at surfaces.

dsDNA modified gold electrodes were prepared by incubating electrodes in thiolated dsDNA of above for 18 h, and rinsed with 10 mM HEPES containing 50 mM $NaClO_4$ completely. For copper assays, the modified electrode was placed into 2mL copper solutions of various concentrations.

Electrochemical measurements

The measurements were conducted using SWV with a CHI 660c eletrochemical analyzer. The optimal SWV parameters were taken as follows: ΔE: 0.004V, amplitude (A): 0.025V, and frequency (ν): 25 Hz. A three-electrode cell consisting of Ag/AgCl reference electrode and platinum counter electrode was used for all electrochemical measurements. All the electrochemical reactions were carried out in 10 mM HEPES containing 50 mM $NaClO_4$, 0.5M NaCl and 0.5M KCl (PH 7.4).

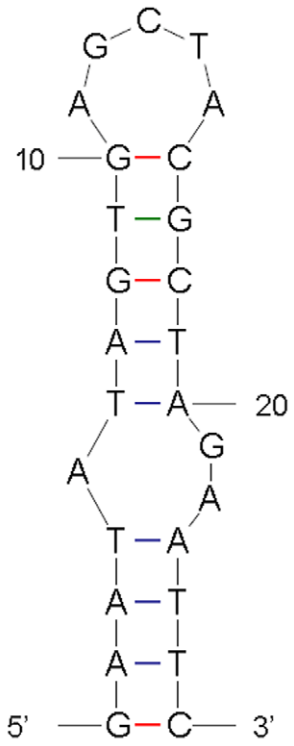


Figure S1: Favorable secondary structure of DNA(2)

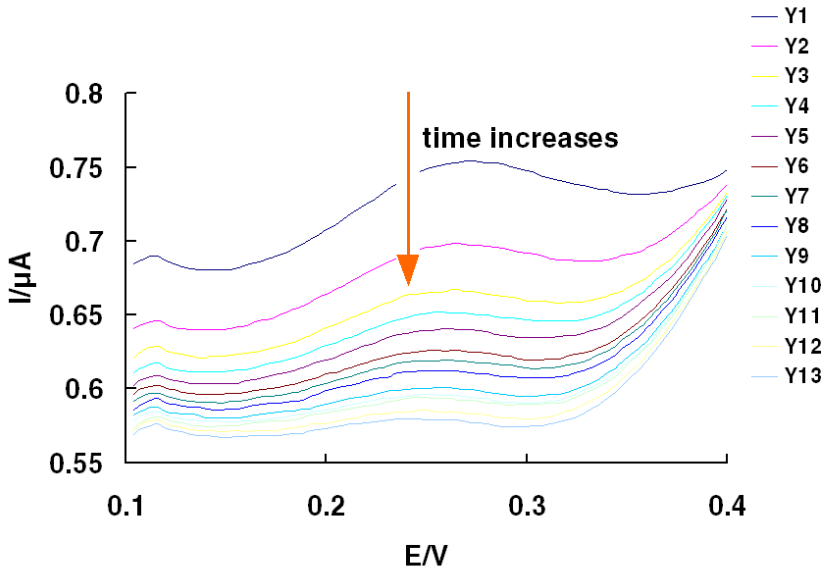


Figure S2: Shown is the sensor electrochemical signal descending with time. The electrochemical measurements were carried out in the 50mM $NaClO_4$、0.5M NaCl and 0.5M KCl without buffer solution HEPES in consecutive 13 times from Y1 to Y13, including 1 μM Cu^{2+}.

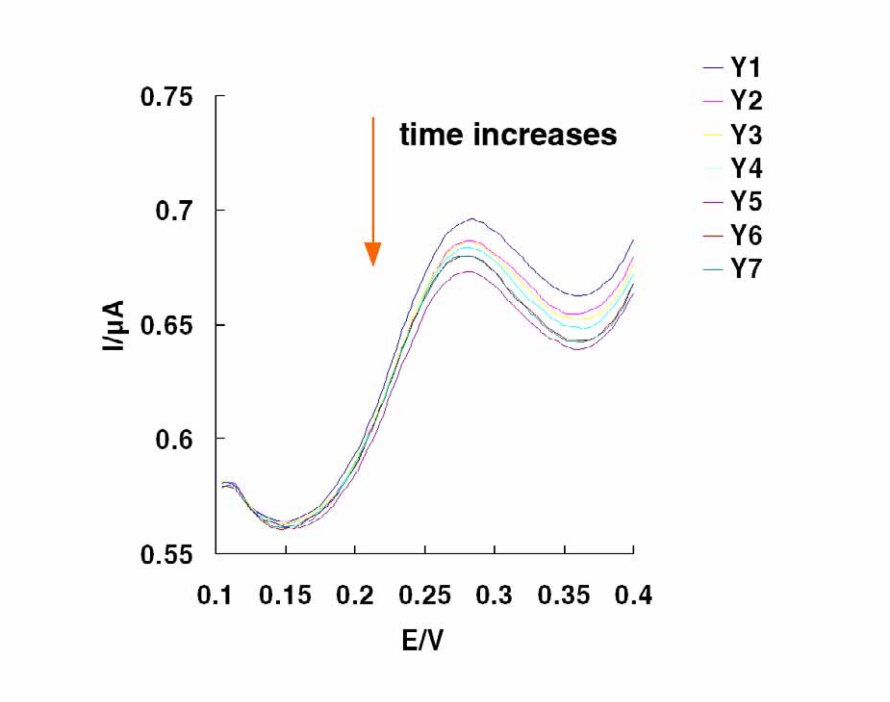


Figure S3: Shown is the sensor electrochemical signal changing with time. The electrochemical measurements were carried out in the 50mM $NaClO_4$、0.5M NaCl and 0.5M KCl with 10 mM HEPES buffer (pH=7.4) in consecutive 7 times from Y1 to Y7, including 1 μM Cu^{2+}.

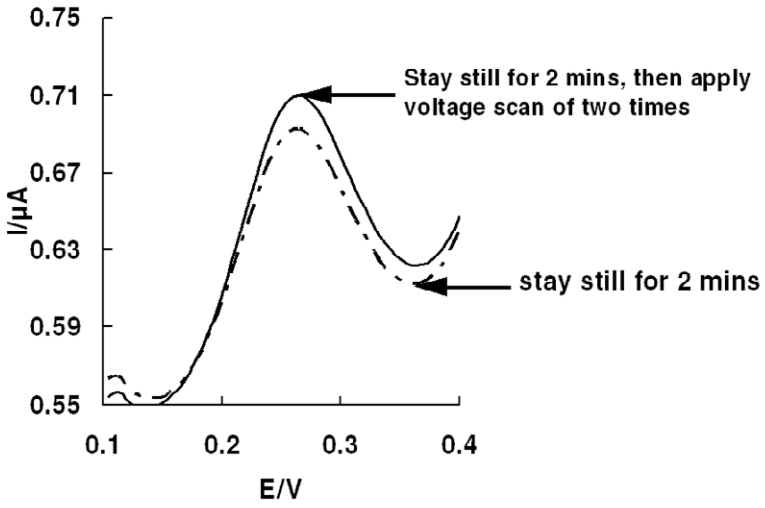


Figure S4: Shown is the sensor signal change via different operation methods. The measurement taken after 2 mins of staying exhibit the lower signal; It gives stronger signal if applied consecutive two times voltage scan thereafter. The electrochemical measurements were carried out in the 50mM NaClO4、0.5M NaCl and 0.5M KCl and 10 mM HEPES, including 3.5 μM Cu^{2+}.

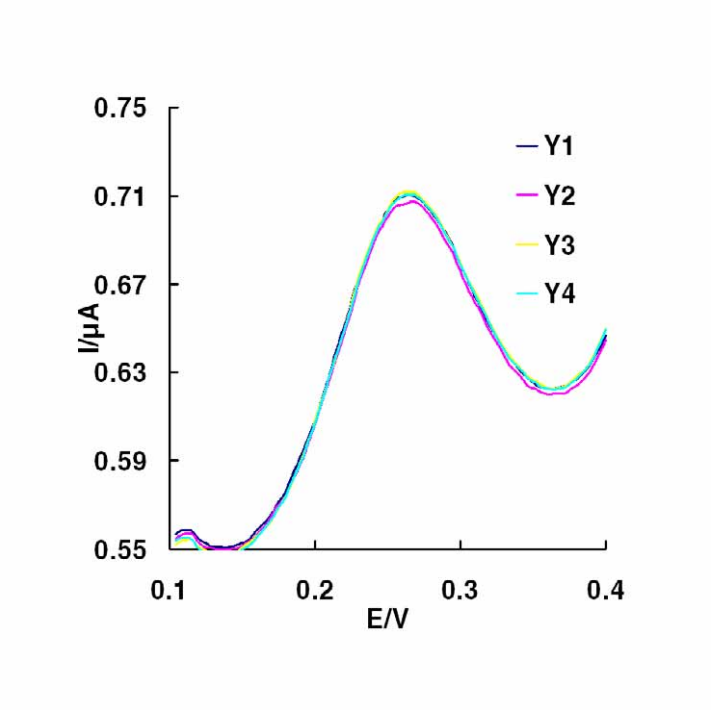
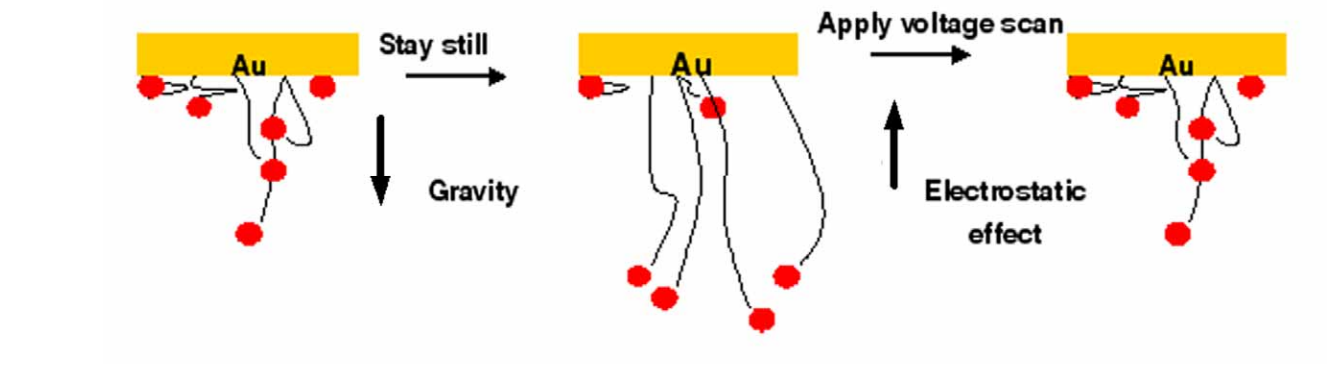


Figure S5: Shown is the sensor signal change with time from Y1 to Y4 by the operation method of applying voltage scan twice. Almost no signal change was observed. The electrochemical measurements were carried out in the 50mM $NaClO_4$、0.5M NaCl and 0.5M KCl and 10mM HEPES, including 3.5 μM Cu^{2+}.



Scheme S1: The proposed schematic illustration of signal change via different operation methods.

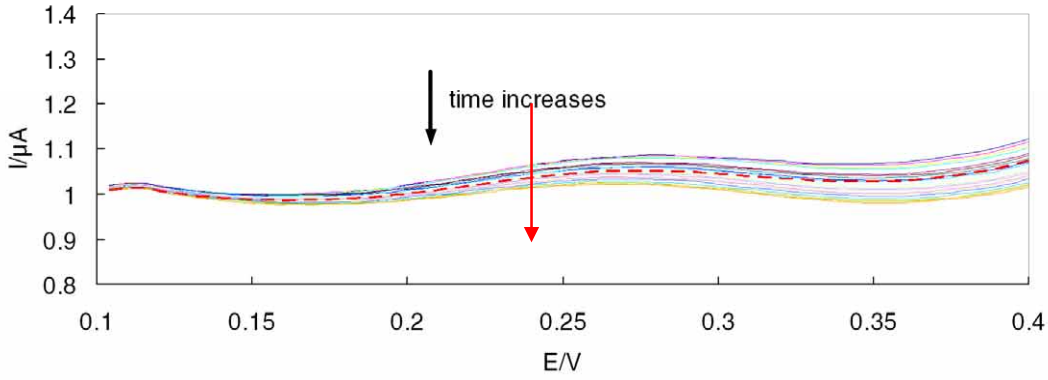


Figure S6: Shown is the base line descending with time. The electrochemical measurements were carried out in the 50mM $NaClO_4$、0.5M NaCl, 0.5M KCl and 10 mM HEPES without Cu^{2+}.

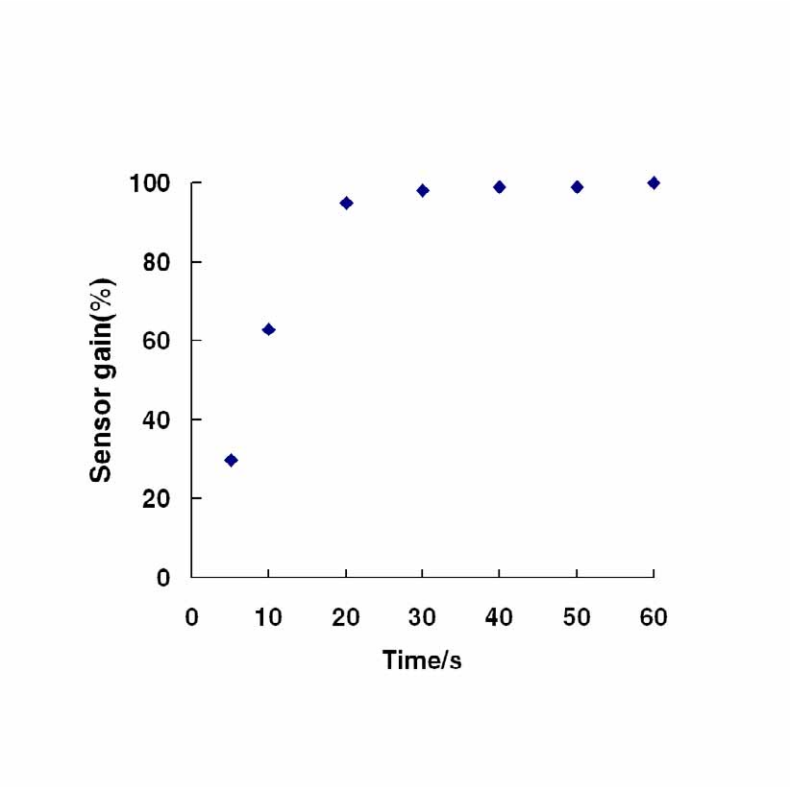


Figure S7: Time dependence of sensor gain. The electrochemical measurements were carried out in the 50mM $NaClO_4$、0.5M NaCl and 0.5M KCl and 10 mM HEPES, including 10 μM Cu^{2+}.