Supporting Information

Asymmetric Nanochannel-Ionchannel Hybrid for Ultrasensitive and Label-free Detection of Copper Ions in Blood

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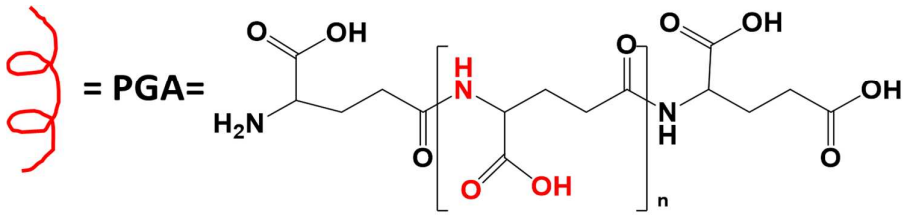

Scheme S1. The chemical structural formula of PGA.

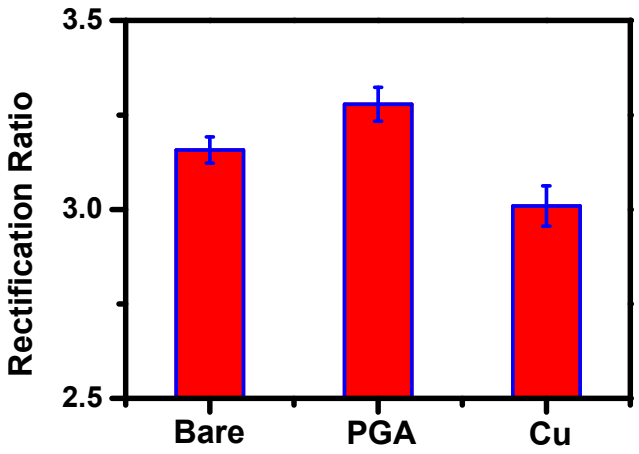

Figure S1. ICR ratio for different processes.

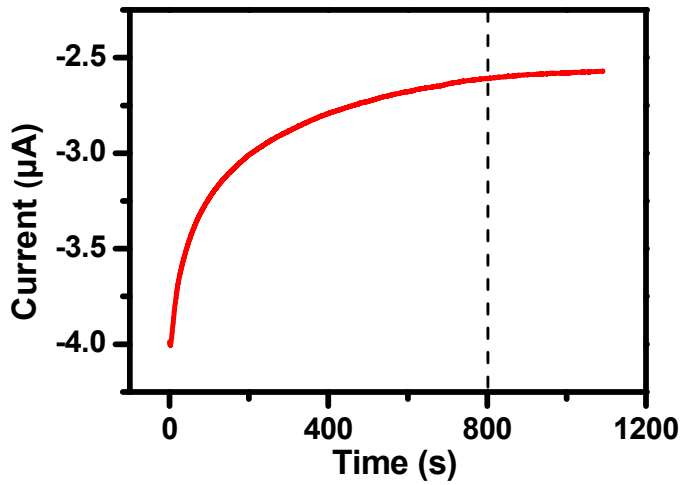

Figure S2. Cu^{2+}-PGA recognition kinetics. The dashed line means the time needed for PGA-Cu^{2+} recognition equilibrium. The Cu^{2+} concentration is 3.37 x 10^{-10} μM.

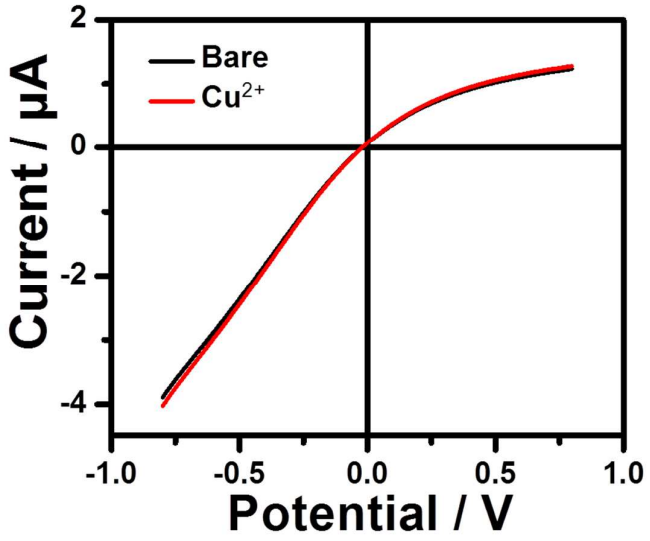

Figure S3. *I-V* curve of PGA-free PAA with and without Cu^{2+} (10 μM).

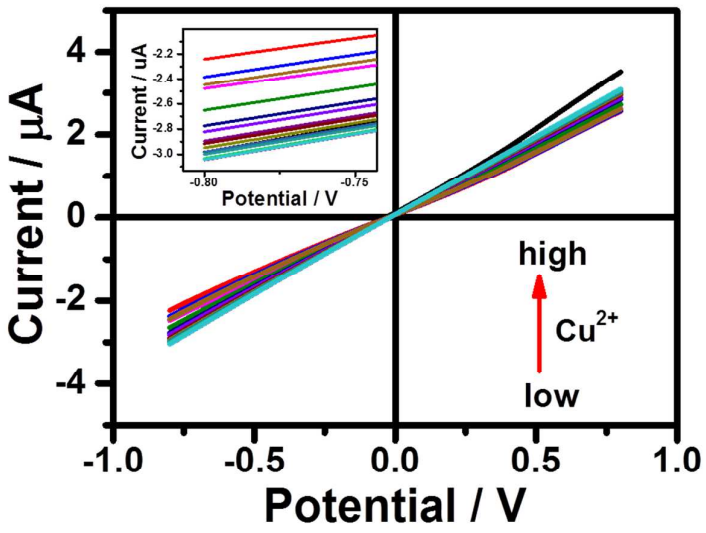

Figure S4. *I-V* curve of PGA- modified symmetric PAA membranes in the present of different Cu^{2+} (the amplify inset).

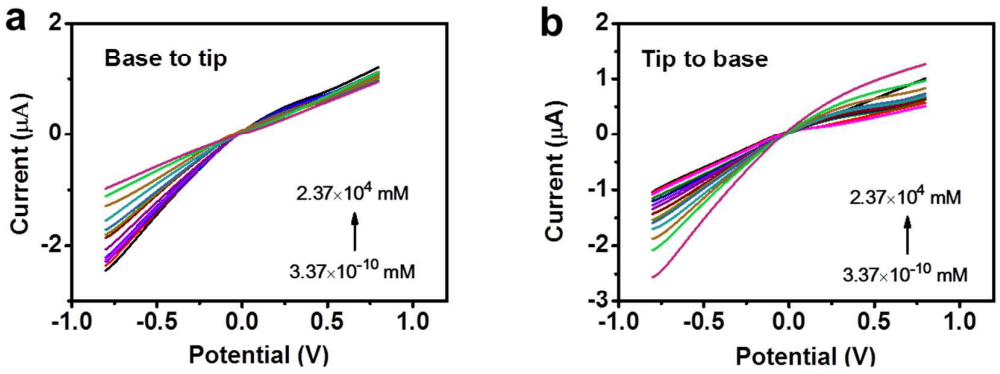

Figure S5. The *I-V* profiles of the PGA modified nanochannel-ionchannel hybrid for detection of Cu^{2+} using different methods. (a) Cu^{2+} ions were added in the nanochannel side of PAA membrane (b) Cu^{2+} ions were added in the ionchannel side of PAA membrane.

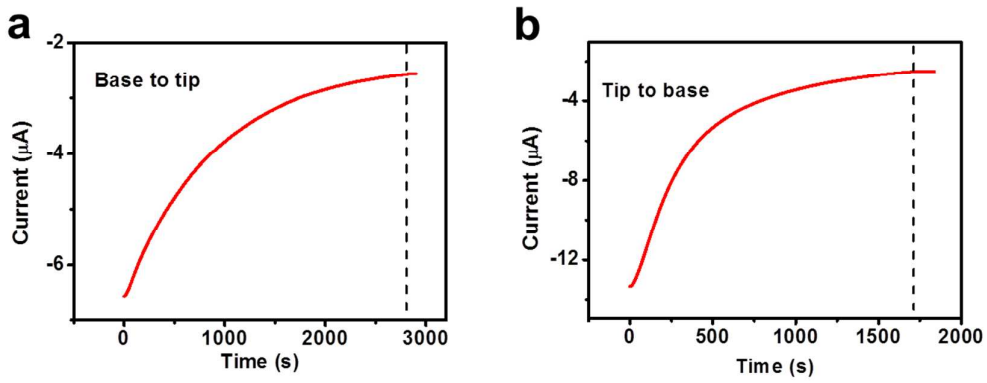

Figure S6. Cu^{2+}-PGA recognition kinetics for different systems. (a) Cu^{2+} ions were added in the nanochannel side of PAA membrane (b) Cu^{2+} ions were added in the ionchannel side of PAA membrane. The dashed line means the time needed for PGA-Cu^{2+} recognition equilibrium. The Cu^{2+} concentration is 3.37 x 10^{-10} μM.

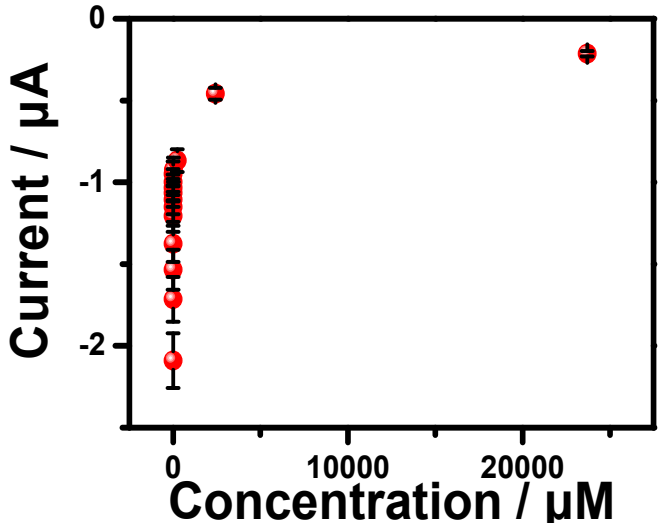

Figure S7. The current values versus of Cu^{2+} concentrations.

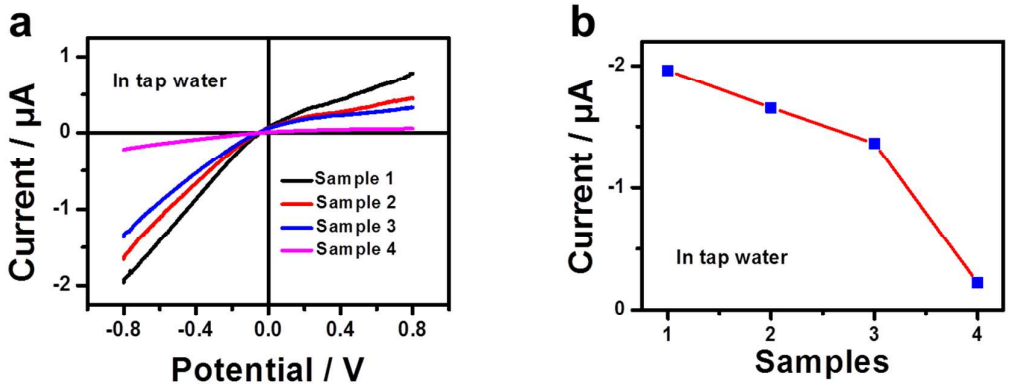

Figure S8. (a) The *I-V* profiles of different concentrations of Cu^{2+} in tap water samples. (Sample 1: no additional Cu^{2+} in tap water; Sample 2: added 5 x 10^{-7} μM in tap water; Sample 3: added 5 x 10^{-3} μM in tap water; Sample 4: added 5 x 10^{5} μM in tap water). (b) The ionic current at -0.8 V versus different tap water samples.

Table S1. Results of the detection of Cu^{2+} in real tap water samples.

Sample	Added Cu^{2+} (μM)	Measured Cu^{2+} (μM)	Recovery (%)
Sample 1	0	2.27 x 10^{-8}	/
Sample 2	5 x 10^{-7}	4.99 x 10^{-7}	99.9
Sample 3	5 x 10^{-3}	4.67 x10^{-3}	93.4
Sample 4	5 x 10^{5}	5.63 x 10^{5}	112.6