Electronic Supplementary Information

A ratiometric electrochemical microsensor for monitoring of Chloride ion *in vivo*

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Experiment Section

Synthesis of TNWSs. Briefly, 1.0 g Rutile titanium dioxide powder (40 nm) was dispersed in 35 mL NaOH aqueous solution (10 M), and followed by ultrasonic treatment to get suspension. Then the suspension was transferred into a high pressure hydrothermal reactor, and processed hydrothermal reaction at 200 °C for 20 h. After filtrating, washing and drying, the TNWSs continued to be ultrasonic dispersed in dd water for further use.

Fabrication of bare carbon fiber microelectrode (CFE). First, a borosilicate capillary was pulled on PC-100 puller (Narishige, Japan) to form a slender tip. Then, a single carbon fiber was stick to the tip of a Cu wire by silver epoxy, which was then kept in an oven at 120 ℃ for 2 h to dry. Next, the carbon fiber was carefully inserted into the slender tip of the above pulled capillary with fiber of 3~5 mm length exposed outside. The fiber was fixed by filling the capillary tip with epoxy resin followed by processing drying at room temperature overnight. Finally, the prepared bare CFE was cut to 1 mm under a microscope. Before modification, the bare CFE was sonicated in acetone, HNO_3 (3 M), NaOH (1 M), dd water each for 5 min.

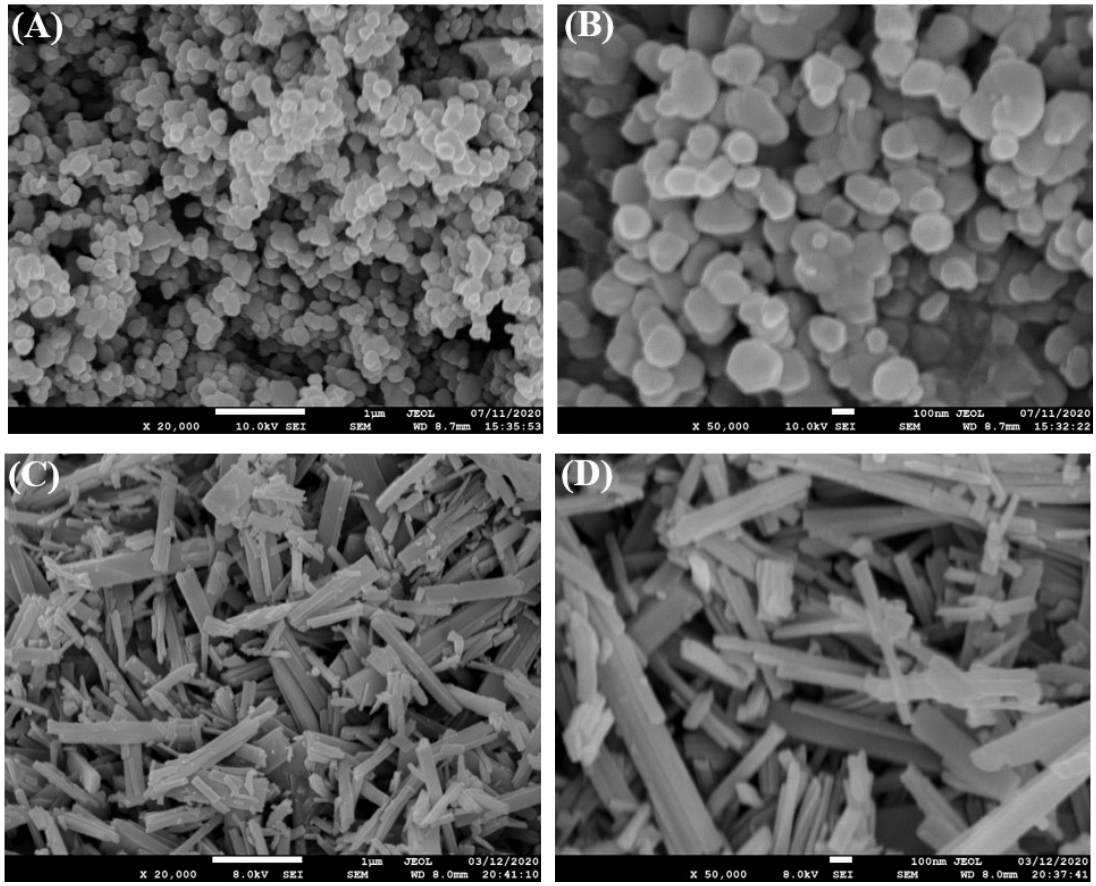

Figure S1. SEM images of (A-B) TiO_2 nanoparticles，(C-D) TNWs.

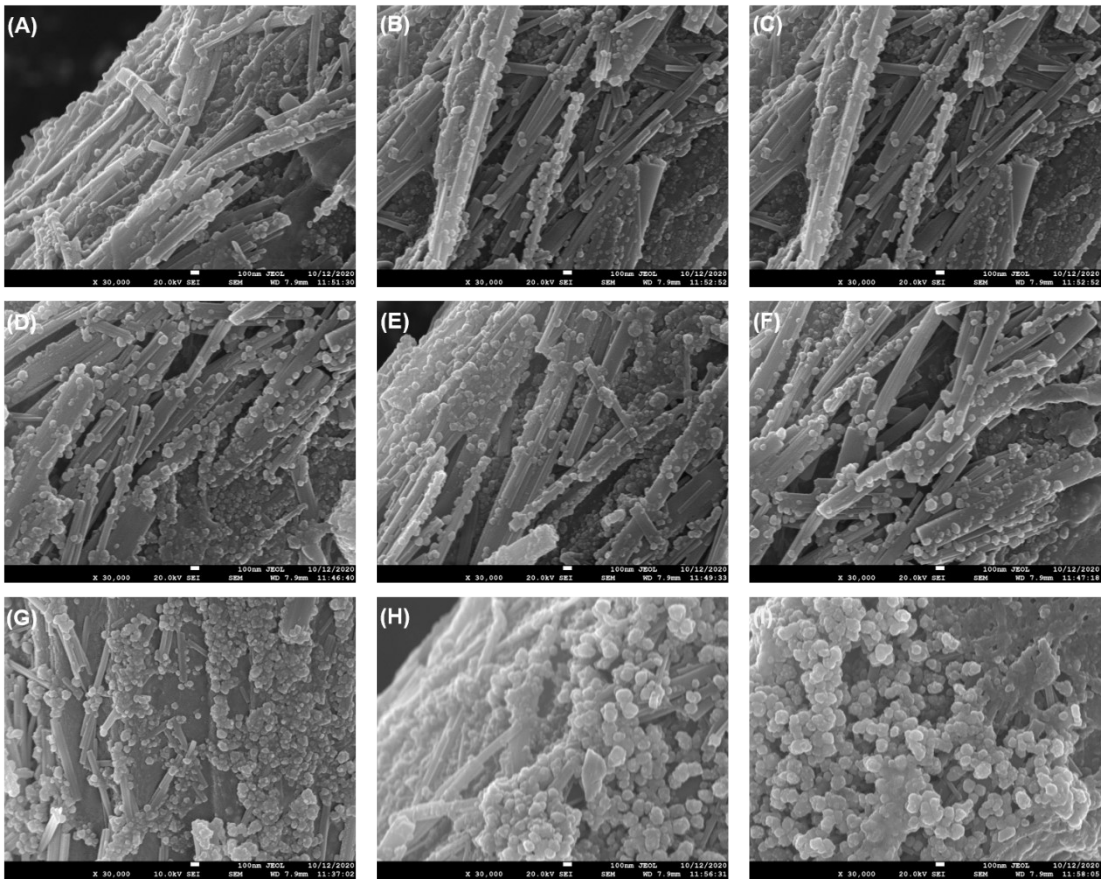

Figure S2. SEM images of CFE/GO/TNWs/Ag electrode, Ag^{+} ions adsorption time: (A-C) 30 min, (D-F) 60 min, (G-I) 90 min. All scale bars shown represent 100 nm.

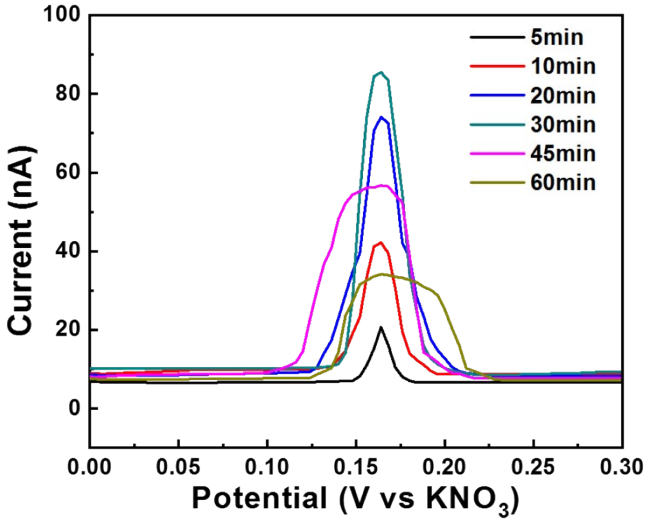

Figure S3. Typical DPVs recorded at CFE/GO/TNWs/Ag^{+} electrodes after immersing in 3 mg/mL AA aqueous solution for 5, 10, 20, 30, 45, 60 min.

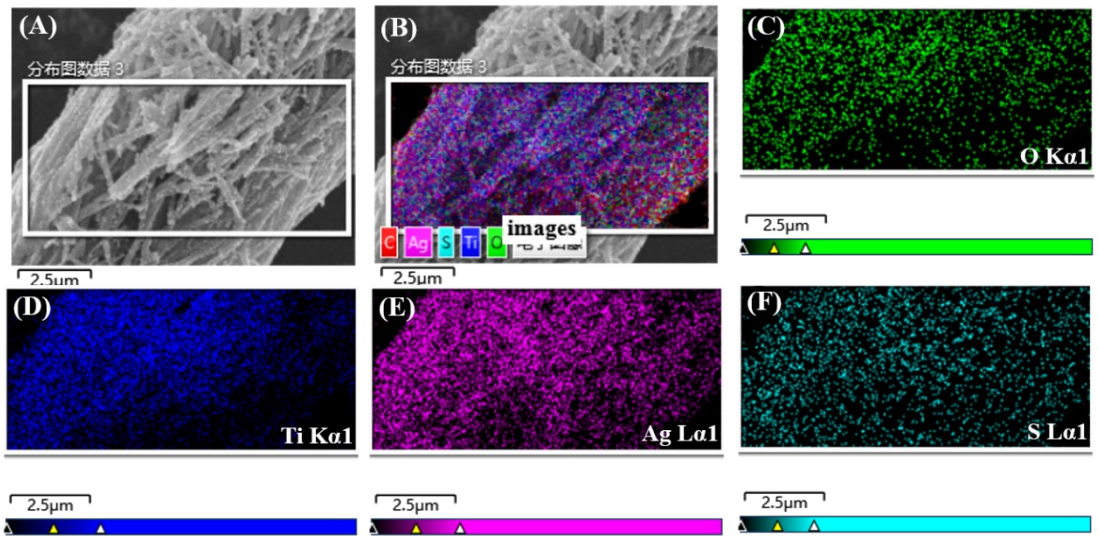

Figure S4. EDS mapping image of (A-B) the CFE/GO/TNWs/Ag/MB electrode, (C) O, (D) Ti, (E) Ag, (F) S.

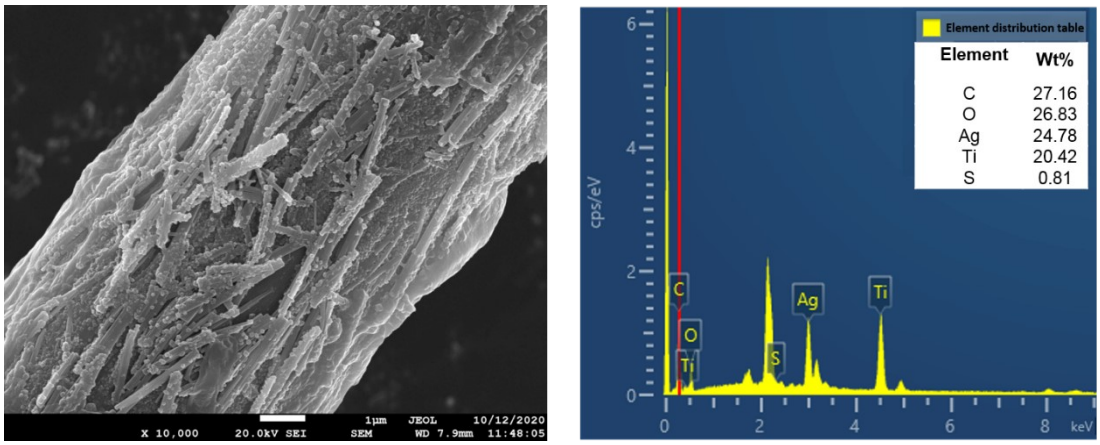

Figure S5. EDX analysis of the CFE/GO/TNWs/Ag/MB electrode.

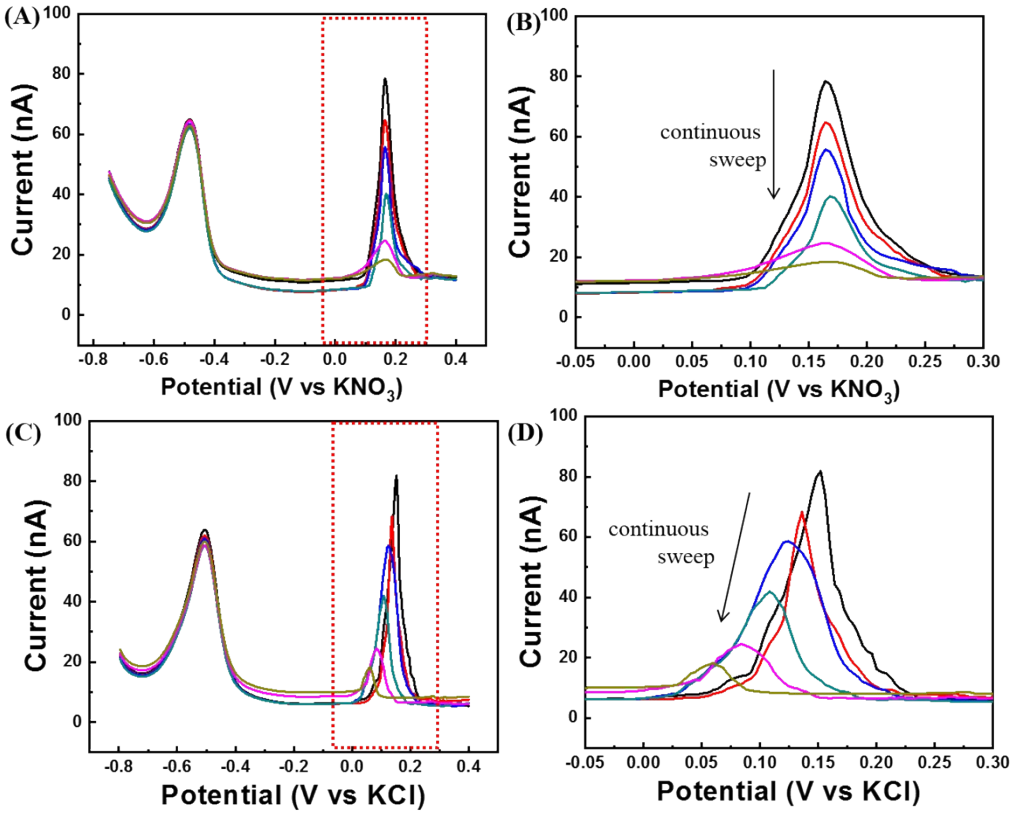

Figure S6. Typical DPVs recorded at CFE/GO/TNWs/Ag/MB electrode in blank PB solution (pH 7.4) using calomel electrode saturated with (A-B) KCl (C-D) KNO_3 as the reference electrode. Note: B, D are the high-magnification images of the marked local area in panel A, C respectively.

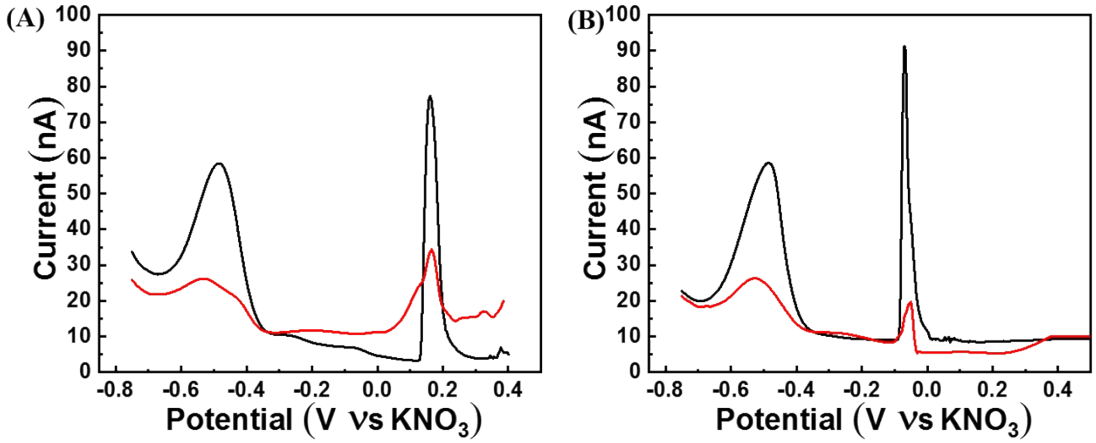

Figure S7. DPVs obtained at CFE/GO/TNWS/Ag/MB electrode (black curve), CFE/GO/Ag/MB electrode (red curve) in 0.1 M PB solution (A) without and (B) with 100 mM Cl^-.

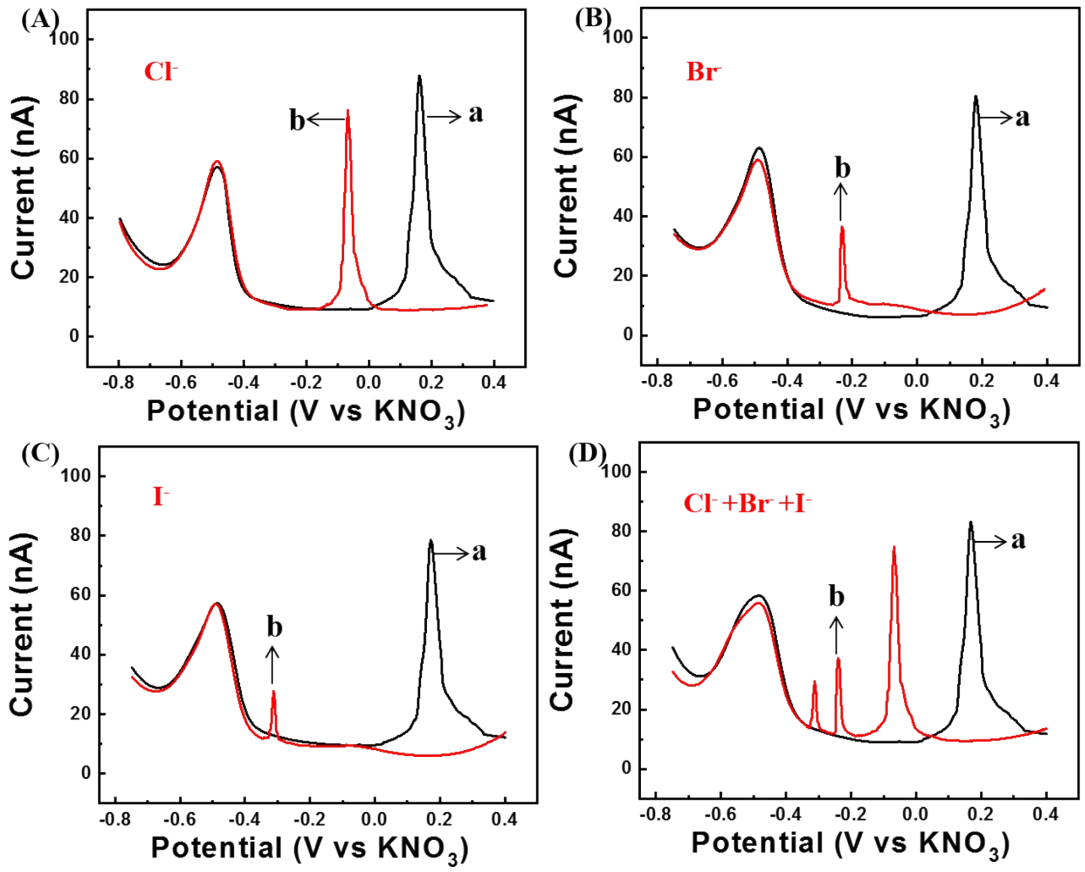

Figure S8. Typical DPVs recorded at CFE/GO/TNWS/Ag/MB electrode in PB solution (pH 7.4) in the absence (curve a) and presence (curve b) of (A) 100 mM NaCl, (B) 100 mM NaBr, (C) 100 mM NaI, (D) 100 mM NaI, 100 mM NaBr and 100 mM NaCl.

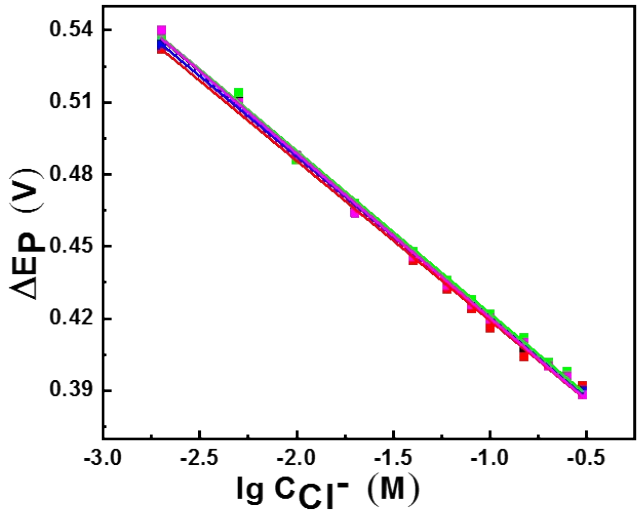

Figure S9. Linear plots obtained at five REMs monitored in 0.1 M PB solution (pH 7.4) in the presence of different concentrations of Cl^- from 1 mM to 300 mM.

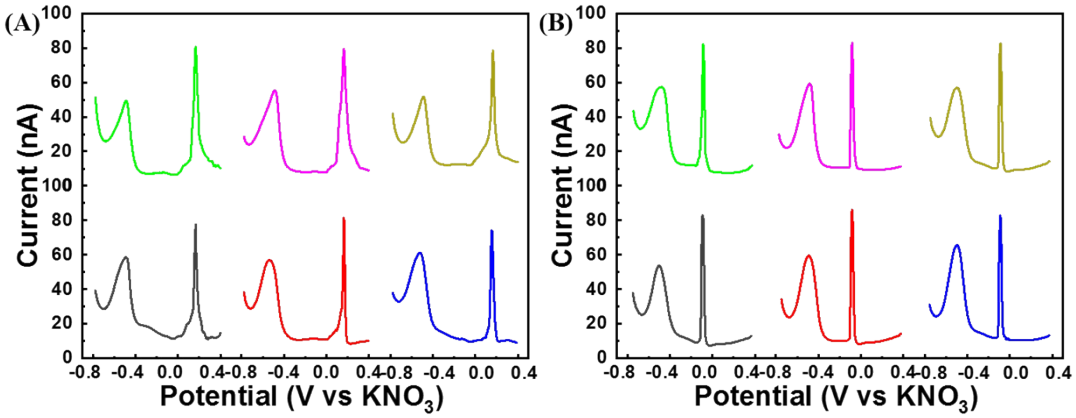

Figure S10. Reproducibility test: DPVs obtained at six REMs in PB solution (pH 7.4) in the (A) absence and (B) presence of 100 mM Cl^-.

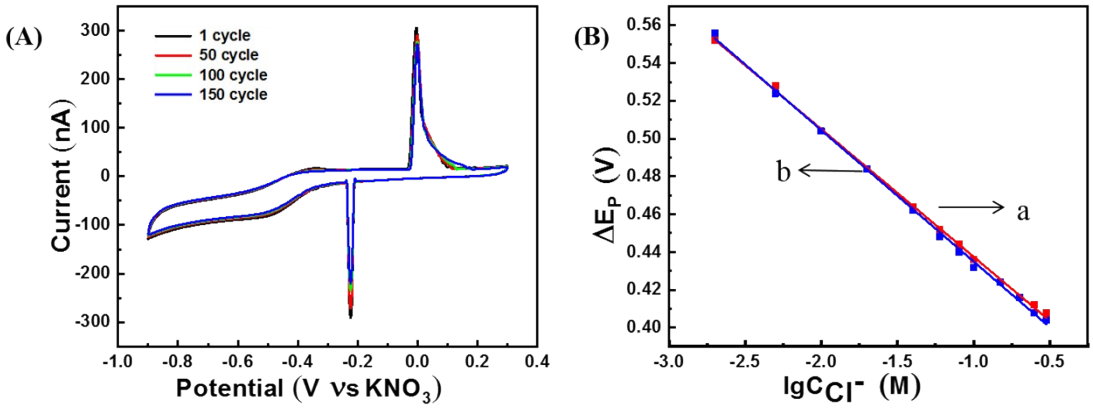

Figure S11. (A) DPVs obtained at the REM that was continuously scanned for 150 cycles in 0.1 M PB solution (pH 7.4) containing 100 mM Cl^-, (B) linear plot obtained at the ECMB before (curve a) and after being stored at 4 ℃ for 20 days (curve b).

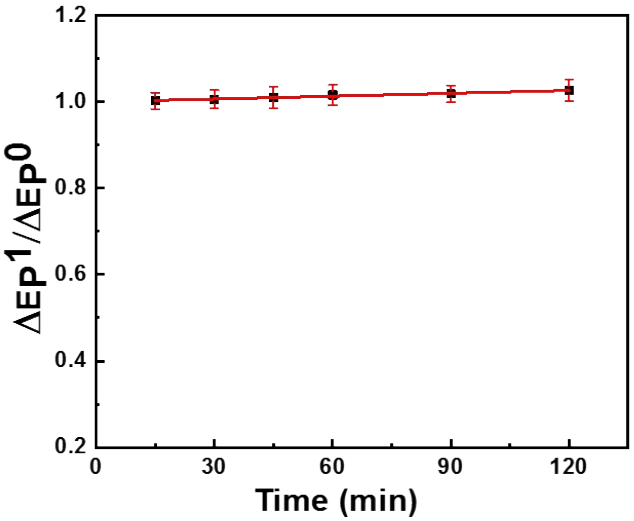

Figure S12. The $\Delta Ep^1/\Delta Ep^0$ values obtained at the REM in PB solution (7.4) containing 100 mM Cl^- after its immersing in 4% BSA for different time. $\triangle Ep^1/\Delta Ep^0 = 2.2104 \times 10^{-4}T + 0.9997$ (r=0.987).

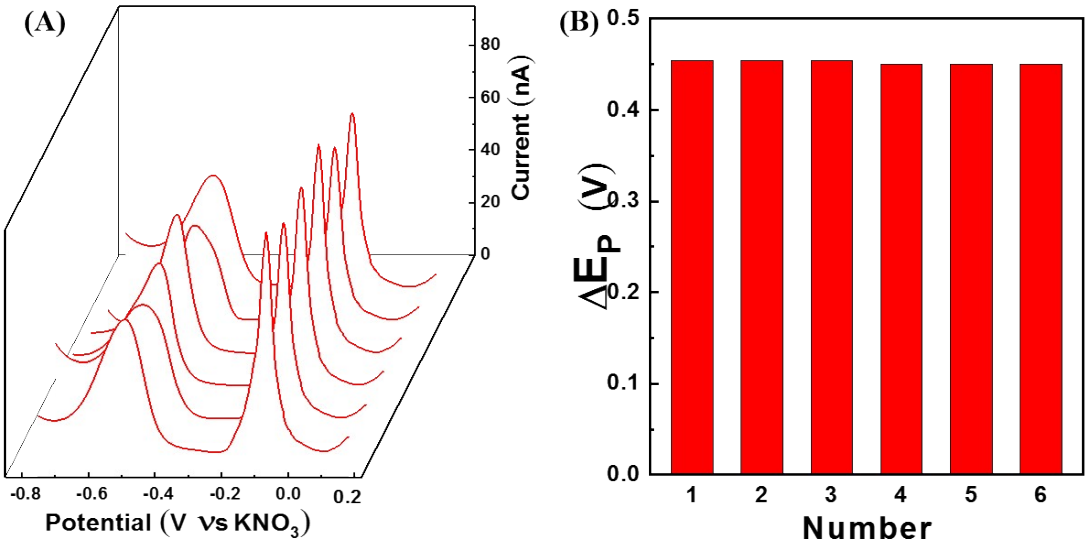

Figure S13. (A) Reproducibility test of six REMs to *in vivo* monitoring of the Cl^- levels in the cortex of rat brain. (B) The obtained ΔE_p values taken from panel A.