Supporting Information

Electrochemical analysis of attoliter water droplets through organic solution by partitioning equilibrium

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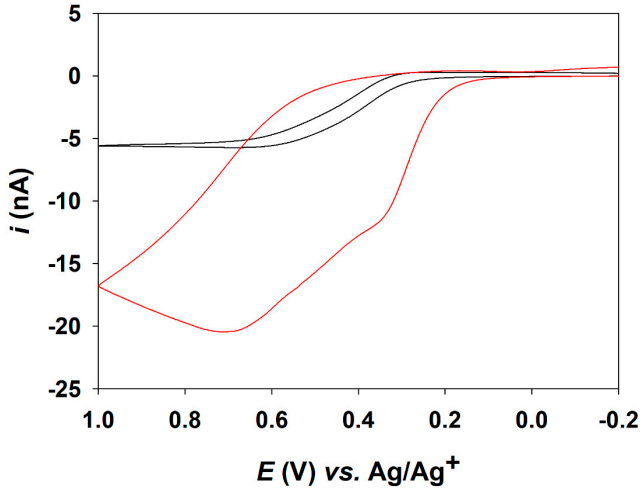

Figure S1. Cyclic voltammetry of 1 mM AP in DCE solution containing 100 mM $TBAPF_6$ (black) and AP saturated DCE solution containing 100 mM $TBAPF_6$ (red). Saturated concentration of AP in DCE solution was estimated using Eq. S1.

$$i_{lim} = 4nD_{AP}r_{UME}C_{AP} \qquad \text{(S1)}$$

Here, i_{lim} is limiting current, n is the number of electrons in the redox reaction, D_{AP} is diffusion coefficient of AP, r_{UME} is the radius of Pt-UME, and C_{AP} is concentration of AP. The calculated saturated concentration of AP in DCE solution was ca. 3.64 mM at 25ºC.

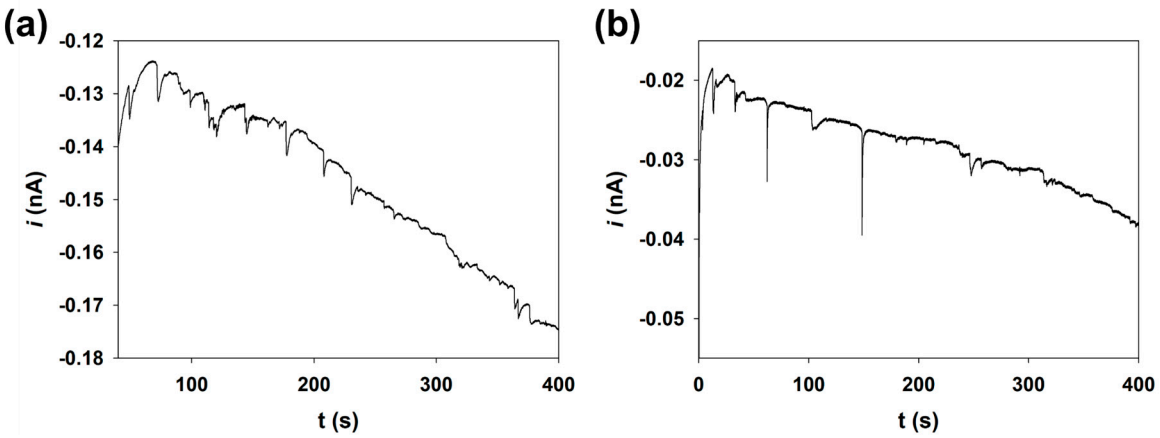

Figure S2 (a), (b) *i-t* curves measured for monitoring the collision of the single water droplets (100 mM $MgSO_4$) using 25 μm Pt UME at +0.6 V *vs.* Ag/Ag^+ in DCE containing 3 mM AP.

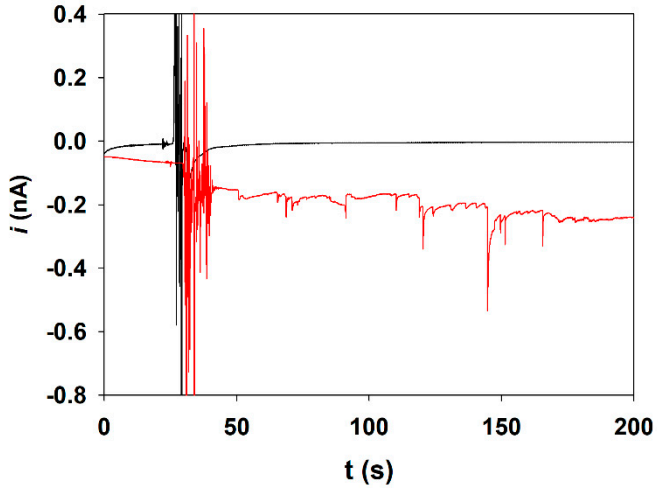

Figure S3. Amperometric *i-t* curve recorded using 25 μm Pt-UME when water droplets were injected at 30s into the the pure DCE solution (black) and DCE solution containing 3 mM AP (red). The large noise signal at 30 s were caused by the injection process of water droplets (e.g., opening of the Faraday cage).