Supporting Information

Exploring Single-Entity Electrochemistry Beyond Conventional Potential Windows: Mechanistic Insights into Hydrazine/Hydrazinium Ion Oxidation

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Preparation of Ultramicroelectrode (UME)

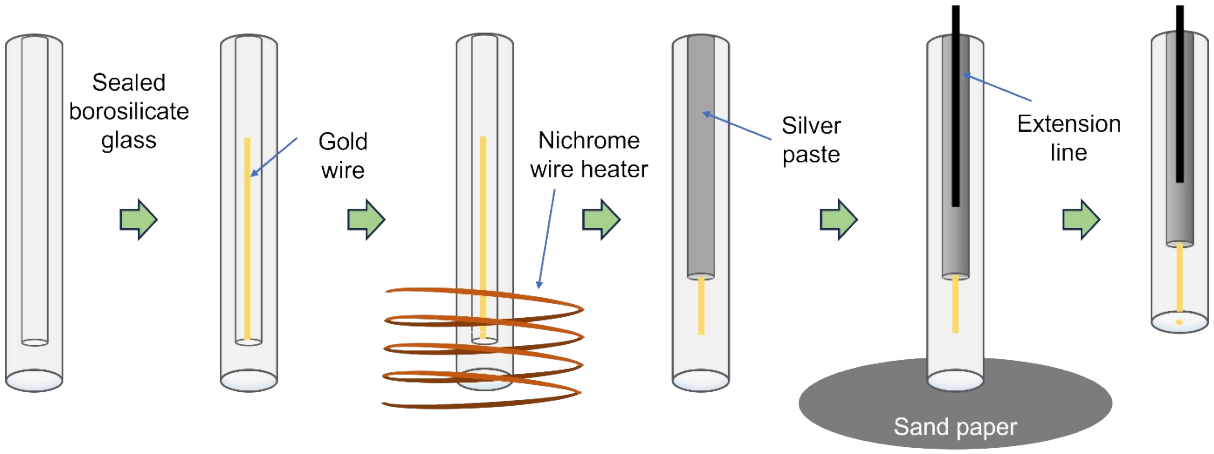

Figure S1. Schematic illustration of the preparation of Au UME.

Single-entity electrochemistry (SEE) measurement

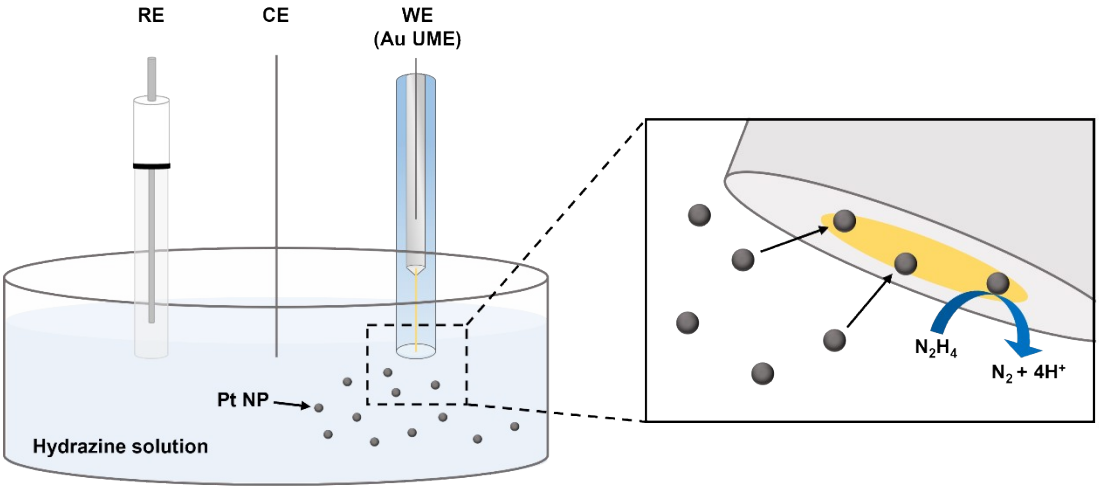

Figure S2. Schematic illustration of the single Pt NP collision on the Au UME for the measurement of SEE signal.

The SEE measurement is conducted as follows. The electrochemical cell is set up inside a Faraday cage, with the Au UME as the working electrode in a buffer electrolyte solution containing hydrazine, as shown in Figure S2. The electrolyte solution contains Pt NPs and hydrazine. A specific potential is applied to the Au UME, and the current is measured. The SEE current signal is generated when the NPs diffuse through the solution and collide with the UME.

Chronoamperometry results when 0 mM hydrazine in electrochemical cell

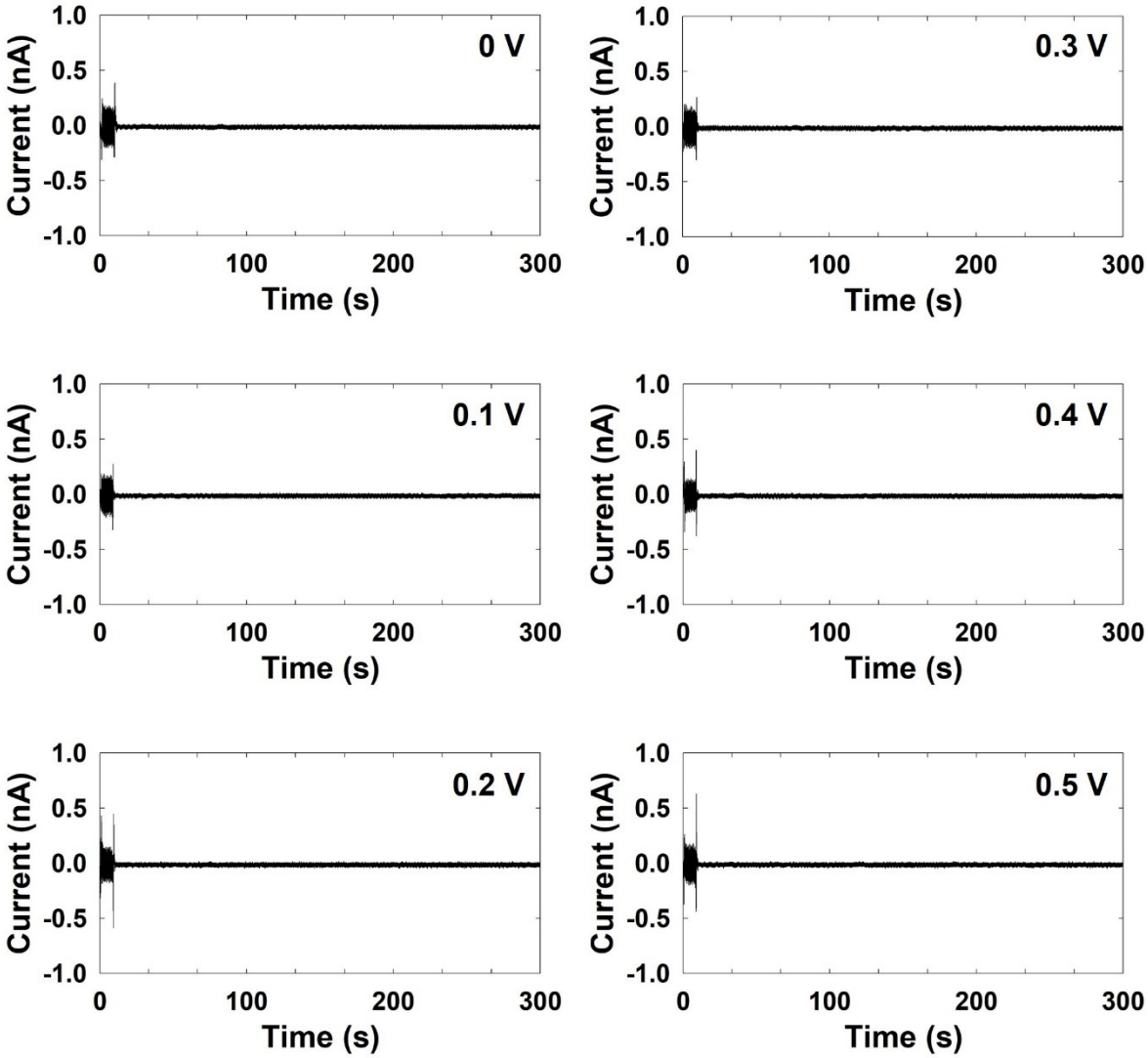

Figure S3. Chronoamperometric results at the various potentials applied Au UME in 50 mM PB (pH 7.0) solution without hydrazine. Concentration of Pt NP was 33 fM. The applied potentials were from 0.0 V to 0.5 V. The data sampling time was 1 ms.

Chronoamperometry results when 0 fM Pt NP in electrochemical cell

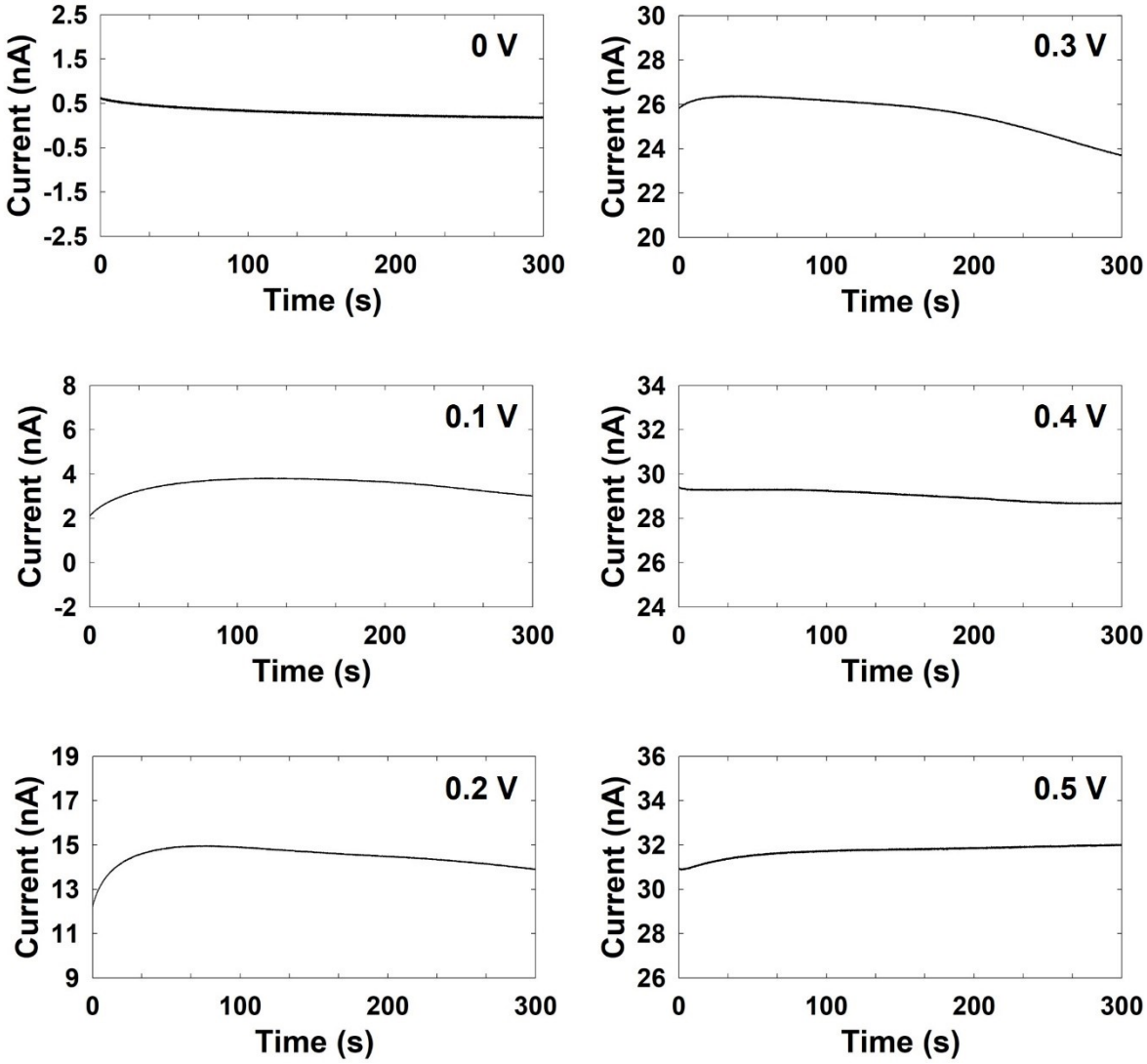

Figure S4. Chronoamperometric results at the various potentials applied Au UME in 50 mM PB (pH 7.0) solution containing 5 mM hydrazine without Pt NP. The applied potentials were from 0.0 V to 0.5 V. The data sampling time was 1 ms.

Investigation for Single-entity electrochemistry of Pt NP when using C fiber UME in hydrazine-hydrazinium equilibrium

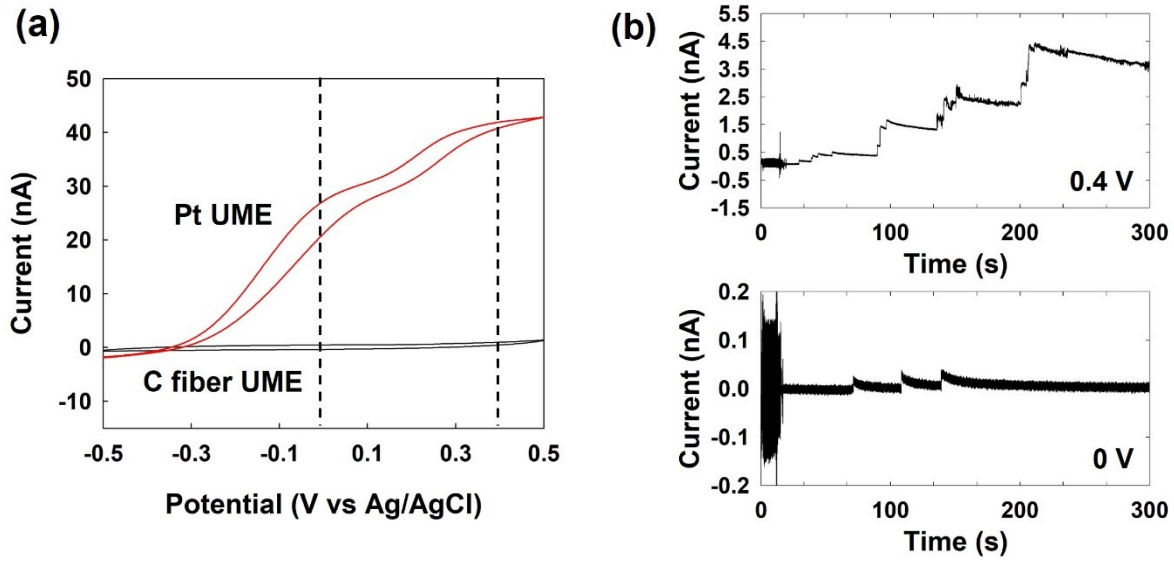

Figure S5. (a) CVs for C fiber (5.5 μm of radius, black) and Pt (5 μm of radius, red) UMEs in 50 mM PB (pH 7.0) solution containing 5 mM hydrazine. The scan rate was 50 mV/s. (b) Chronoamperograms obtained depending on applied potential onto C fiber UME with 33 fM of Pt NP. The electrochemical cell was 50 mM PB (pH 7.0) containing 5 mM hydrazine. The data sampling time was 1 ms.

Investigation for Single-entity electrochemistry of Pt NP when using C fiber UME in pH 6 to 8.

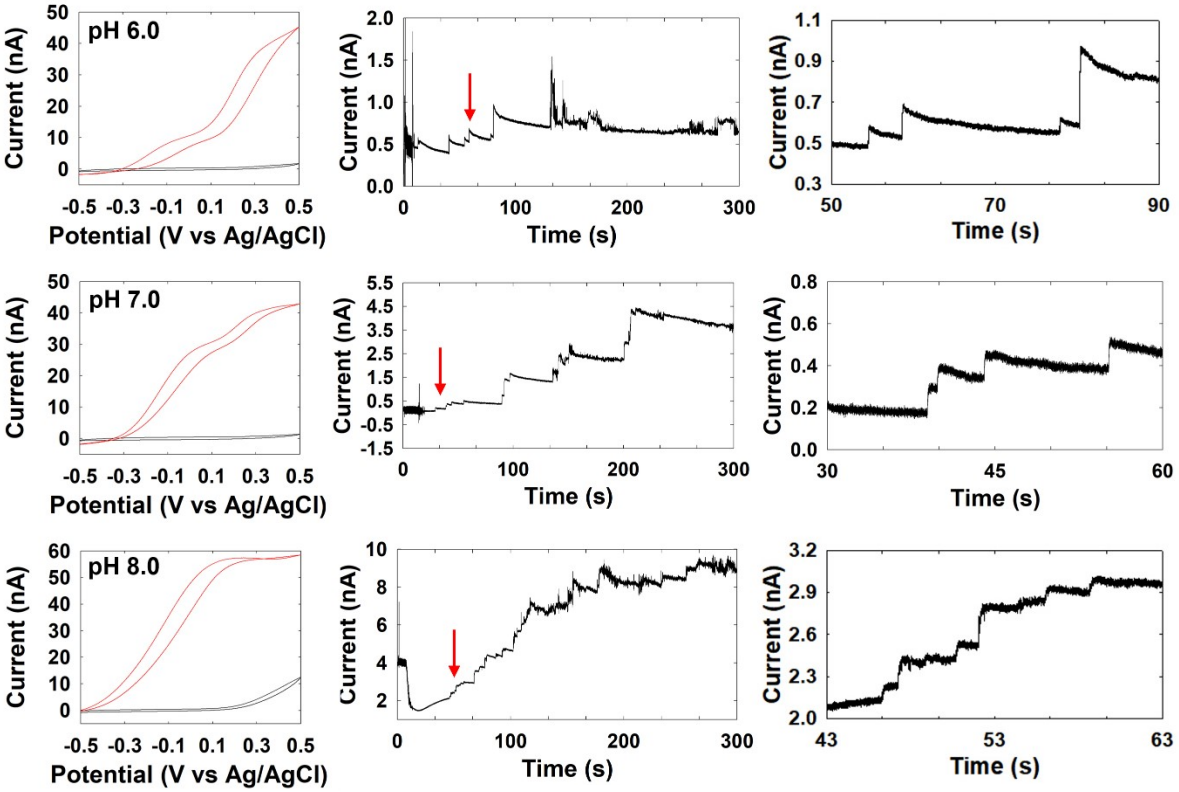

Figure S6. CVs of hydrazine oxidation in the C fiber (black) and Pt UME (red) in 50 mM buffer solution containing 5 mM hydrazine. Next, CA results obtained by SEE of Pt NP at the Au UME in 50 mM PB (pH 6 to 8) solution containing 5 mM hydrazine and 33 fM of Pt NP. The data sampling time was 1 ms. The applied potential of Au UME was 0.4 V.

Investigation for Single-entity electrochemistry of Pt NP in the potential window I at pH 9 and 10.

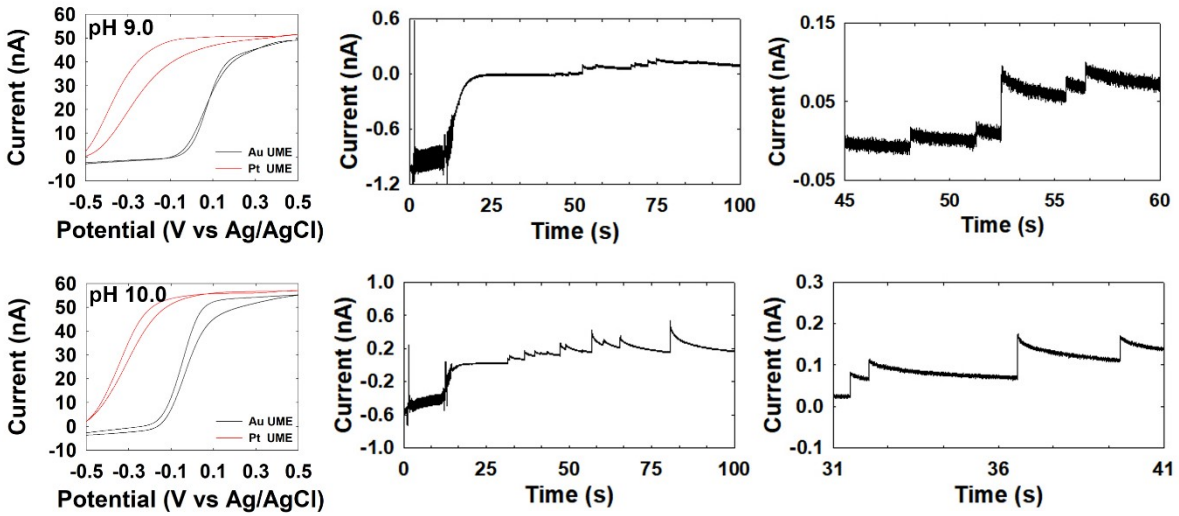

Figure S7. CVs of hydrazine oxidation in the Au (black) and Pt UME (red) in 50 mM buffer solution containing 5 mM hydrazine. Next, CA results obtained by SEE of Pt NP at the Au UME in 50 mM BB (pH 9 and 10) solution containing 5 mM hydrazine and 33 fM of Pt NP. The data sampling time was 1 ms. The applied potential of Au UME was -0.3 V.

Investigation of hydrogen evolution reaction (HER) Interference.

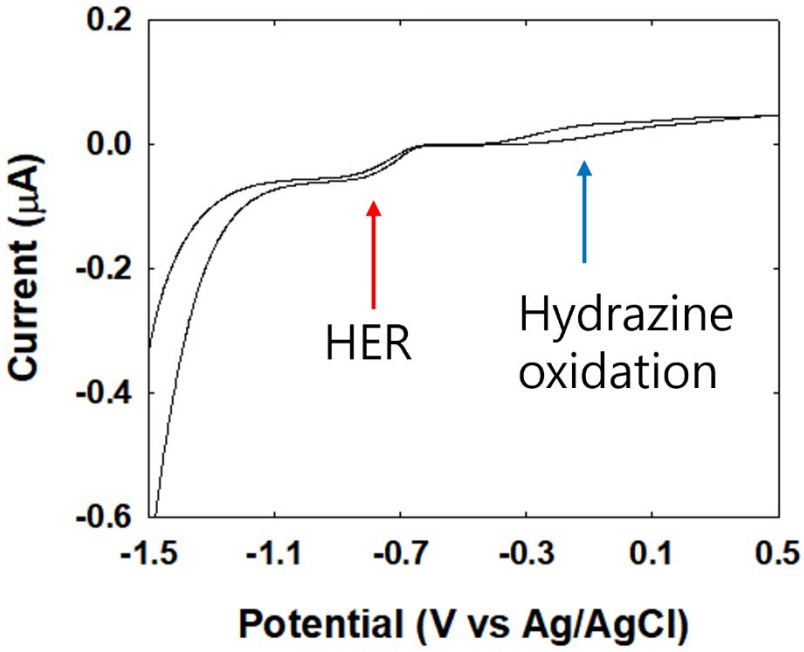

Figure S8. CVs of hydrazine oxidation and HER in the Au UME in 50 mM buffer solution containing 5 mM hydrazine.