Electronic Supplementary Material (ESI) for Chemical Science.

Revisiting a classical redox process on a gold electrode by operando ToF-SIMS: where does the gold go?

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Contents:

S-1 Experimental part:

S-1.1 Chemicals and instruments.

$K_3Fe(CN)_6$ and KCl of analytically pure were purchased from Sigma-Aldrich (Shanghai, China). Polydimethylsiloxane (PDMS) for microfluidic EC cell fabrication was obtained from Dow Corning Corporation (Shanghai, China). Ultrapure water (18 MΩ·cm) from Millipore system was used in the preparation of all solutions.

ToF-SIMS measurement was performed using a ToF-SIMS V spectrometer (IONTOF GmbH, Germany). A 30 keV Bi_3^+ primary ion beam was used in all measurements. Target current was ca. 0.32 pA. Primary ion beam size was optimized to ca. 250 nm. To compensate accumulated charge on sample surface, a low energy electron flood gun was used. Mass spectra in negative mode was calibrated to O^-, OH^-, Au^- and Au_3^-.

S-1.2 Fabrication of the microfluidic EC cell.

The vacuum compatible microfluidic EC cell was fabricated as following: the three electrodes were sputter coated onto the SiN wafer. An SU-8 photoresist silicon mold was used to form PDMS micro-cell. The SiN wafer and PDMS cell were irreversibly bonded via air plasma pretreatment. An inlet and outlet were drilled through the PDMS block to inject solution into the micro-cell. After being filled with the solution, the whole cell was sealed and mounted onto a customized ToF-SIMS sample holder for subsequent ToF-SIMS measurements.

S-2 Supplementary figures.

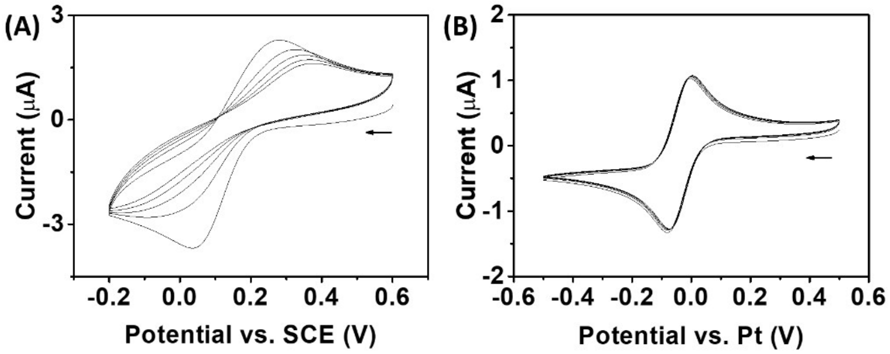

Fig. S-1. Cyclic voltammetry of 1 mM $K_3Fe(CN)_6$ with 1 mM KCl solution in (A) a beaker using bulk electrodes (WE: Au; CE: Pt; RE: SCE) and (B) a micro-EC cell using micro electrodes (WE: Au; CE: Pt; RE: Pt). Scan rate = 100 mV/s.

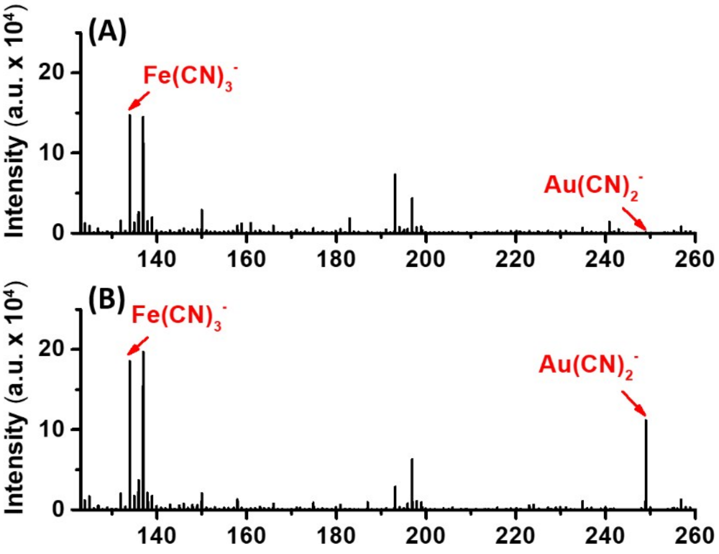

Fig. S-2. Negative mass spectra of the electrolyte taken out of the EC cell before (A) and after (B) CV measurement (100 scans). The electrolyte contains 1 mM $K_3Fe(CN)_6$ and 1 mM KCl. Scan range was from 0.8 V to -0.1 V (vs. NHE). Scan rate = 50 mV/s.

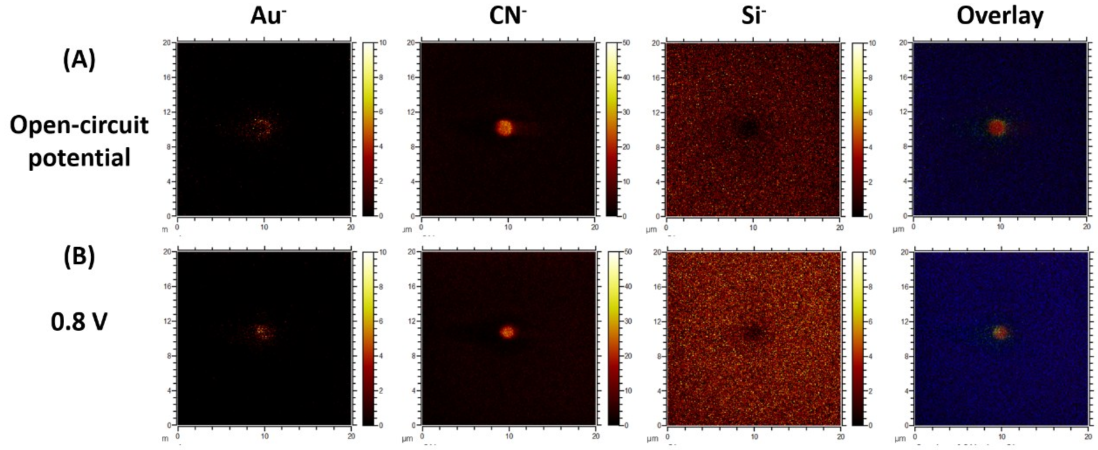

Fig. S-3. Chemical mapping images of Au^-, CN^-, Si^- and the overlay of Au^- (green), CN^- (red), Si^- (blue) at the electrode-electrolyte interface under (A) open-circuit potential; (B) 0.8 V (vs. NHE). Analysis area for each image was 20×20 μm².

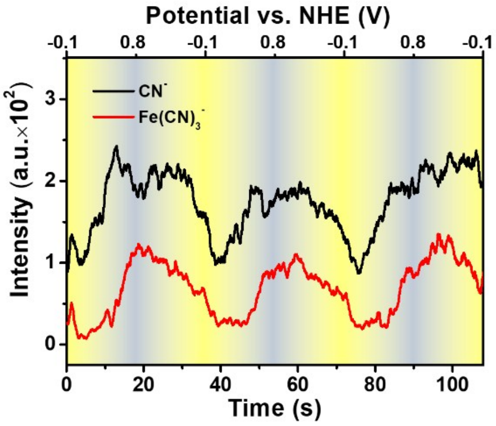

Fig. S-4. Potential-resolved variations of CN^- and $Fe(CN)_3^-$ at the electrode-electrolyte interface in the solution of 1 mM $K_3Fe(CN)_6$ with 1 mM KCl. Scan rate in the measurement was 50 mV/s. Three cycles were conducted in the measurement.