

Supporting Information for: Electrochemistry of Single Droplets of Inverse (Water in Oil) Emulsions

Haozhi Zhang¹, Lior Sepunaru¹, Stanislav V. Sokolov¹, Eduardo Laborda², Christopher Batchelor-McAuley¹,

Richard G. Compton¹ (✉)

¹ Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

² Departamento de Química Física, Facultad de Química, Universidad de Murcia, 30100 Murcia, Spain

Experimental

The chemicals used in the experiments were $K_4Fe(CN)_6$ (99%, BDH, Poole, UK), Cyclohexane (99.8%, Honeywell Chemicals), $TBA^+ ClO_4^-$, $TBA^+ BF_4^-$, $TBA^+ PF_6^-$, $TBA^+ CF_3SO_3^-$ (99%, Fluka), $TBA^+[FAP]^-$ (98%+, Merck), $[C_{16}mim]^+[NTf_2]^-$ (97%+, Queens), $K_3Fe(CN)_6$, Dichloromethane, Span 80 (99.8%+, Sigma-Aldrich). All aqueous solutions were prepared with deionized Milli-Q water.

The w/o emulsions were prepared by constant injecting a total of 1 mL of 0.50 M aqueous solution over 20 min into a mixture of 2 mL cyclohexane, 2 mL dichloromethane and 50 μ L (1%) of span 80 while stirring at room temperature. The solution was left stirred for 4 hrs before electrochemical measurement to allow the emulsions to stabilize. For the electrochemical measurement, the stock emulsions were diluted (x20) with 0.10 M of electrolyte solution in 1:1 Cyclohexane: Dichloromethane.

A 7 μ m diameter carbon fibre microdisk electrode (Goodfellow, Cambridge, UK) was used as the working electrode, the electrode was polished with 1.0 μ m, 0.3 μ m, and 0.05 μ m aluminium oxide (Buehler Ltd., USA) slurries on a Buehler polishing pad prior to each measurement. Electrochemical measurements were performed with an in-house built low noise potentiostat^[1] with a 3-electrode set-up housed inside a Faraday cage, with a silver wire pseudo-reference electrode and platinum wire counter electrode. The cyclic voltammograms were measured at a scan rate of 10 mV s⁻¹, unless stated otherwise.

The dark field imaging was done using a Zeiss Axio Examiner A1 microscope using a $\times 20$ air objective (NA = 0.5, EC Plan-Neofluar). Image acquisition was provided by a Hamamatsu ORCA-Flash 4.0 Digital CMOS camera (Hamamatsu, Japan). Camera exposure control and most image analysis was provided by the software Zen 2 (blue edition, Carl Zeiss Ltd., Cambridge U.K.) The solution was x 20 diluted and injected into a home-made sandwiched structure cell using a clean microscopic slide for dark field imaging." (For further explanation on the cell design, the reader is referred to ref [2].

DLS measurements were performed using an ALV/CGS-3 Compact Goniometer operating at an angle of 25 degrees. The software used to analyse the collected data was the ALV-Correlator. 2 ml of each x20 diluted sample was transferred to microcuvettes with a specified path length of 10 mm. The measurements were made under thermostated conditions at 25 °C. For each sample, 10 runs of 30 s were performed, with 10 repeats. The intensity size distribution was obtained from the autocorrelation function using the general purpose mode.

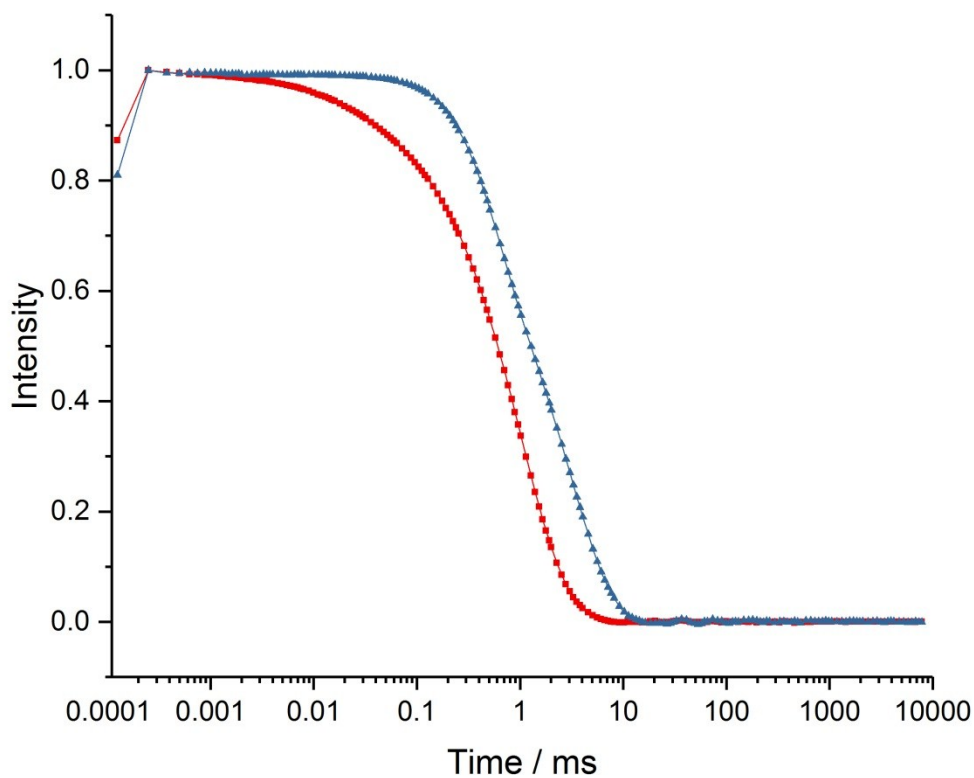


Fig. S1.a DLS Correlation function. (a) 25nm radius silver nanoparticle (red) used for calibration and (b) 269 nm ferrocyanide W/O emulsion (blue).

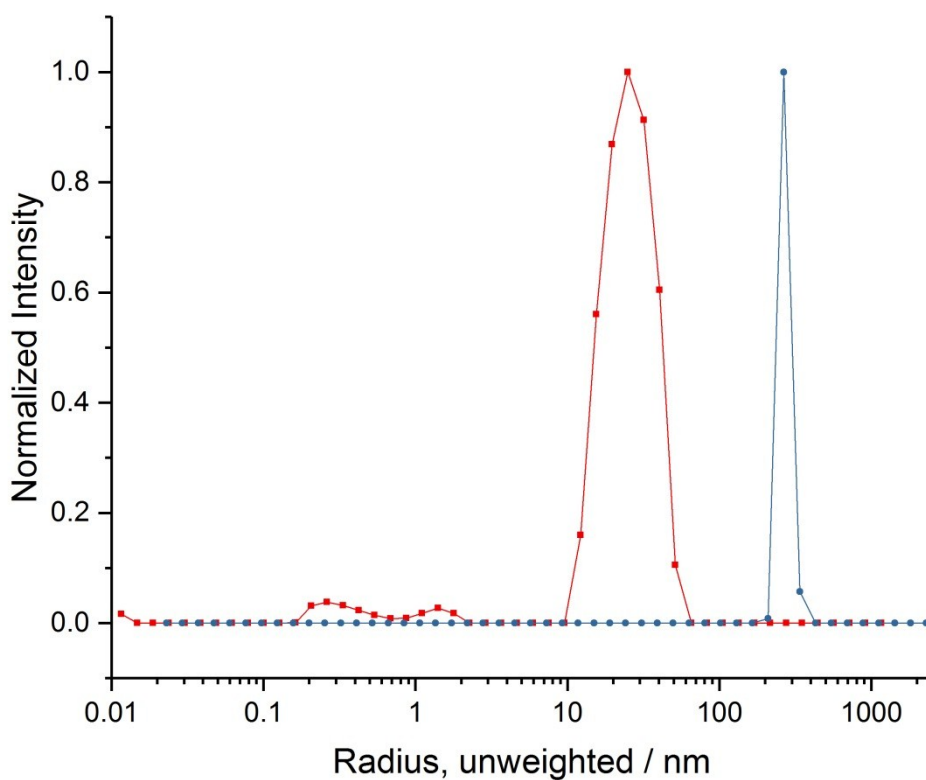


Fig. S1.b DLS radius distribution. (a) 25nm radius silver nanoparticle (red) used for calibration and (b) 269nm ferrocyanide W/O emulsion (blue).

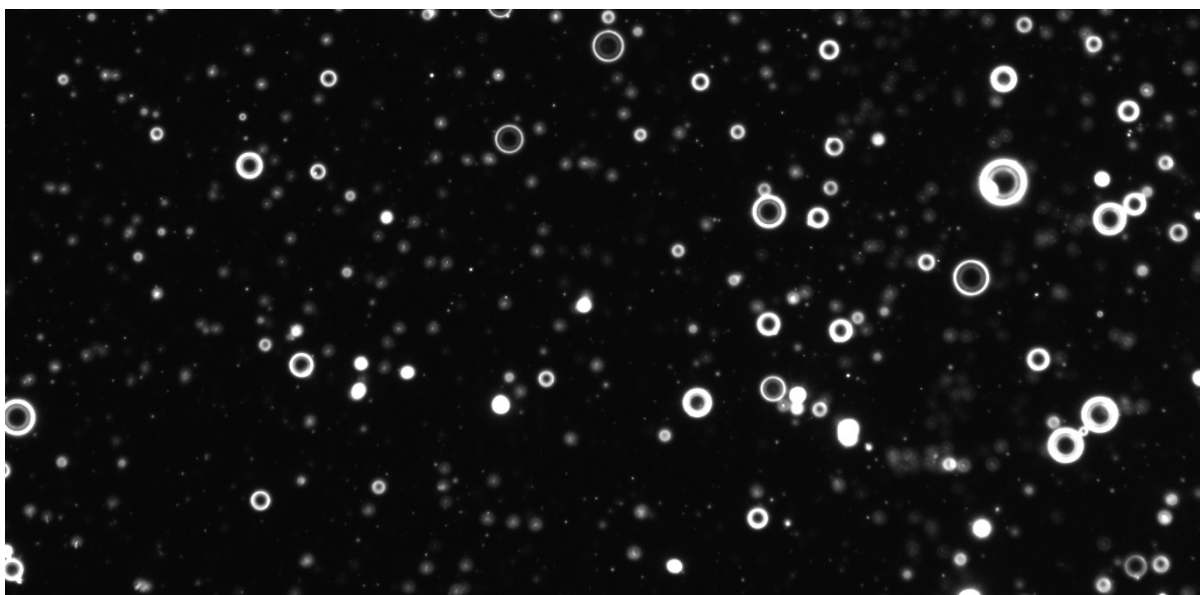


Fig. S1.c Dark field image of x200 magnification

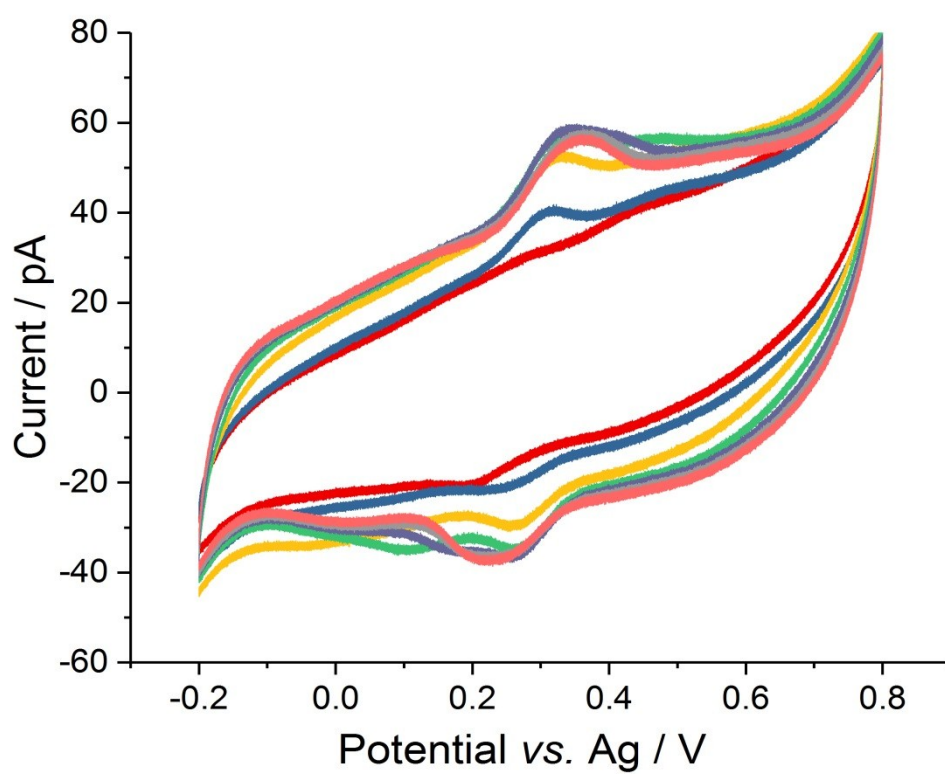


Fig. S2a Cyclic voltammetry of $K_4Fe(CN)_6$ W/O emulsion oxidation in 0.1 M $[C_{16mim}]^+ [NTf_2]^-$ cyclohexene/dichloromethane solution over 30 min with 5 min intervals.

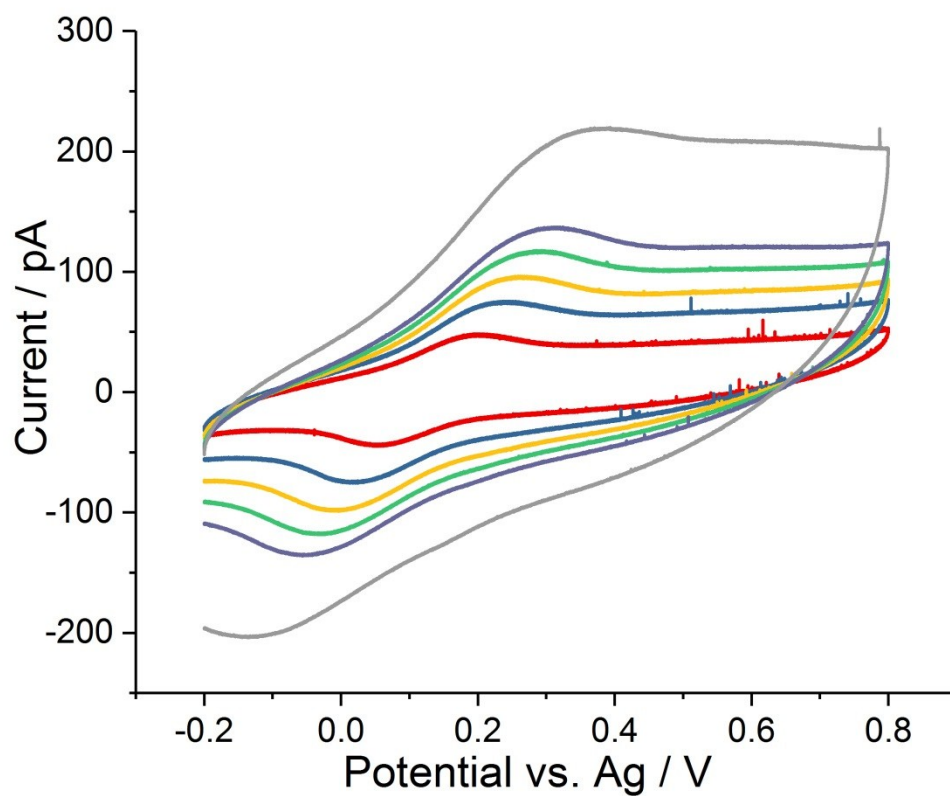


Fig. S2b Cyclic voltammetry of $\text{K}_4\text{Fe}(\text{CN})_6$ W/O emulsion oxidation in 0.1M $\text{TBA}^+\text{ClO}_4^-$ cyclohexene/dichloromethane solution at various scan rates, 10 mV s^{-1} (red), 20 mV s^{-1} (blue), 30 mV s^{-1} (yellow), 40 mV s^{-1} (green), 50 mV s^{-1} (purple), 100 mV s^{-1} (grey)

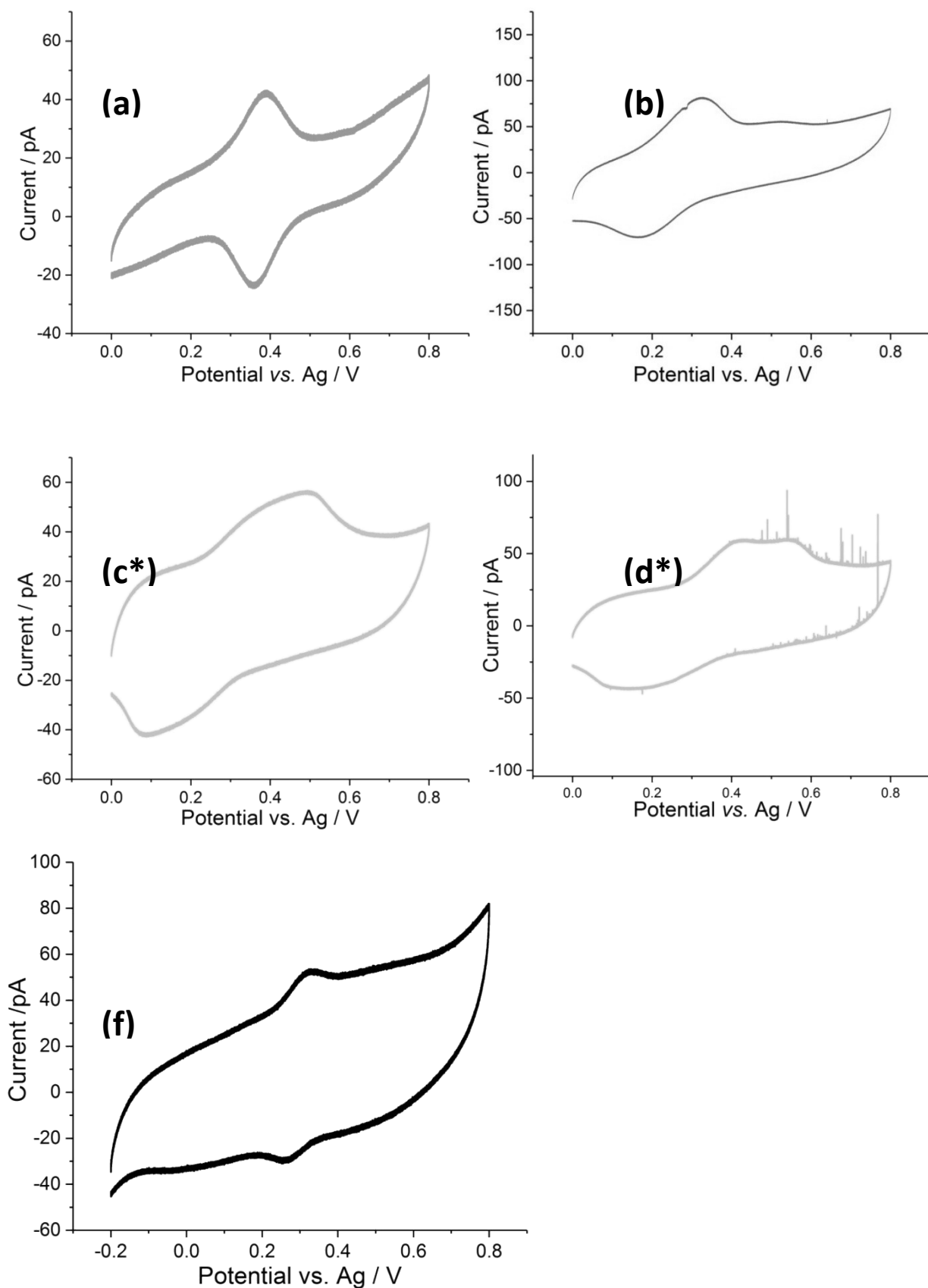


Fig. S3 Cyclic voltammetry of 0.5 M $K_4Fe(CN)_6$ W/O emulsion oxidation in a cyclohexene/dichloromethane solution containing different electrolytes at 10 mV s^{-1} scan rate. (a) 0.1 M $TBA^+PF_6^-$, (b) 0.1 M $TBA^+CF_3SO_3^-$, (c) 0.1 M $TBA^+[FAP]^-$, (d) 0.1 M $TBA^+BF_4^-$, (e) $[C_{16mim}]^+[NTf_2]^-$. The slow oxidation processes likely occur due to either small electrolyte contamination in the oil phase and/or potassium diffusion from the water to the oil phase.* The two peaks observe may reflect both ion insertion and desertion processes during the slow scan.

‘Lower limit’ estimation of the droplets size from ‘nano-impacts’ experiments:

Assuming a spherical droplet and 100% oxidation of the droplet content, the mean radius of the water droplets were determined using the following equation:

$$Q = \frac{4\pi r^3}{3} \times N_A [C] e^-$$

where Q is the coulombic charge of the spike, r is the radius of the emulsion, N_A is the Avogadro number [C] is the concentration of potassium ferrocyanide in the emulsion [mol/ m³] and e^- is the elementary charge. After rearranging the equation, the droplet radius associated with each spike can be determined from:

$$\left(Q \times \frac{3}{4\pi N_A [C] e^-} \right)^{1/3} = r$$

It is worth noting, that here the radius is extracted from the observed charge injection during single droplet collision. However, in the case of partial oxidation (not 100 % of the charge is injected) the calculated radius will reflect the lower limit of the droplet radius.

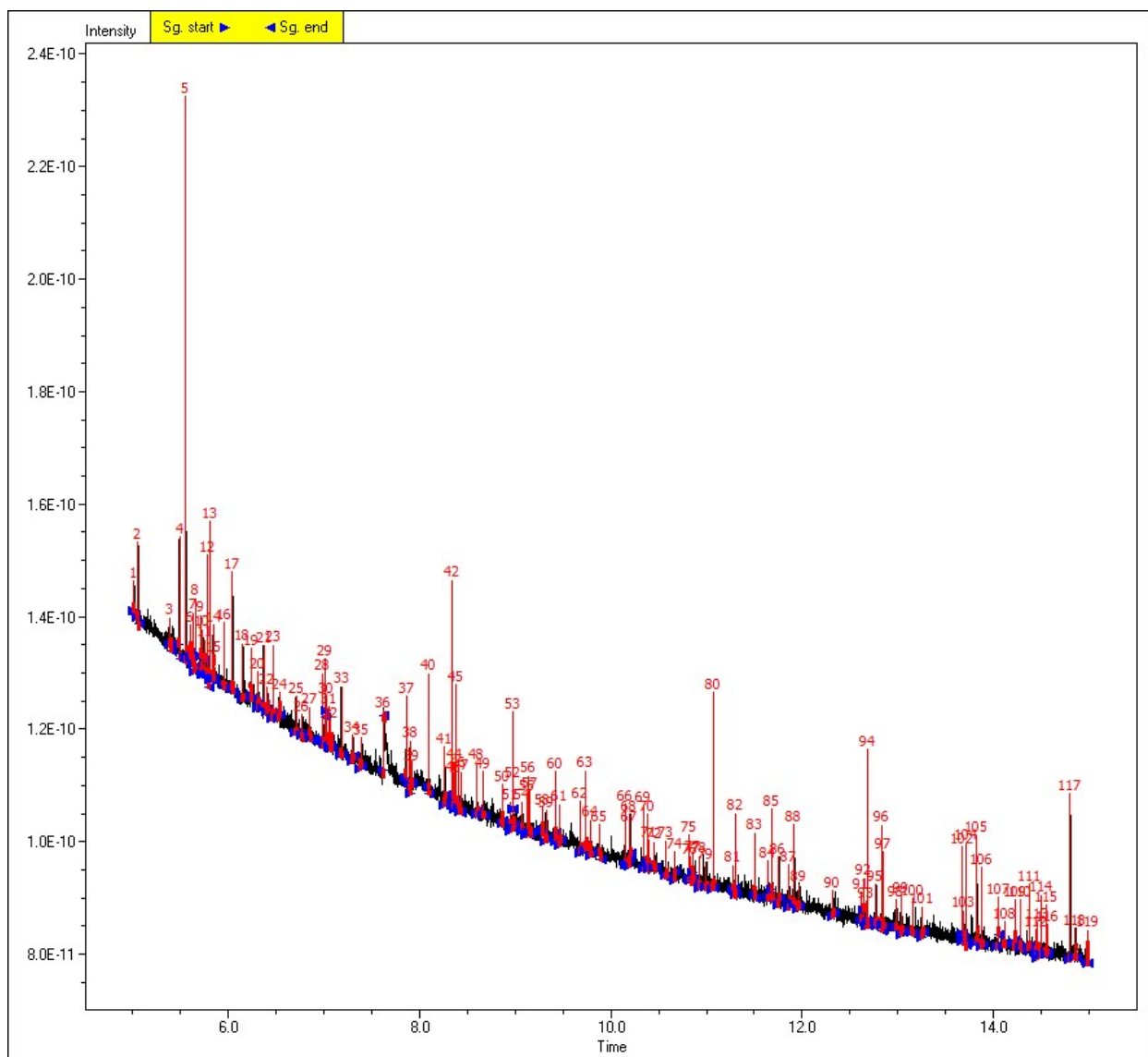


Fig. S4 Representative chronoamperometric measurement of 0.5 M $K_4Fe(CN)_6$ emulsion oxidation with 0.1 M $TBA^+ClO_4^-$ in the oil phase at 0.8 V vs Ag. The 119 spikes shown during 10 s interval were detected using SignalCounter software, developed by Dario Omanovic–(Centre for Marine and Environmental Research, Ruder Boskovic Institute, Croatia).^[3]

Reference

- [1] C. Batchelor-McAuley, J. Ellison, K. Tschulik, P. L. Hurst, R. Boldt, R. G. Compton, *Analyst* **2015**, *140*, 5048–5054.
- [2] C. Batchelor-McAuley, C. Little, S.V. Sokolov, E. Kätelhön, G. Zampardi, R.G Compton, *Analytical Chemistry*, **2016**, *88*, 11213-11221.
- [3] J. Ellison, K. Tschulik, E. J. E. Stuart, K. Jurkschat, D. Omanović, M. Uhlemann, A. Crossley, R. G. Compton, *ChemistryOpen* **2013**, *2*, 69–75.