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Temporal Behavior of the Individual Soft Microparticles: Understanding the Detection by Particle Impact Electrochemistry

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Temporal Behavior of the Individual Soft Microparticles: Understanding the Detection by Particle Impact Electrochemistry

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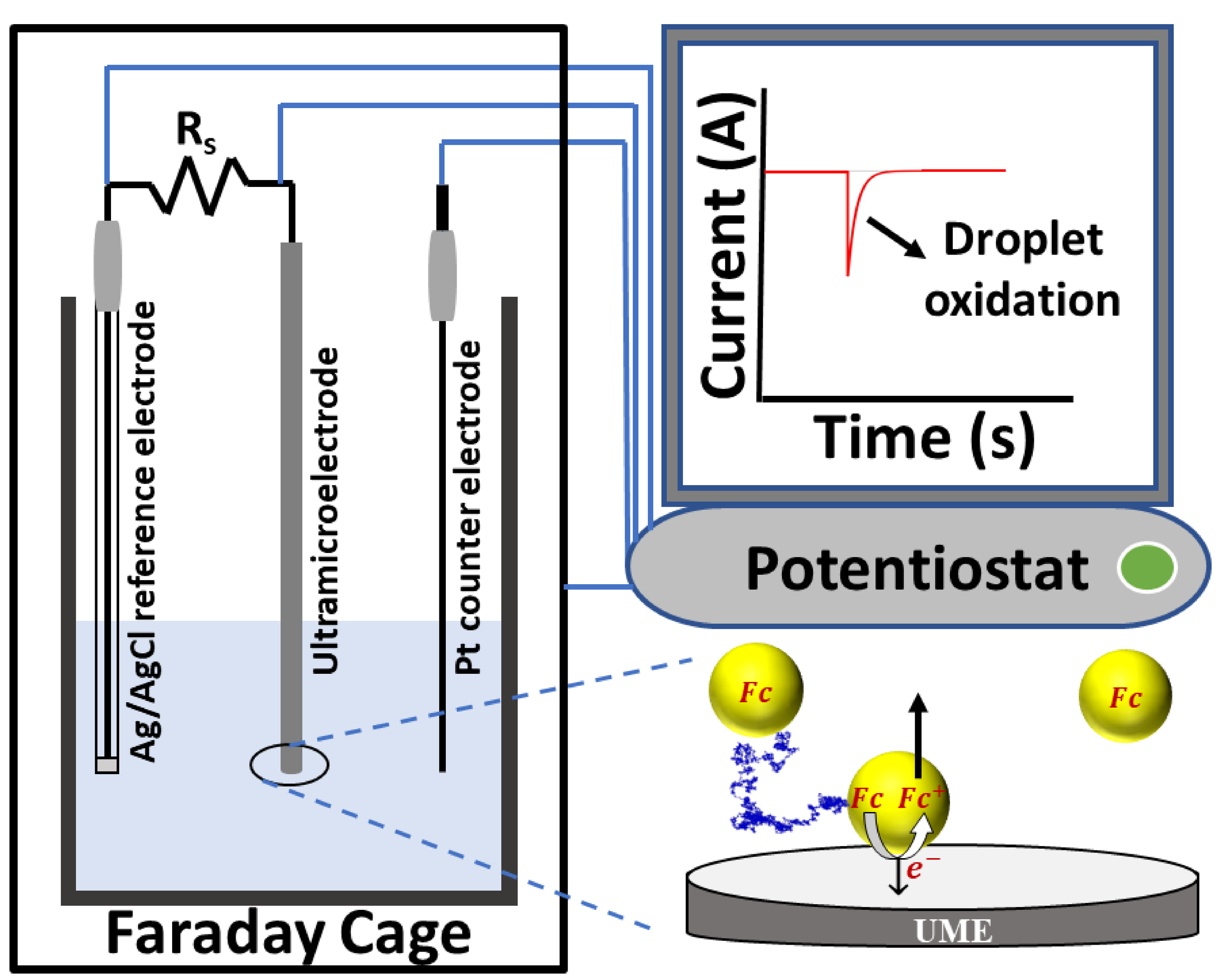
Abstract : Droplets loaded with ferrocene (Fc) were analyzed by the Particle Impact Electrochemistry (PIE) technique using a Carbon Ultramicroelectrode (UME). The technique successfully characterized the size and polydispersity of the emulsion droplets. A 3D Random walk lattice simulation with MATLAB was used to model for the random motion and collision dynamics of the droplets. The simulation indicated the stochastic nature of the droplet motion. The smaller droplets are faster compared to the larger droplets. Unlike nanoparticles, the droplet collision associated with adsorption on the surface of the electrode generating a similar spike-like current response to real-time experiments.

Introduction

- PIE detects the electrochemical current changes upon collisions of individual micro or nanoparticles at the UME surface .[1]
- This technique is a rapid, low cost, and analyze one analyte at a time.[1-4]
- Quantitative information on the collision and adsorption dynamics of the soft-microparticles (absence of crystalline structure) will enable the PIE to characterize them. [3,5]

Hypothesis

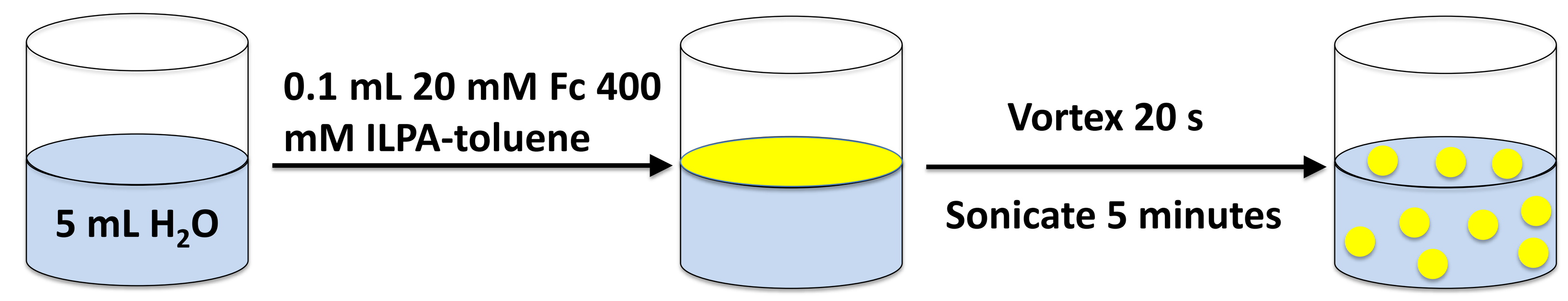
- Emulsion droplets (Soft Microparticles) loaded with redox species will react electrochemically on the surface of the disk UMEs.
- The collisional behavior of the droplets with UMEs can be investigated by random walk simulation.



Methods:

Preparation of 20 mM Fc-toluene-in-water emulsion ⇨ Characterize the emulsion by PIE technique ⇨ Investigate collision dynamics by random walk model. ⇨ Simulate the current

Preparation and stability of emulsion



ILPA = Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide

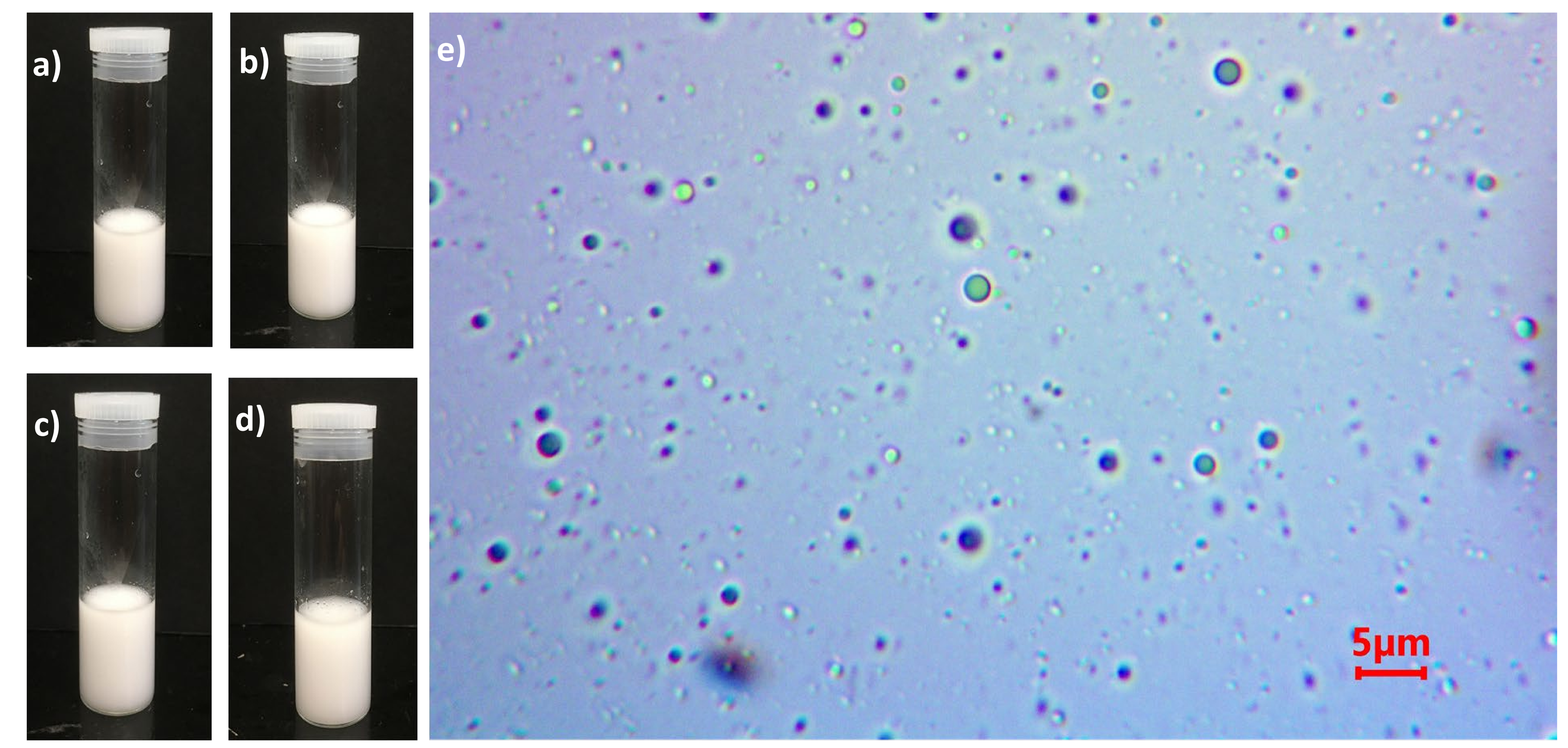


Figure: Toluene in water emulsion. (A) Emulsion after 5 minutes. (B) Emulsion after 1 hour. (C) Emulsion after 2 hours. (D) Emulsion after 5 hours. (E) Microscopic image of emulsion

Inhouse made UME

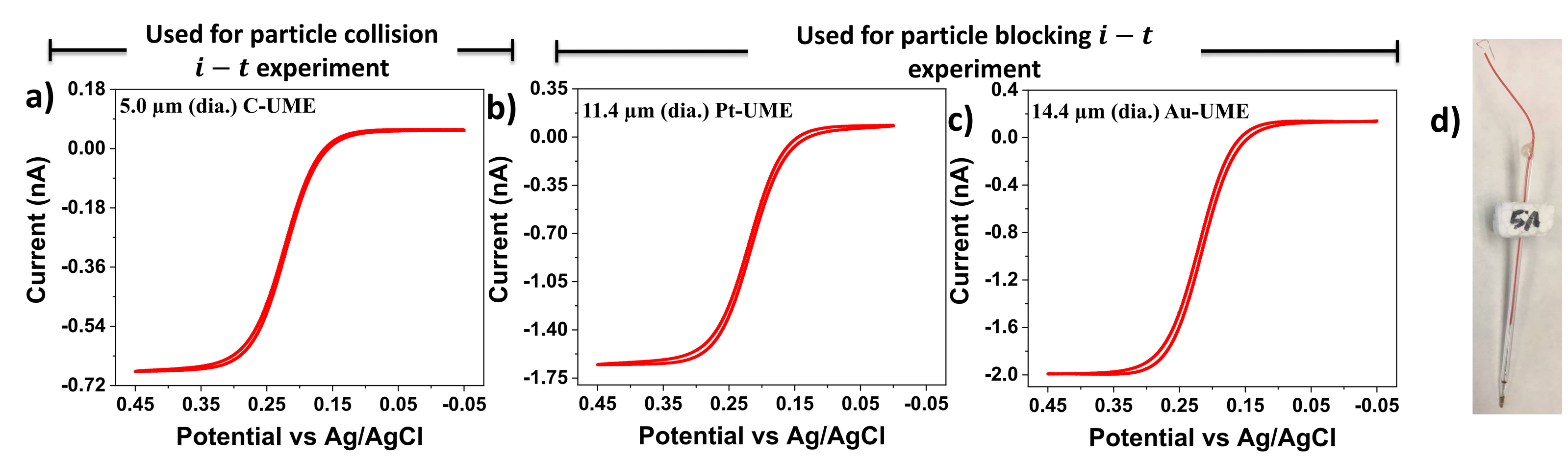


Figure: (A),(B),(C) Cyclic voltammograms of inhouse made disk UMEs for 1 mM Ferrocenemethanol and 0.1 M KCl aqueous solution at a scan rate of 10 mV/s. (D) Inhouse made UME

Characterization of emulsion by PIE

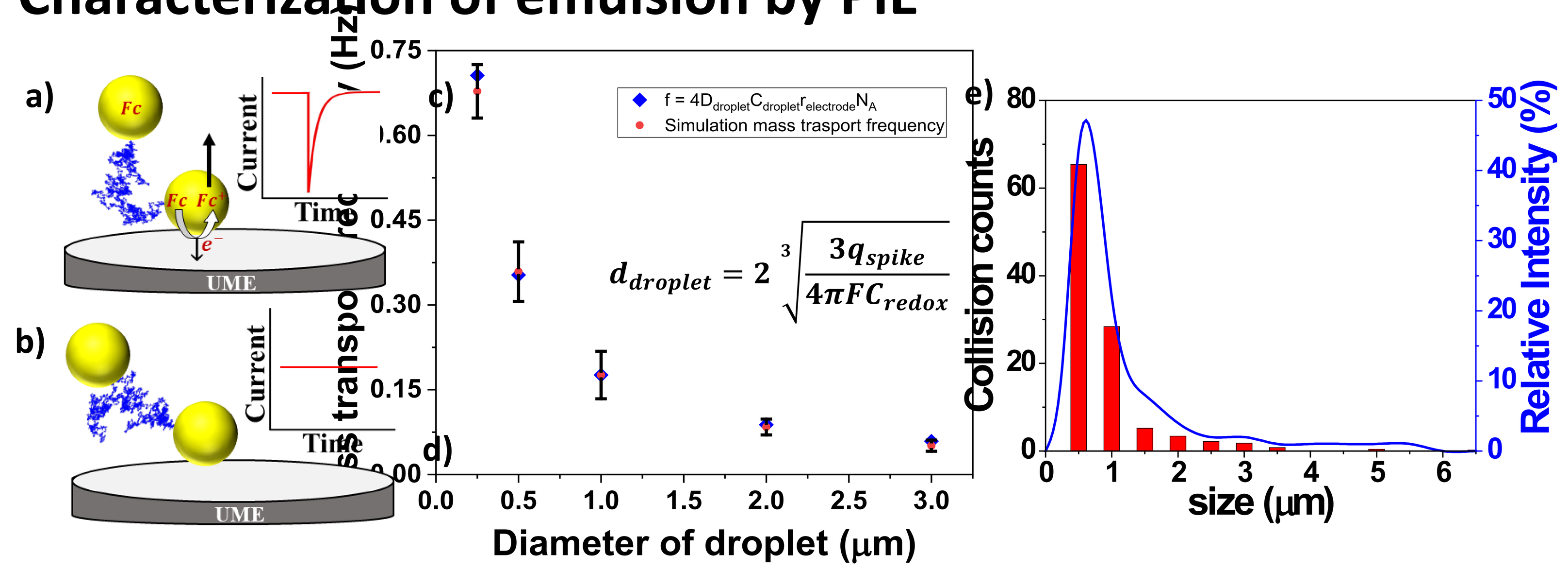


Figure: Schematic diagram of Amperometric $i-t$ curve (A) 20 mM Fc-toluene droplet, (B) Empty droplet. Experimental Amperometric $i-t$ curve for toluene in water emulsions with 50 pM emulsions with a 5.0 μm (diameter) C-UME at a potential +0.7V vs Ag/AgCl (C) 20 Mm Fc-toluene droplet, (D) Empty droplet. (E) Comparison of droplet size distributions obtained by PIE technique (Red bar) and Dynamic Light Scattering (blue line) data.

	Average size (PIE) (μm)	Average size (DLS) (μm)	Average charge per droplet (pC)	Average current per droplet (pA)	Observed frequency (Hz)	Theoretical frequency (Hz)
20 mM Fc-emulsion	0.7 ± 0.1	1.0 ± 0.2	1.4 ± 0.5	−1.2 ± 0.3	0.11 ± 0.01	0.15

Droplet diffusion over migration

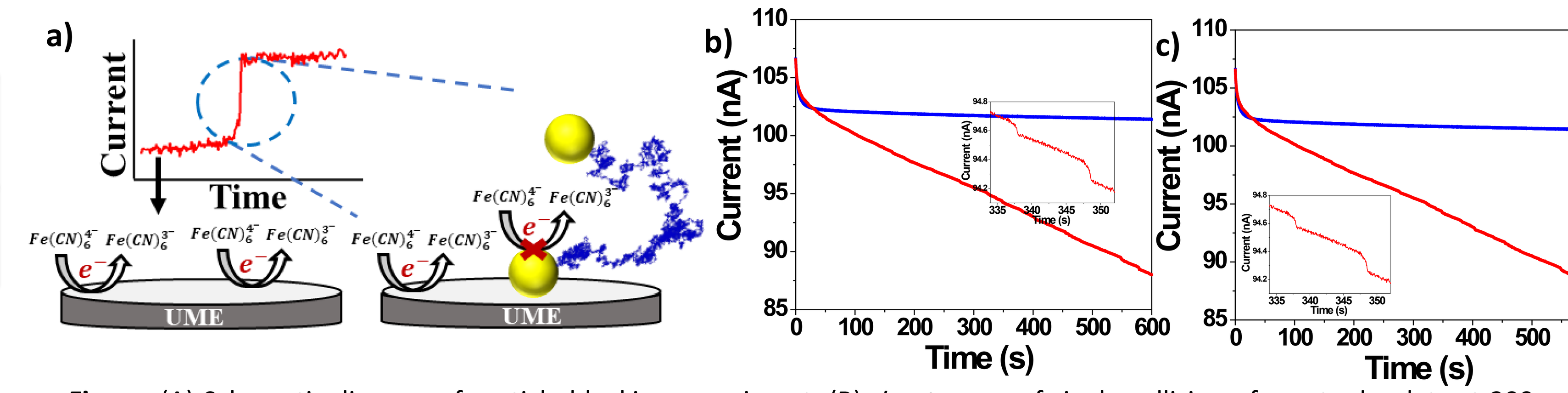


Figure: (A) Schematic diagram of particle blocking experiment. (B) $i-t$ curve of single collision of empty droplets at 200 mM $K_4Fe(CN)_6$ and 100 mM KCl aqueous solution with a 11.4 μm (dia.) Pt-UME biased at +0.4 V vs Ag/AgCl. (C) $i-t$ curve of single collision of empty droplets at 40 mM $Ru(NH_3)_6Cl_3$ and 100 mM KCl aqueous solution with a 14.4 μm (dia.) Au-UME biased at -0.4 V vs Ag/AgCl. Concentration of droplets is 1.5 pM. Staircase current decrease (Red line) and control experiment (Blue line).

3D random walk simulation

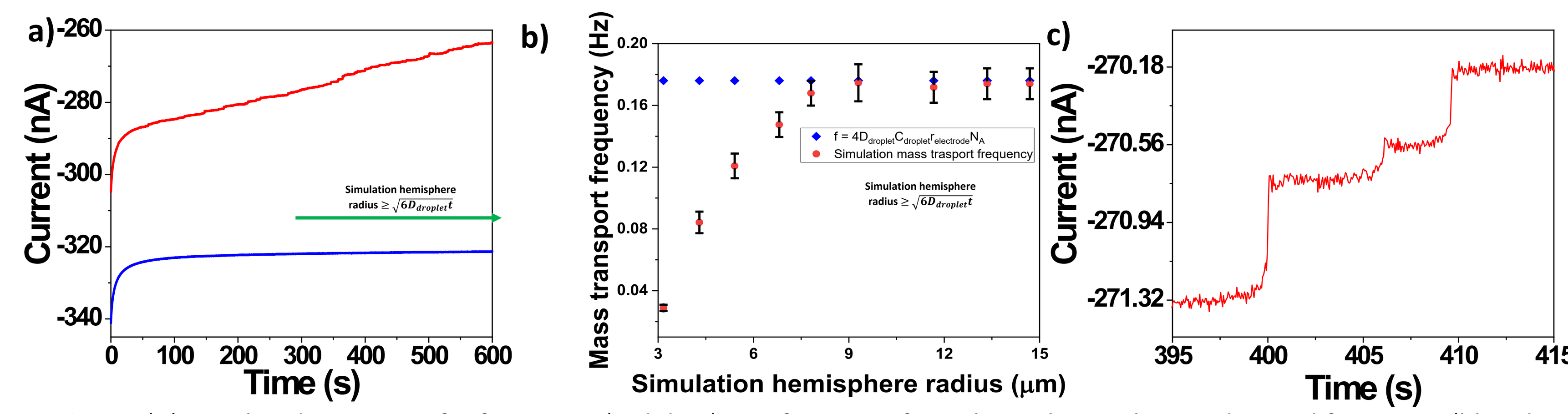


Figure: (A) Simulated mass transfer frequency (red dots) as a function of simulation hemisphere radius and frequency (blue dots) for infinite boundary for 20 seconds simulation runtime of a 1.0 μm (diameter) droplet. (B) Simulated mass transfer frequency (red dots) and theoretical mass transfer frequency (blue dots) as a function of droplet diameter at different simulation runtimes. Droplet concentration 50 pM, diameter of UME 6 μm. (C) Collisional (simulation) and mass transfer frequency (simulation) of droplets with a 6 μm diameter of electrode as a function of ratio of droplet and electrode diameter.

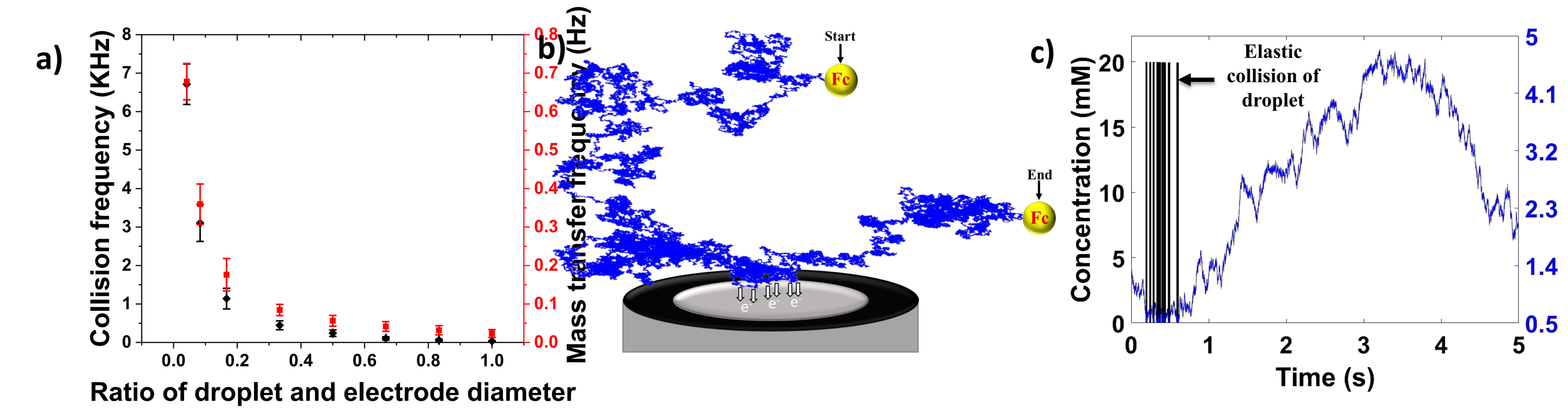


Figure: (A) Effective contact radius of the Fc-loaded emulsion droplet as a function of droplet diameter during the amperometric $i-t$ curve (PIE) experiment. (B) Simulated 5 seconds 3D random walk of a 1.0 μm (diameter) droplet with a 6.0 μm (diameter) of electrode. (C) Change of concentration resulting of multiple collision of the 1.0 μm (diameter) 20 mM Fc toluene droplet with a 6.0 μm (diameter) of electrode (Black) and z-axis profile of droplet motion (Blue).

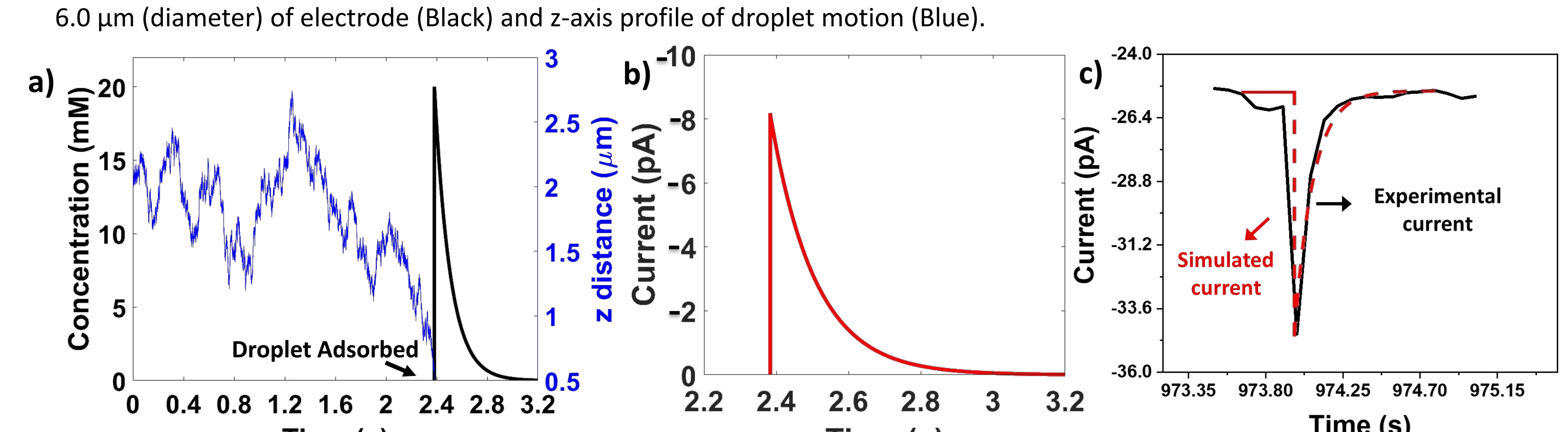


Figure: (A)) Change of concentration resulting of adsorption of the 1.0 μm (diameter) 20 mM Fc toluene droplet on a 6.0 μm (diameter) of electrode (Black) and z-axis profile of droplet motion (Blue). (B) Oxidation current of 1.0 μm (diameter) 20 mM Fc toluene droplet adsorbed on the surface of electrode. (C) Comparison of experimental and simulated current of a 1.0 μm (diameter) 20 mM Fc toluene droplet.

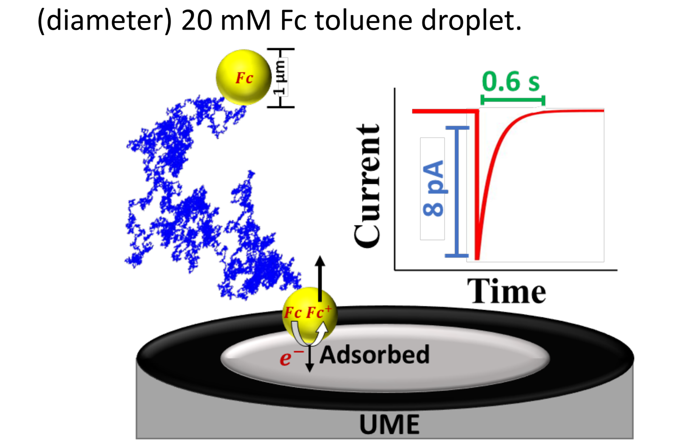


Figure: Simulated 3D random walk of the 1.0 um 20mM Fc toluene droplet on a 6.0 um electrode with irreversible adsorption on the electrode surface. (Inset) Simulated current of the droplet.

Conclusion

- PIE technique successfully detected the polydisperse 20 mM Fc emulsion droplets.
- The droplets:
  - ❖ have stochastic motion in the solution.
  - ❖ undergo irreversible adsorption on the surface of electrode.
  - ❖ oxidize following the bulk electrolysis model.

Reference:

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