Supporting Information

Millisecond Coulometry via Zeptoliter Droplet Collisions on an Ultramicroelectrode

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It is noteworthy to discuss the use of electrochemical collisions in determining the concentration of a colloidal suspension. The frequency at which nanoparticles collide with the electrode surface, assuming mass transport to the electrode is controlled only by diffusion, is given by

$$f^{dif} = 4DCr_{elec}N_A \qquad \text{Eq. 1}$$

where D is the diffusion coefficient, estimated by the Stokes-Einstein relationship, C is the concentration of nanoparticles, r_{elec} is the radius of the electrode, and N_A is Avagadro's number. This equation can give insight into the concentration of a colloidal suspension, which is necessary after filtration of the droplets. Common concentrations found using this technique were between 0.1 and 7 pM. The assumption that mass transport is controlled mainly by diffusion is likely valid due to the fact that little or no faradaic current is flowing at the electrode surface for reactor-type collision experiments.

Solubility of species from SciFinder:

Species	**Solubility in Water (pH 7, mol/L)**
Fc	Insoluble
TTF	Sparingly (2.7e-5)
TPrA	Soluble (6.98)
DPH	Sparingly (1.3e–3)

Ferrocene

Experiment	ne^-	Std. Dev. (%)	DLS Std. Dev. (%)
1	0.89	27	22
2	0.91	21	22
3	0.93	13	15
4	0.98	16	15
5	0.94	21	20
6	1.1	23	20
7	0.97	21	24

TTF

Experiment	E_{appl} (V)	ne^-	Std. Dev. (%)	Mechanism
1	0.4	0.87	20	E
2	0.5	0.93	15	E
3	0.95	1.94	18	EE
4	1	1.89	17	EE
5	0.5	0.92	22	E
6	0.5	0.95	18	E
7	1	1.93	20	EE
8	1	1.89	20	EE

Aliphatic Amines

Amine	E_{appl} (V)	ne^-	Std. Dev. (%)	Mechanism
TPrA	0.9	1.78	34	ECE
TPrA	0.9	1.90	29	ECE

Diphenylhydrazine

Experiment	Eapp (V)	ne^-	Std. Dev. (%)
1	0.8	3.70	28
2	0.8	4.48	12
3	0.8	4.06	7

Tables S1. Values of *n* calculated for different experiments using various analytes at certain applied potentials (E_{appl}) and standard deviation from electrochemistry and DLS, as well as the proposed mechanistic pathway, where E is an electrochemical reaction, EE is multi-electron transfers and C is a chemical reaction.

The following tables give representative charge data over different experiments for different analytes:

Ferrocene Charge Data:

Q / fC	Q/C	n, d = 60.85
14.7	1.47E-14	0.803561648
15.7	1.57E-14	0.858225705
21.2	2.12E-14	1.158878022
18.5	1.85E-14	1.011285067
17.9	1.79E-14	0.978486632
19.6	1.96E-14	1.07141553
14.7	1.47E-14	0.803561648
17.3	1.73E-14	0.945688198
19.6	1.96E-14	1.07141553
18.5	1.85E-14	1.011285067
13.9	1.39E-14	0.759830401
16.8	1.68E-14	0.918356169
14.4	1.44E-14	0.78716243
18.1	1.81E-14	0.989419444
16.9	1.69E-14	0.923822574
22.6	2.26E-14	1.235407703
11.5	1.15E-14	0.628636663
23.7	2.37E-14	1.295538167
17.9	1.79E-14	0.978486632
19.1	1.91E-14	1.044083501
18.7	1.87E-14	1.022217878
19.6	1.96E-14	1.07141553
21.8	2.18E-14	1.191676457
18.6	1.86E-14	1.016751472
15.8	1.58E-14	0.863692111
14.6	1.46E-14	0.798095242
18.3	1.83E-14	1.000352255
15.7	1.57E-14	0.858225705
20.2	2.02E-14	1.104213965
19.4	1.94E-14	1.060482719
24.1	2.41E-14	1.31740379
		0.986421737
		0.157258005
		16%

Q / fC	Q/C	n, d = 60.85
12.2	1.22E-14	0.702469584
13.1	1.31E-14	0.75429111
15.9	1.59E-14	0.915513638
18.2	1.82E-14	1.047946428
19.4	1.94E-14	1.117041797
12.7	1.27E-14	0.731259321
15.6	1.56E-14	0.898239795
11.8	1.18E-14	0.679437794
13.9	1.39E-14	0.80035469
16.9	1.69E-14	0.973093112
17.4	1.74E-14	1.001882849
19.5	1.95E-14	1.122799744
17	1.7E-14	0.978851059
18.6	1.86E-14	1.070978218
17.2	1.72E-14	0.990366954
13.9	1.39E-14	0.80035469
16.9	1.69E-14	0.973093112
16.4	1.64E-14	0.944303375
17.2	1.72E-14	0.990366954
17.5	1.75E-14	1.007640796
18.1	1.81E-14	1.042188481
13.7	1.37E-14	0.788838795
15.5	1.55E-14	0.892481848
16.8	1.68E-14	0.967335164
17.9	1.79E-14	1.030672586
		0.928872076
		0.125842124
		13.50%

Q/pC	Q/C	n
0.0139	1.39E-14	0.501615056
0.0199	1.99E-14	0.718139541
0.0202	2.02E-14	0.728965765

0.022	2.2E-14	0.79392311
0.0243	2.43E-14	0.876924163
0.0256	2.56E-14	0.923837801
0.0273	2.73E-14	0.985186405
0.0275	2.75E-14	0.992403888
0.027	2.7E-14	0.974360181
0.029	2.9E-14	1.046535009
0.0301	3.01E-14	1.086231165
0.035	3.5E-14	1.263059494
		0.907598465
		0.191917537
	Spread	21%

TPrA Charge Data:

Q / pC	Q / C	ne
0.024	2.4E-14	0.980076154
0.022	2.2E-14	0.898403142
0.067	6.7E-14	2.736045931
0.02	2E-14	0.816730129
0.069	6.9E-14	2.817718944
0.067	6.7E-14	2.736045931
0.03	3E-14	1.225095193
0.048	4.8E-14	1.960152309
0.032	3.2E-14	1.306768206
0.034	3.4E-14	1.388441219
0.027	2.7E-14	1.102585674
0.037	3.7E-14	1.510950738
0.024	2.4E-14	0.980076154
0.065	6.5E-14	2.654372918
0.052	5.2E-14	2.123498334
0.034	3.4E-14	1.388441219
0.035	3.5E-14	1.429277725
0.043	4.3E-14	1.755969777
0.05	5E-14	2.041825322
0.045	4.5E-14	1.837642789
0.06	6E-14	2.450190386

TTF Charge Data:

E_1 = 0.5 V

0.051	5.1E-14	2.082661828
0.045	4.5E-14	1.837642789
0.06	6E-14	2.450190386
0.051	5.1E-14	2.082661828
		1.783738601
		0.614962535

Q / pC	Q / C	ne
0.067	6.7E-14	2.7360
0.069	6.9E-14	2.8177
0.067	6.7E-14	2.7360
0.03	3E-14	1.2251
0.048	4.8E-14	1.9602
0.032	3.2E-14	1.3068
0.034	3.4E-14	1.3884
0.027	2.7E-14	1.1026
0.037	3.7E-14	1.5110
0.024	2.4E-14	0.9801
0.065	6.5E-14	2.6544
0.052	5.2E-14	2.1235
0.034	3.4E-14	1.3884
0.035	3.5E-14	1.4293
0.043	4.3E-14	1.7560
0.05	5E-14	2.0418
0.045	4.5E-14	1.8376
0.06	6E-14	2.4502
0.051	5.1E-14	2.0827
0.045	4.5E-14	1.8376
0.06	6E-14	2.4502
0.051	5.1E-14	2.0827
	4.66364E-14	1.9045
		0.5547

Q / pC	n_e
0.011	0.754514206
0.013	0.891698607
0.016	1.097475208
0.016	1.097475208

0.014	0.960290807
0.01	0.685922005
0.01	0.685922005
0.011	0.754514206
0.012625	0.865976532

E_2 = 0.95 V	
Q / pC	n_e
0.021	1.440436211
0.016	1.097475208
0.033	2.263542617

E_1 = 0.5 V	
Q / pC	n_e
0.014	0.960290807
0.015	1.028883008
0.015	1.028883008
0.017	1.166067409
0.02	1.37184401
0.0162	1.111193648

E_2 = 1.0 V	
Q / pC	n_e
0.012	0.823106406
0.012	0.823106406
0.014	0.960290807
0.032	2.194950417
0.034	2.332134818
0.045	3.086649023
0.048	3.292425625
0.028142857	1.9303805

E_1 = 0.5 V	
Q / pC	n_e
0.012	0.823106406
0.012	0.823106406
0.015	
0.014	0.960290807
0.015	1.028883008
0.041	2.812280221
0.042	2.880872422
0.022	1.509028411
0.019	1.30325181
0.03	2.057766016
0.028	1.920581614
0.014	0.960290807
0.025	1.714805013
0.034	2.332134818
0.027083333	1.857705431
0.017	1.166067409
0.014166667	0.971722841

E_2 = 1.0 V	
Q / pC	n_e
0.021	1.440436211
0.035	2.400727018
0.026	1.783397213
0.033	2.263542617
0.028	1.920581614
0.033	2.263542617
0.03	2.057766016
0.026	1.783397213
0.026	1.783397213
0.031	2.126358216
0.0289	1.982314595

Diphenylhydrazine Charge Data:

E = 0.8 V	
Q/ C	*n*
3.29E-13	3.83
2.27E-13	2.65
3.00E-13	3.51
3.53E-13	4.12
3.50E-13	4.08
2.65E-13	3.10

4.15E-13	4.85
3.70E-13	4.32
3.72E-13	4.34
2.93E-13	3.42
3.81E-13	4.45
4.09E-13	4.78
3.31E-13	3.86
4.32E-13	5.04
2.18E-13	2.54
1.90E-13	2.22
1.95E-13	2.28
3.71E-13	4.33
1.76E-13	2.06
4.65E-13	5.43
2.34E-13	2.74
2.10E-13	2.45
4.38E-13	5.12
2.33E-13	2.72
4.50E-13	5.26
1.45E-13	1.69

2.27E-13	2.65
3.30E-13	3.85
3.17E-13	**3.70**

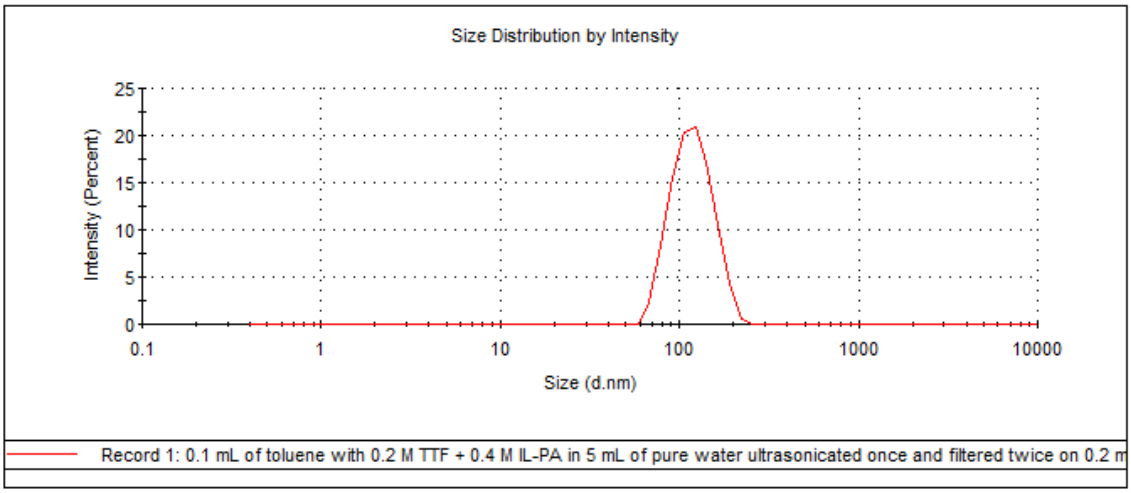
E = 0.8 V	
Q/ C	*n*
1.71E-13	5.17
1.63E-13	4.92
1.37E-13	4.14
1.40E-13	4.21
1.31E-13	3.95
1.48E-13	4.48

E = 0.8 V	
Q/ C	*n*
1.74E-13	3.84
1.94E-13	4.28
1.84E-13	4.06

Tables S2. Values of n_e calculated from charge (Q) by integrating each collision current spike using various analytes and standard deviation (d).

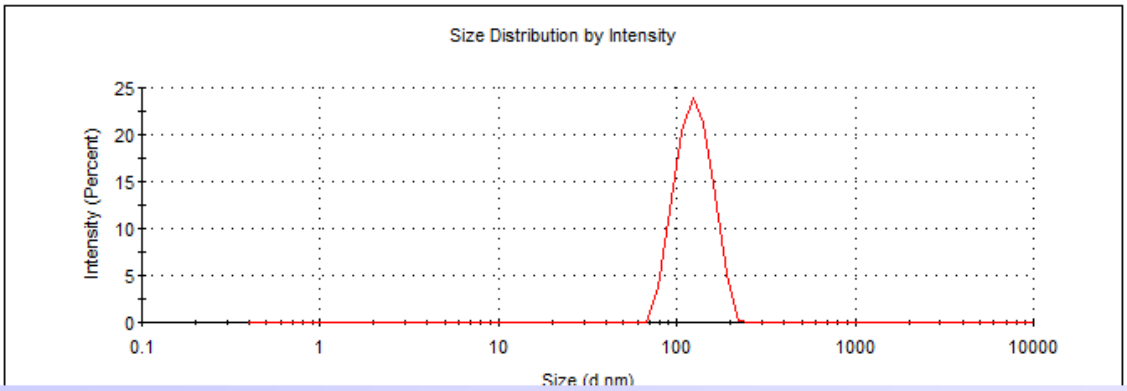
DLS of droplets with 200 mM TTF after 2 filtrations:

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 113.2	Peak 1:	120.2	100.0	30.33
PdI: 0.051	Peak 2:	0.000	0.0	0.000
Intercept: 0.954	Peak 3:	0.000	0.0	0.000
Result quality : Good				



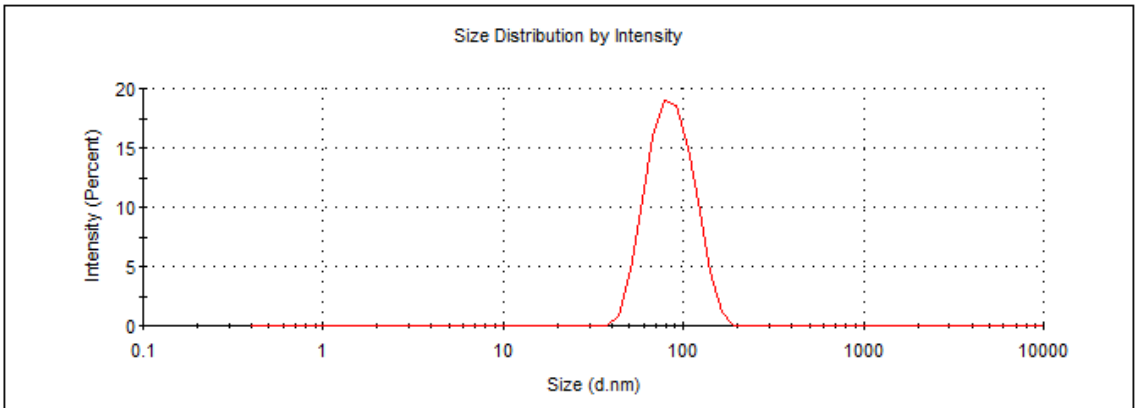
DLS of droplets with 200 mM Ferrocene after 2 filtrations:

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 121.7	Peak 1:	127.1	100.0	28.08
PdI: 0.022	Peak 2:	0.000	0.0	0.000
Intercept: 0.943	Peak 3:	0.000	0.0	0.000
Result quality : Good				



DLS of droplets with 1 M TPrA after 2 filtrations:

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 81.43	Peak 1:	87.76	100.0	24.72
PdI: 0.065	Peak 2:	0.000	0.0	0.000
Intercept: 0.952	Peak 3:	0.000	0.0	0.000
Result quality : Good				



DLS of droplets with 200 mM DPH after 1 filtration

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 178.7	Peak 1:	183.8	100.0	37.44
PdI: 0.026	Peak 2:	0.000	0.0	0.000
Intercept: 0.959	Peak 3:	0.000	0.0	0.000
Result quality : Good				

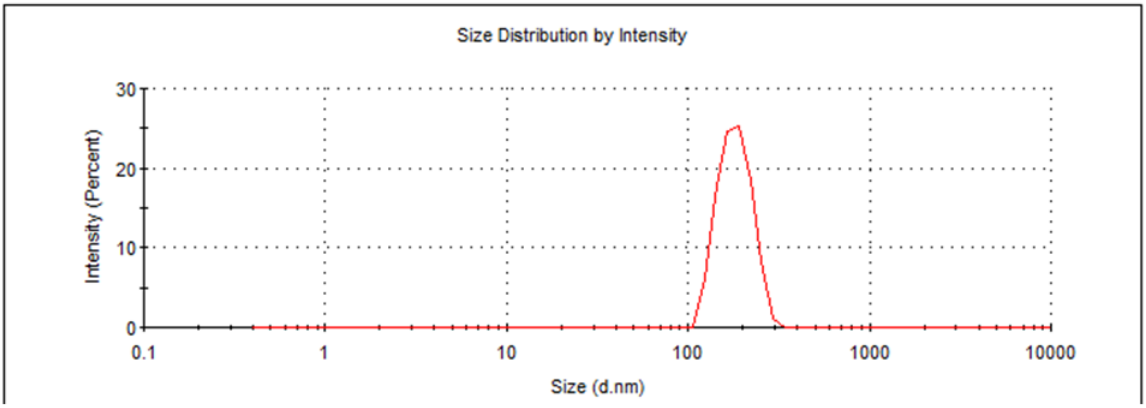


Figure S1. DLS measurements of emulsion solutions with various analytes after filtering through a filter with pore diameter of 200 nm.

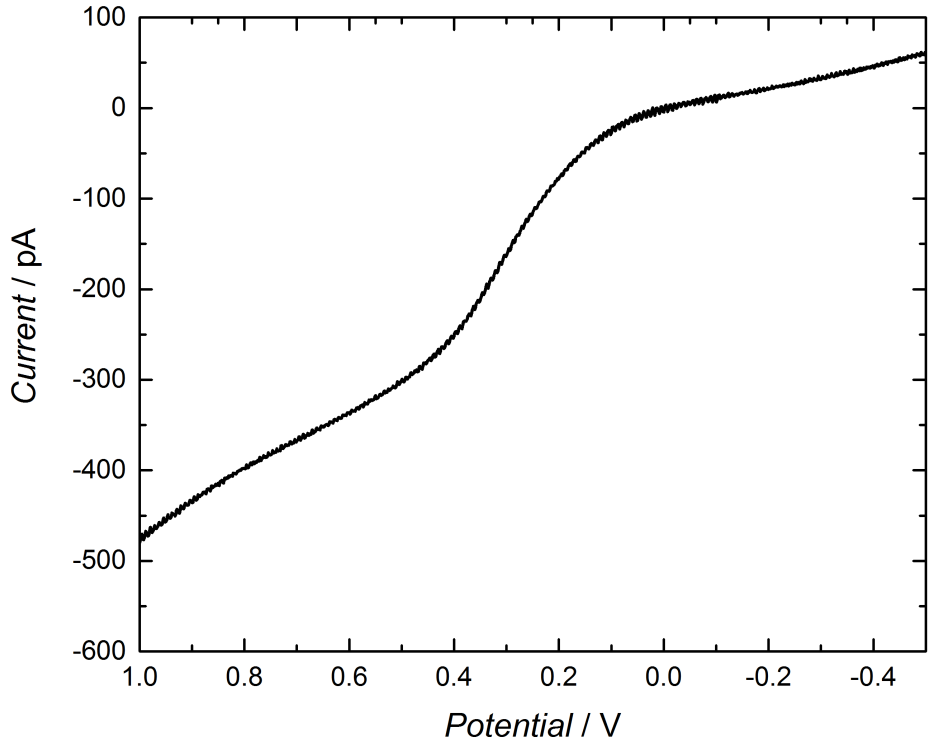


Figure S4. Oxidation of 8 mM 1,2-diphenylhydrazine in toluene containing 400 mM phosphonium-amide ionic liquid as the supporting electrolyte versus a Ag quasi-reference electrode on a 4 μm Pt ultramicroelectrode working electrode. The scan rate was 500 mVs^{-1}.