Electronic Supplementary Material *for*

Ionic Conductivity Enhancement of Sputtered Gold Nanoparticle-in-Ionic Liquid Electrolytes

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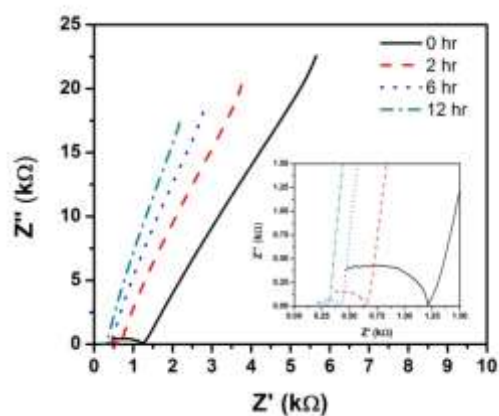[3] Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

Fig. S1 EIS of [emim][EtSO$_4$] left in atmosphere for the indicated time showing how the humidity in the atmosphere is affecting the electrochemical properties.
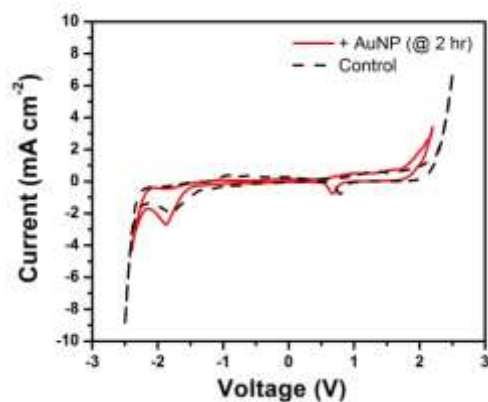
Fig. S2 CV measurements showing breakdown of [emim][EtSO$_4$] with nanoparticles 2 h after deposition (red) and without nanoparticles (black). Electrochemical windows: Au –2.23 to 2.02 V @ 2 mA cm^{-2} and control –2.32 to 2.29 V @ 2 mA cm^{-2}.
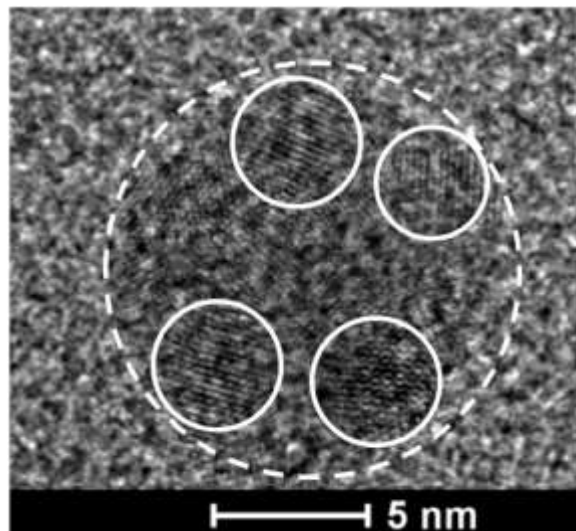

Fig. S3 Agglomeration of small nanoparticles within 30 minutes of deposition caused by grid preparation. Circles represent a few selected regions showing different crystal orientation, verifying agglomeration.
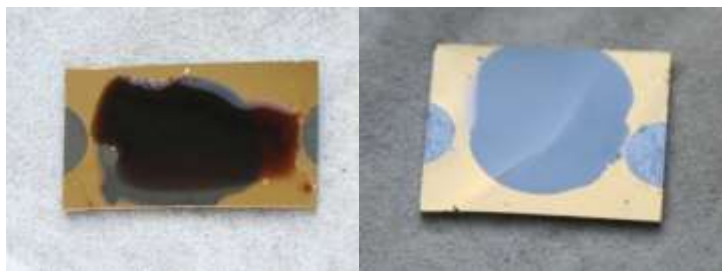
Fig. S4 Photographs post-Au deposition of (Left) [C$_6$mpy][Tf$_2$N] and (right) [P$_{14,666}$][Cl]. No color change or SPR peak was observed in the [P$_{14,666}$][Cl] indicating very little or no nanoparticle growth.
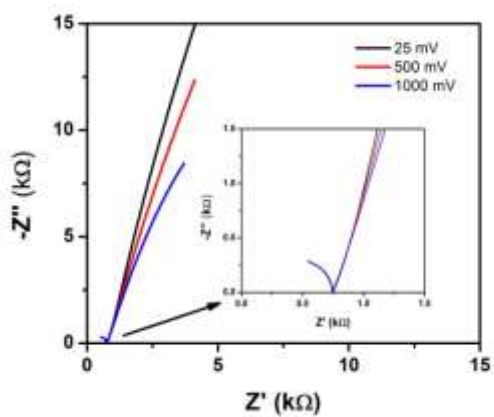

Fig. S5 EIS measurements at various signal amplitudes showing the HF components are unaffected by signal amplitude.

Table S1 (A) EIS modelling results for neat [emim][EtSO$_4$]

Time (hr)	Lead		Ion Circuit					Bulk		Counterion Circuit				
	L_{lead} [μH]	R_{lead} [Ω]	R_{ct1} [Ω]	σ (CPE$_{W1}$) [μS s^n]	n (CPE$_{W1}$)	σ (CPE$_{cdl1}$) [μS s^n]	n (CPE$_{cdl1}$)	R_{hf} [Ω]	C_{hf} [pF]	R_{ct2} [Ω]	σ (CPE$_{W2}$) [μS s^n]	n (CPE$_{W2}$)	σ (CPE$_{cdl2}$) [μS s^n]	n (CPE$_{cdl2}$)
0.33	0.375	5.0	21.3	58.1	0.36	0.598	0.78	1310.0	1.26	20.3	0.838	0.34	0.131	1.00
2	0.347	4.9	33.7	65.3	0.41	0.494	0.80	1137.8	1.28	29.4	0.342	0.57	0.118	1.00
7.5	0.484	5.1	10.6	137	0.36	0.295	0.83	1589.7	1.18	34.4	0.281	0.62	0.107	0.99
12	0.463	5.7	13.0	332	0.29	0.492	0.80	1706.9	1.21	16.4	0.344	0.63	0.118	1.00
20	0.434	6.9	19.8	255	0.31	0.910	0.77	1677.5	1.33	24.8	0.364	0.57	0.132	1.00

(B) EIS modelling results for Au NPs

Time (hr)	Lead		Ion Circuit					Bulk		Counterion Circuit				
	L_{lead} [μH]	R_{lead} [Ω]	R_{ct1} [Ω]	σ (CPE$_{W1}$) [μS s^n]	n (CPE$_{W1}$)	σ (CPE$_{cdl1}$) [μS s^n]	n (CPE$_{cdl1}$)	R_{hf} [Ω]	C_{hf} [pF]	R_{ct2} [Ω]	σ (CPE$_{W2}$) [μS s^n]	n (CPE$_{W2}$)	σ (CPE$_{cdl2}$) [μS s^n]	n (CPE$_{cdl2}$)
0.33	0.100	5.6	8.3	126	0.38	0.757	0.78	309.8	2.11	20.4	0.836	0.56	0.179	1.00
2	0.293	5.3	26.5	55.6	0.42	0.539	0.80	858.2	1.39	38.8	0.411	0.56	0.126	1.00
7.5	0.465	6.5	34.5	57.4	0.42	0.299	0.83	1662.2	1.22	47.7	0.331	0.61	0.102	1.00
12	0.468	5.5	23.3	145	0.34	0.449	0.80	1840.9	1.22	20.5	0.472	0.57	0.107	1.00
20	0.429	10.0	21.5	238	0.31	0.737	0.77	1871.8	1.27	51.5	0.396	0.57	0.135	1.00

(C) EIS modelling element ratios (AuNP/Control)

| Time (hr)	Lead		Ion Circuit					Bulk		Counterion Circuit				
	L_{lead}	R_{lead}	R_{ct1}	σ (CPE$_{W1}$)	n (CPE$_{W1}$)	σ (CPE$_{cdl1}$)	n (CPE$_{cdl1}$)	R_{hf}	C_{hf}	R_{ct2}	σ (CPE$_{W2}$)	n (CPE$_{W2}$)	σ (CPE$_{cdl2}$)	n (CPE$_{cdl2}$)
0.33	0.27	1.11	0.39	2.17	1.06	1.27	1.00	0.24	1.68	1.00	1.00	1.64	1.36	1.00
2	0.84	1.09	0.79	0.85	1.02	1.09	1.00	0.75	1.09	1.32	1.20	0.98	1.07	1.00
7.5	0.96	1.27	3.25	0.42	1.18	1.01	0.99	1.05	1.04	1.39	1.18	0.98	0.96	1.01
12	1.01	0.97	1.79	0.44	1.19	0.91	0.99	1.08	1.01	1.26	1.37	0.91	0.91	1.00
20	0.99	1.45	1.09	0.93	1.01	0.81	1.01	1.12	0.96	2.08	1.09	1.01	1.02	1.00
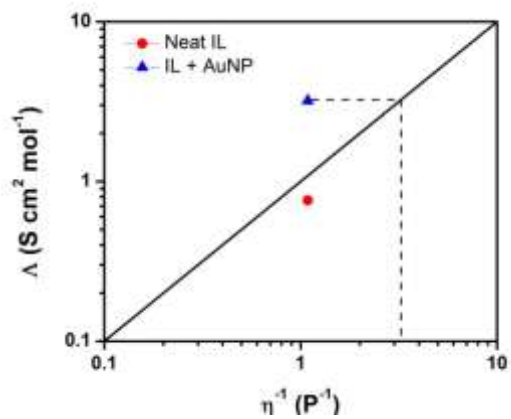
Fig. S6 Walden plot of [emim][EtSO4] before and after AuNP deposition using reported values for the molar conductivity (Λ) and viscosity (η) as referenced in the main article and assuming viscosity does not change post-deposition. The molar conductivity after deposition was calculated using the reported value multiplied by the experimental conductivity ratio of AuNP in IL and neat IL.
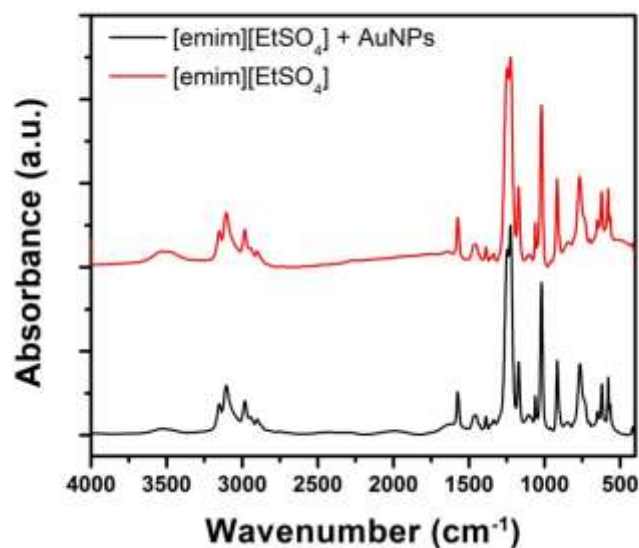
Fig. S7 FTIR spectra of [emim][EtSO4] with (black) and without (red) AuNPs. Other than small peak changes due to slightly different concentrations of moisture,[1] there are no significant peak changes. Results normalized with respect to the peak at 1225 cm^{-1}.
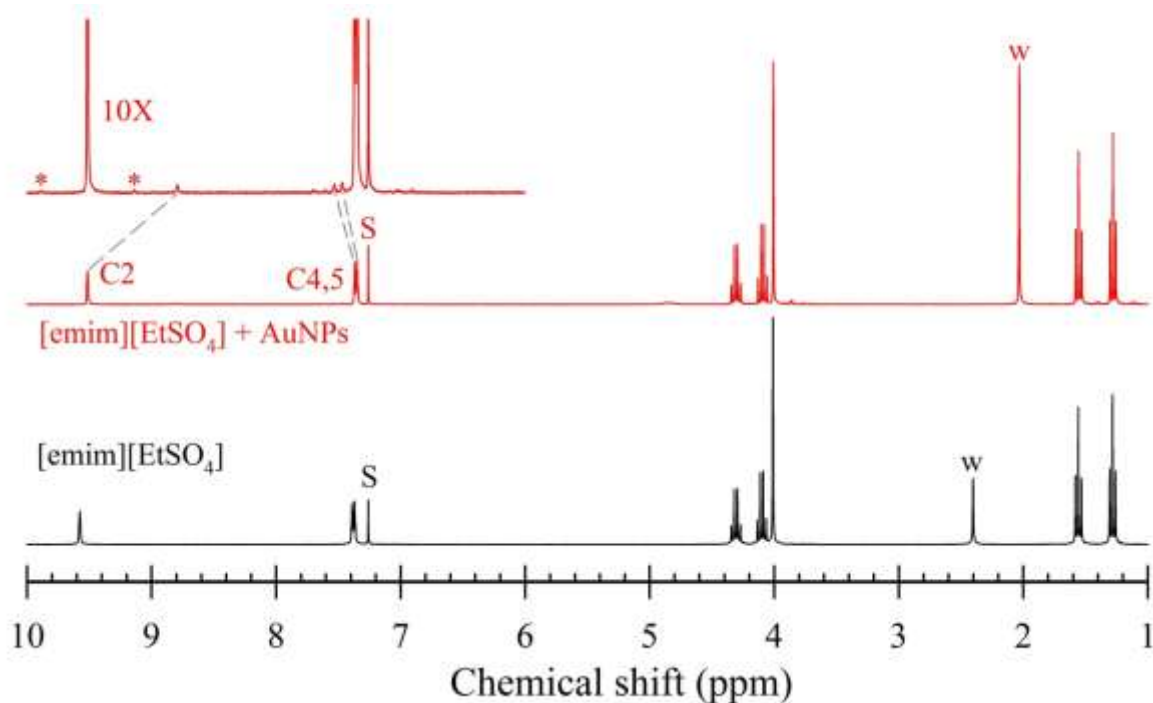

Fig. S8 ^{1}H-NMR spectra of [emim][EtSO$_4$] in CDCl$_3$ (bottom) and [emim][EtSO$_4$] containing AuNPs in CDCl$_3$ (top) at 300 MHz. Signals marked by S and w arise from the residual solvent peak (δ = 7.26 ppm) and water (no attempt was made to keep the solvents dry prior to NMR analysis), respectively, and * denotes spinning sidebands.

S6

References

1.   Q.-G. Zhang, N.-N. Wang and Z.-W. Yu, *J. Phys. Chem. B*, 2010, **114**, 4747-4754.