Supporting Information

Electrolyte-mediated assembly of graphene-based supercapacitors using adsorbed ionic liquid/non-ionic surfactant complexes

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1. Characterization of dispersion in the absence of rGO:

Figure S1: Characterization of microemulsion. a) Rh B labeled EMImTFSI in water at various concentration of IL, b) Rh B labeled EMImTFSI dispersed in water after addition of 0.4 mg/ml of P123, c) DLS of microemulsions of EMImTFSI/P123 in water at different weight ratio of IL/P123 at 4 mg/ml of P123

Figure S1a shows various volumes of EMImTFSI, a hydrophobic IL (labeled with Rh B to provide visual contrast), in water and Figure S1b shows the same concentration of IL when 0.4 mg/ml P123 is added to the mixture (all the three vials have 0.4 mg/ml of P123). As depicted in Figure S1b, after addition of P123, the IL disperses in water, resulting in the formation of a transparent solution for tested ratios of IL/P123. The transparency indicates that the dispersed phase is significantly smaller in size than the wavelength of visible light (<< 400 nm). These result, however, are taken at the concentrations lower than the cmc of P123 ($C_{P123} = 0.4$ mg/ml vs. $C_{CMC} = 1.70$ mg/ml). In order to analyze the interaction in the presence of micelles, we performed DLS analysis at a higher concentration of P123 (i.e., $C_{P123} = 4$ mg/ml) and IL (This is done to increase

the total kcps to ~100 which is often needed for a reliable result). For IL/P123 ratio of 1 and 2, a transparent dispersion was resulted. However, we noticed when the ratio of IL to P123 reaches 3, the dispersion changes from transparent to cloudy. Figure 1c shows DLS analysis of the dispersions when different ratio of IL/P123 existed in the solution. According to this result, for the ratio of IL/P123 of 1 and 2, a uniform dispersion with droplet sizes ~10 nm is formed, which is close to the value reported for aqueous micelles of P123, ¹ implying the formation of mixed micelle with IL. However, with the IL/P123 ratio to 3, the droplet sizes follow a bimodal distribution, where the average sizes of the smaller droplets is ~ 20 nm with the appearance of a larger droplets showing particle sizes of ~ 200 nm (equal to the maximum pore size of the filter paper). From the above results, it can be inferred that addition of excess amount of IL results in swelling of the micelles up to a certain level above which unstable agglomerates with larger diameters appear. However, this is not the case for $C_{P123} = 0.4$ mg/ml. it should be noted that EMImTFSI is slightly soluble in water, therefore, at lower concentrations of the surfactant shown in Figure 1b, a sizeable amount of the added IL can be solubilized in water without the aid of the surfactant, therefore, the surfactant will only solubilize a portion of the added IL, while the rest will be dissolved in water. As it was already mentioned in the method section, the 0.4 mg/ml P123 (i.e., 80 wt. % P123 for electrode fabrication) was the highest concentration of surfactant used in electrode making process. Therefore, we can safely say that before adding rGO, all of our dispersions form stable solution in water.

1.2 0.8 2nd Cycle 2nd Cycle 10th Cycle 1.0 10th Cycle 0.6 0.8 0.4 0.6 I (mA) I (mA) 0.4 0.2 0.2 0.0 0.0 -0.2 -0.2 -0.4 -0.4 -0.6 -0.6 -0.8 0.0 0.5 1.5 2.0 2.5 3.0 0.5 2.0 2.5 1.0 0.0 1.0 1.5 3.0 Voltage (V) Voltage (V)

2. Work in cycle comparisons for 60%P control and 60%P (3) electrodes:

Figure S2: Electrolyte imbibition through cycling. a) 60%P Control (no IL), b) 60%P(3)

3. Specific capacitance, gravimetric and volumetric energy densities and power densities of the rGO/IL/P123 composites.

Table S1. Calculated specific capacitance, gravimetric and volumetric energy densities and power densities of the rGO/IL/P123 composites.

Material	Specific	Gravimetric energy	Volumetric energy	Power density
	capacitance	density (Wh/kg _{active material})	density (Wh/L)	(W/kg _{active material})
	(F/g_{active})			
	material)			
10%	81	25	28	544
10%(1)	107	33	25	621
10%(2)	93	29	21	353
10%(3)	101	32	19	339
20%	72	22	13	189
20%(1)	85	27	14	375
20%(2)	158	49	27	326
20%(3)	98	31	12	274
40%	96	44	12	318
40%(1)	143	13	13	105

40%(2)	156	49	14	402
40%(3)	140	44	9	360
60%	130	41	14	209
60%(1)	158	44	8	293
60%(2)	161	50	7	374
60%(3)	199	62	8	349



Figure S3. Plot of gravimetric and volumetric energy densities as a function of P123 wt. % (IL:P123= 3). The gravimetric energy densities are calculated with respect to active material weight only (red triangles) and the weight including active material, ionic liquid, and surfactant (red squares) showing that a significant drop in gravimetric energy density occurs when inactive mass is considered, which is also consistent with the trend in volumetric energy densities (right-hand Y axis). The blue arrow directs to the upper limit of achievable volumetric energy density for a 60% P(3) electrode, if we were able to achieve the estimated density of the electrode, ~ 1.4 g/cm³ for a fully dense composite while retaining the ionic liquid-accessible surface area, i.e., 88 Wh/L at a gravimetric capacitance of 200 F/g, assuming a 3 V operational potential window. Note that the grey dotted lines are provided as a guide to the eye.



Figure S4. Estimated energy densities as a function of CG for various weight percentages of P123 (IL:P123 =3). The energy densities that are calculated considering total mass, including non-active components, i.e., active material+ionic liquid+surfactant (blue squares) are also given for comparison, along with energy densities estimated using only active material mass (red spheres), showing that gravimetric energy density drops substantially when inactive mass is considered. Note that "per kg" and "per g" values on the Y- and X-axis labels, respectively correspond to either active material weight only (red spheres) or [active material + ionic liquid + surfactant] weight, (blue squares).



Figure S5. Ragone plot constructed for the 20 % P(2) electrodes (per volume), compared with several graphene-based supercapacitors previously reported .

Reference	Mass	Ι	CG	Cv	EG	Ev	Electrolyte	Binder	Density	ESR
	Loading	(A/g)	(F/g)	(F/cm ³)	(Wh/kg)	(Wh/L)	(VW)	additive	(g/cm ³)	(Ω)
	(mg/cm ²)									
Curved	6.6	1	154	46.2	58.6	27.5	EMImBF ₄	5 wt%	0.3	3.31
Graphene ²							(4V)	SuperP		
								10 wt%		
								PTFE binder		
a-MEGO ³	2.5	1.4	165	59.8	70.6	25.4	BMImBF4/AC	5 wt% PTFE	0.36	3.1
							(3.5 V)	binder		
Compressed	4.3	1.2	147	110	63	48	BMImBF4/AC	5 wt% PTFE	0.75	8.3
a-MEGO ⁴							(3.5 V)	binder		
as-MEGO ⁵	1.3	2.1	173	102	74	44	EMImTFSI/AC	5 wt% PTFE	0.59	4.2
	10.4	1.1	129	58	55	25	(3.5V)	binder	0.45	
Porous 3D	4	1	231	92	98	39	EMImBF4	10 wt%	0.4	0.26
Graphene ⁶							(3.5 V)	PTFE binder		
Laser ascribed	0.036	5	276	13.2	117.4	5.6	EMImBF4	NA	0.046	
Graphene							(3.5 V)			
(LSG) ⁷										
Chemically	3.73	1.33	99	49	21.5	10.7	Et4NBF4/AN	5 wt% PTFE	0.5	0.65
reduced							(2.5 V)	binder		
graphene ⁸										
Carbide	15	0.3	160	85	50	26.5	EMImTFSI	NA	0.53	
Derived							(3 V)			
Carbon ⁹										
EM-CCG ¹⁰	1	1	167	209	71	89	EMImBF4/AN	NA	1.25	
	10	1	126	158	52	65	(3.5 V)		1.25	
HGF ¹¹	1	1	289	205	123	87	EMImBF4 (3.5	NA	0.71	2.6
	10	1	246	174	105	74	V)		0.71	
acGr/SWNT ¹²	0.6	1	172	275	95.6	101.3	EMImBF4 (4V)	NA	1.06	
GCNS-SC 13	5	1	152	80.6	64.6	34.2	EMImTFSI	5 wt% PVDF	0.53	0.27
							(3V)	binder		
Our Work	1	1	243.7	80 (20	50 (20	26.6 (20	EMImTFSI	NA	0.54	0.03
			(60 %	% P(2))	% P(2))	% P(2))	(3V)			
			P(3))							
IM-rGO (60%	0.7-1.5	1	189	142	59	4	EMImTFSI	NA	0.75	
IL) ¹⁴							(3V)			
rGO/IL gel	0.5-1	0.2	140	64	43.73	20.125	EMImBF4/3V	NA	0.46	
(60% IL) ¹⁵										
PGP ¹⁶		1	152	140	84	77	BMImBF4/4V	3 wt% PTFE	0.9	

Table S2. Comparison of electrochemical performance of our electrodes vs. similar systems reported in the literature.

binder						
					binder	



4. Work in cycle comparison for 20%P(2) and 60%P(3) electrodes:

Figure S6. Comparison of 2nd and 10th cycle for a) 20%P (2) and b) 60%P(3)



5. Comparison of GCD and EIS for control rGO and rGO/P123 composites:

Figure S7. Comparison of the GCD and EIS impedance for rGO, 20%P control and 60%P control electrodes. a) Nyquist plot comparisons, b) GCD comparisons at 10 A/g, the 5th cycle

Figure S7 a and b compare the Nyquist plot and GCD plot for rGO control, 20%P control (i.e., no IL) and 60%P control electrodes. According to Figure S4a, the rGO electrode has both largest charge transfer resistance and ohmic resistance, while with increasing 20 wt. % of surfactants, the ohmic resistance and charge transfer resistance reduce first and then increase with further increasing the surfactant to 60 wt.%. As surfactant act as a spacer, at low weight fraction of surfactant, they help separate the rGO sheets so the IL can penetrate into electrode's pore and reduce the ionic resistance. While increasing the amount of surfactant, will still separate the rGO sheets, therefore, less IL can diffuse through the already filled electrode with surfactant, leading to reduction of the ionic conductivity and an increase in the resistance. According to GCD plot (Figure 7Sb), the same trend as the EIS data can be seen with rGO electrode having the largest voltage drop and ESR as a result. Adding 20 % of P123 has reduced the voltage drop to 0.29 V, but increasing the surfactant further has an adverse effect on the total cell resistance as it can be seen from the increased voltage drop.



6. EDX mapping of the 20%P(2) electrode:

Figure S8. EDS mapping of 20%P(2) electrode surface. a) SEM image of the surface, b) composition of C element, b) composition of N element, d) composition of F element, e) composition of S element, f) composition of O element

7. Morphological Characterization of 20%P(2) electrodes:

Figure S9 a and b show, the relatively smooth surface morphology of the 20%P(2) electrodes with some sparse irregularities related to rGO sheets emanating from the flat surface. This layered structure is better observed in cross sectional views in Figure S9 c and d. The carbon coating on the Al foil has $\sim 1 \mu m$ thickness, separating the electrode material from the current collector. A slight gap can be seen between the carbon coating and the electrode materials as a result of poor adhesion. Therefore, improving the interface adhesion can further improve the interfacial resistance and rate performance of the device. In addition, areas with large air gaps can be noticed throughout the electrode cross section (Figure S9c and d). These gaps are possibly air that is trapped while pressing the electrode/electrolyte composite using the hydraulic press.



Figure S9. Morphological characterization of surface and cross sectional view of 20% P(2). a and b) Surface morphology, c and d) Cross sectional view of electrodes

8. Balancing the electrode's mass for improved electrochemical stability window:



Figure S10. Improvement in stability window of 20%P(2) electrode using mass balancing method. The mass ratio, $m_{+ev} / m_{-ev} = 2.34 / 1$

9. References

- Schillén, K.; Jansson, J.; Löf, D.; Costa, T. Mixed Micelles of a PEO-PPO-PEO Triblock Copolymer (P123) and a Nonionic Surfactant (C12EO6) in Water. A Dynamic and Static Light Scattering Study. J. Phys. Chem. B 2008, 112 (18), 5551–5562.
- (2) Liu, C.; Yu, Z.; Neff, D.; Zhamu, A.; Jang, B. Z. Graphene-Based Supercapacitor with an Ultrahigh Energy Density. *Nano Lett.* **2010**, *10* (12), 4863–4868.
- (3) Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science* 2011, *332* (6037), 1537–1541.
- (4) Murali, S.; Quarles, N.; Zhang, L. L.; Potts, J. R.; Tan, Z.; Lu, Y.; Zhu, Y.; Ruoff, R. S. Volumetric Capacitance of Compressed Activated Microwave-Expanded Graphite Oxide (a-MEGO) Electrodes. *Nano Energy* 2013, 2 (5), 764–768.
- (5) Kim, T.; Jung, G.; Yoo, S.; Suh, K. S.; Ruoff, R. S. Activated Graphene-Based Carbons as Supercapacitor Electrodes with Macro- and Mesopores. *ACS Nano* **2013**, *7* (8), 6899–6905.
- (6) Zhang, L.; Zhang, F.; Yang, X.; Long, G.; Wu, Y.; Zhang, T.; Leng, K.; Huang, Y.; Ma, Y.; Yu, A.; Chen, Y. Porous 3D Graphene-Based Bulk Materials with Exceptional High Surface Area and Excellent Conductivity for Supercapacitors. *Sci. Rep.* **2013**, *3* (1), 1408.

- (7) El-Kady, M. F.; Strong, V.; Dubin, S.; Kaner, R. B. Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors. *Science* **2012**, *335* (6074), 1326–1330.
- (8) Stoller, M. D.; Park, S.; Zhu, Y.; An, J.; Ruoff, R. S. Graphene-Based Ultracapacitors. *Nano Lett.* **2008**, *8* (10), 3498–3502.
- (9) Largeot, C.; Portet, C.; Chmiola, J.; Taberna, P.-L.; Gogotsi, Y.; Simon, P. Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor. *J. Am. Chem. Soc.* **2008**, *130* (9), 2730–2731.
- (10) Yang, X.; Cheng, C.; Wang, Y.; Qiu, L.; Li, D. Liquid-Mediated Dense Integration of Graphene Materials for Compact Capacitive Energy Storage. *Science* 2013, 341 (6145), 534– 537.
- (11) Xu, Y.; Lin, Z.; Zhong, X.; Huang, X.; Weiss, N. O.; Huang, Y.; Duan, X. Holey Graphene Frameworks for Highly Efficient Capacitive Energy Storage. *Nat. Commun.* **2014**, *5* (1), 4554.
- (12) Pham, D. T.; Lee, T. H.; Luong, D. H.; Yao, F.; Ghosh, A.; Le, V. T.; Kim, T. H.; Li, B.; Chang, J.; Lee, Y. H. Carbon Nanotube-Bridged Graphene 3D Building Blocks for Ultrafast Compact Supercapacitors. *ACS Nano* **2015**, *9* (2), 2018–2027.
- (13) Tian, W.; Gao, Q.; Tan, Y.; Li, Z. Unusual Interconnected Graphitized Carbon Nanosheets as the Electrode of High-Rate Ionic Liquid-Based Supercapacitor. *Carbon* **2017**, *119*, 287–295.
- (14) She, Z.; Ghosh, D.; Pope, M. A. Decorating Graphene Oxide with Ionic Liquid Nanodroplets: An Approach Leading to Energy-Dense, High-Voltage Supercapacitors. *ACS Nano* **2017**, *11* (10), 10077–10087.
- (15) Pope, M. A.; Korkut, S.; Punckt, C.; Aksay, I. A. Supercapacitor Electrodes Produced through Evaporative Consolidation of Graphene Oxide-Water-Ionic Liquid Gels. *J. Electrochem. Soc.* **2013**, *160* (10), A1653–A1660.
- (16) Li, H.; Tao, Y.; Zheng, X.; Li, Z.; Liu, D.; Xu, Z.; Luo, C.; Luo, J.; Kang, F.; Yang, Q.-H. Compressed Porous Graphene Particles for Use as Supercapacitor Electrodes with Excellent Volumetric Performance. *Nanoscale* **2015**, *7* (44), 18459–18463.