

Supplementary Materials: High-Performance Graphene Based Electrochemical Double Layer Capacitors Using 1-Butyl-1-Methylpyrrolidinium Tris (Pentafluoroethyl) trifluorophosphate Ionic Liquid as Electrolyte

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Exfoliation Process:

The liquid-phase exfoliation (LPE) of graphene was performed using a similar method followed by Colemann et al. [1]. In brief, bulk graphite was first soaked in isopropyl alcohol (IPA). An initial concentration of 10mg/ml was used. During exfoliation, the sample was subjected to four hours of bath sonication, during which the water in the bath was changed out every hour in order to prevent the build-up of heat. IPA was used as a solvent in order to prevent the sheets from reforming into bulk clusters through van der Waals forces. The surface tension of IPA overcomes the van der Waals forces, allowing for few-layer dispersions to be generated with this process [2–4]. The resulting solution was then centrifuged at 1500 rpm for 45 min. The centrifuge speed and duration can be varied in order to produce dispersions of different size and layer quantity. The speed and duration chosen produced flakes of roughly \approx 8-14 layers and \approx 200-500 nm diameter. Upon completion, the supernatant liquid was then decanted into glass vials to be used for testing.

Characterization:

In order to verify the structure of the resulting product, high-resolution transmission electron microscopy (HR-TEM), ultraviolet-visible spectroscopy (UV-VIS), X-ray photoelectron spectroscopy (XPS) and atomic force/scanning probe microscopy (AFM/SPM) were used. For HR-TEM investigations, a JEOL JEM-2100F station was used, in order to achieve magnifications upwards of 100,000 \times such that the degree of layering in the samples could be observed. Samples for HR-TEM were drop-cast onto carbon-coated copper TEM grids for testing. Raman measurements were performed using a Horiba Scientific Explora. Scans were obtained using 25% power (6.25 mW) for five rounds of 30 s data collection with a 532 nm laser. For the AFM/SPM results, a Veeco Multimode V station was used. Once a flake was found at lower magnifications, a more in-depth scan was taken of 6.41 μ m by 6.41 μ m dimensions, with a scan rate of 0.996 Hz and 512 samples taken per line across 512 lines (512 by 512 resolution). Once collected, section height profiles were extracted from the data at observed flake boundaries in order to determine the actual layer height of the prepared sample.

All the ionic electrolytes used in this study was purchased from commercial vendors and was used without further modifications. BMIM-PF6 98+% was purchased from Acros Organics (CAS: 174501-64-5, Pittsburgh, PA, USA) and BMP-FAP EMD Millipore (4.91084.0025, Burlington, MA, USA). 6 M KOH was prepared from solid KOH powder obtained from Fisher Scientific (CAS: 1310-58-3, Hampton, NH, USA).

Supplementary Figures:

UV-VIS spectroscopy and XPS analysis of liquid-phase exfoliated graphene sample is presented in Figure S1. UV-VIS absorption spectroscopy data shown in Figure S1a shows the graphene characteristic peak at around 270 nm wavelength [5]. XPS data also shows C 1s characteristic peak at \approx 285 eV binding energy (Figure S1b,d). Similarly, the O peak was around 531eV (Figure S1c).

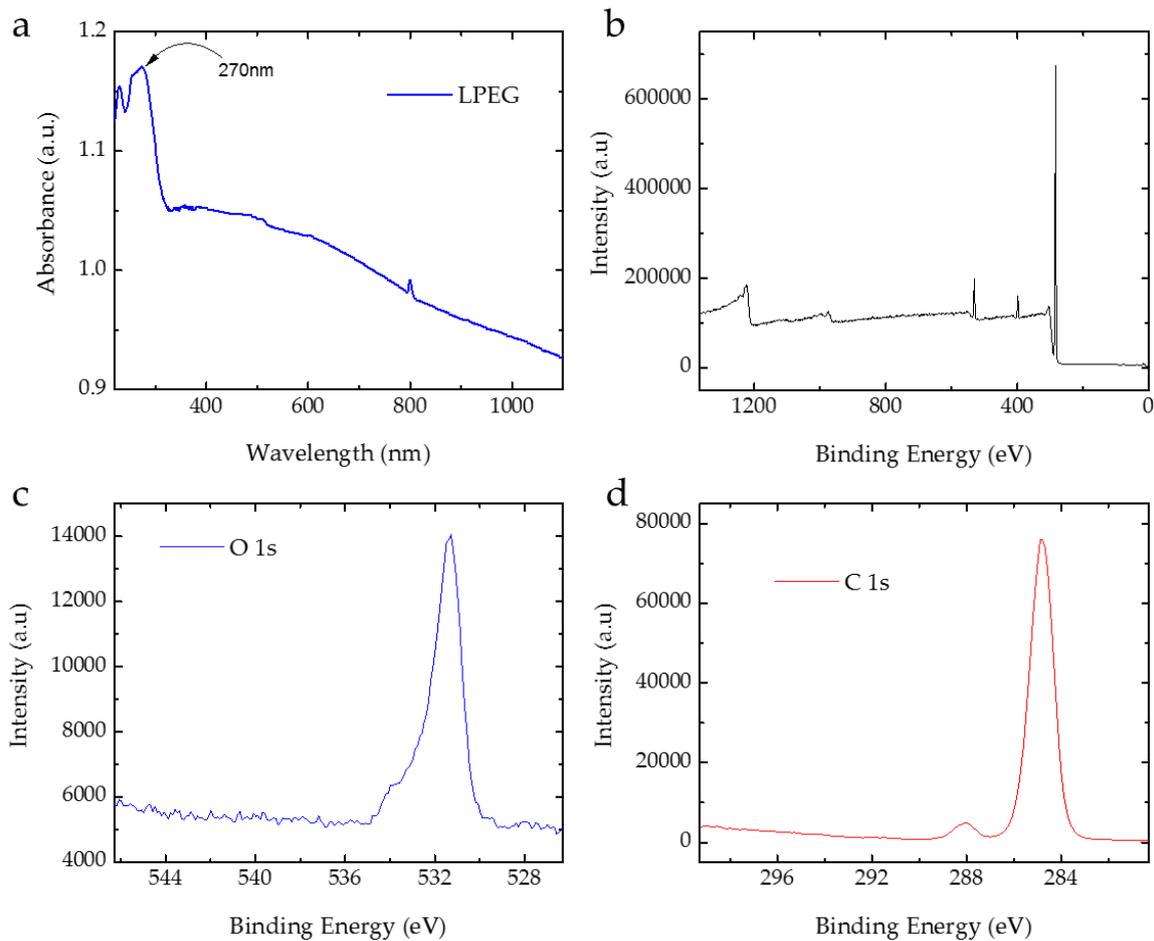


Figure S1. (a) UV-VIS absorbance spectroscopy of LPEG, (b) XPS analysis survey scan, (c) O 1s scan, and (d) C 1s scan.

The CV plots for bulk graphite powder are presented in Figure S2a. Symmetric charge return and reversible response is observed across voltage windows up to 5V. However, once standard CV calculations were performed, as seen in the results of Figure S2b, it was observed that the resulting specific capacitance of the prepared samples of LPEG outperformed the bulk graphite samples by roughly two orders of magnitude.

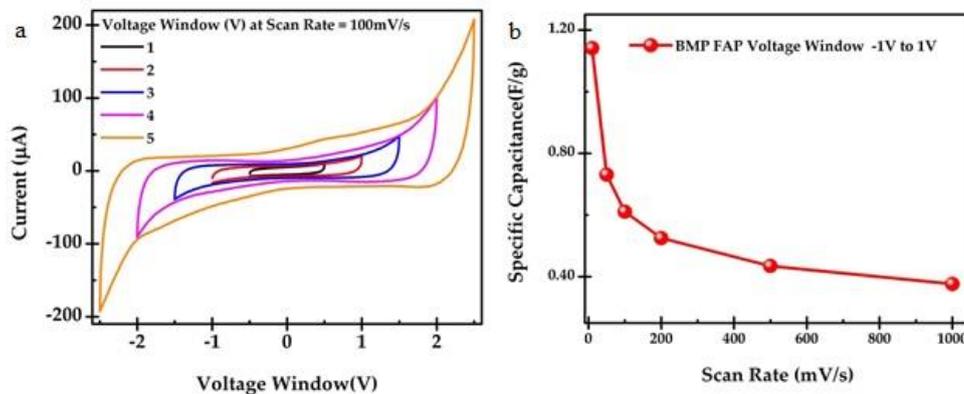


Figure S2. (a) Cyclic voltammogram plot for bulk graphite powder in BMP-FAP, and (b) the resulting specific capacitance vs scan rate used.

The CV plots for LPE graphene in 6M KOH and BMIM-PF6 is presented above in Figure S3a and S3c respectively. Symmetric response with good charge return is observed with both electrolytes. In the range of voltage windows used, no Faradaic peak response is observed in either CV plot. Figure S3b,d present the specific capacitance versus scan rate performance for 6M KOH and BMIM-PF6, respectively. The resulting performance values are less than half of the performance demonstrated with LPE graphene in BMP-FAP electrolyte.

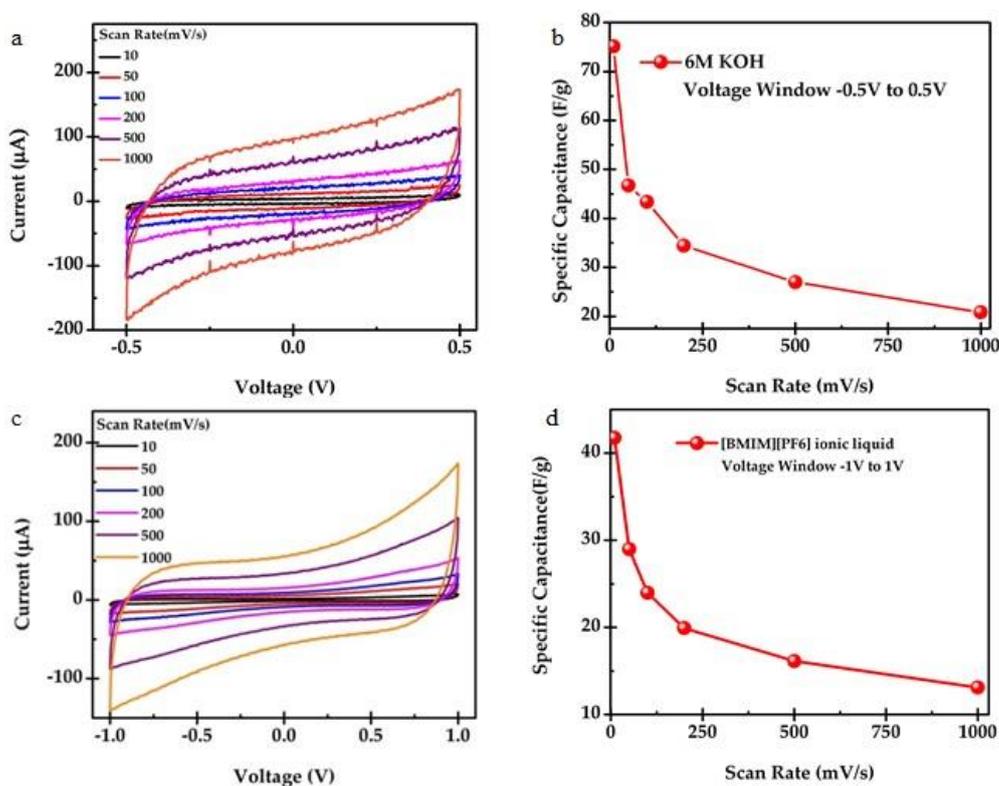


Figure S3. (a) Cyclic voltammetric plot of LPE graphene in 6M KOH aqueous electrolyte, and (b) the resulting specific capacitance vs scan rate used. (c) Cyclic voltammetric plot of LPE graphene in BMIM-PF6 ionic liquid electrolyte, and (d) the resulting specific capacitance vs scan rate used.

Table S1: Table S1 presents the specific capacitance (C_{sp}) (in F/g) for all scan rates and voltage windows that were taken for LPE graphene. Only one of the devices tested is presented below.

Electrolyte	ΔV	Specific Capacitance (C_{sp}) in F/g at Different Scan Rates (mV/s)					
		@ 1000	@ 500	@ 200	@ 100	@ 50	@ 10
BMP-FAP	1V	6.5	7.6	9.6	11.3	14.5	28.6
	2V	10.4	12.4	15.9	20.1	25.8	50.5
	3V	16.5	19.5	24.8	30.8	39.4	72.8
	4V	24.6	28.6	35.8	43.9	55.4	95.2
	5V	37.6	43.3	53.7	65.3	80.5	138
	6V	61.7	71.5	86.4	100.8	122.5	224.2
BMIM-PF6	1V	6.7	8	9.8	11	12.8	18.8
	2V	13.1	16.1	19.9	24	29	41.8
6M KOH	1V	20.8	27	34.4	43.4	46.7	75.1

References

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