Supporting Information

High performance Na-O_2 batteries and printed micro-supercapacitors based on water-processable, biomolecule-assisted anodic graphene

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Figure S1. Digital photograph of a bottle containing an aqueous anodic graphene dispersion at a concentration of 2 mg mL^{-1} derived from derived from 0.1 M AMP.

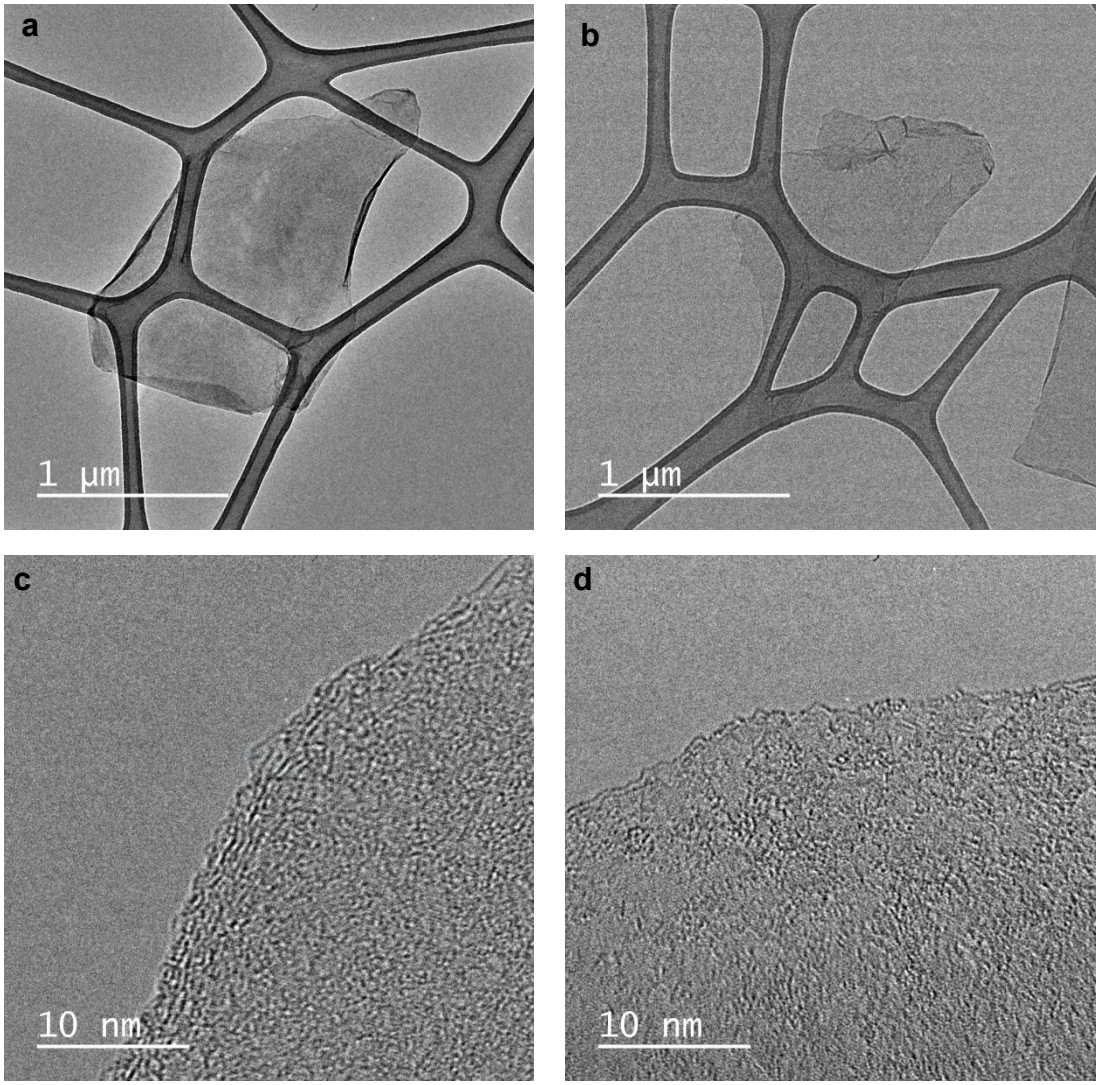

Figure S2. (a,b) TEM images of individual graphene nanosheets and **(c,d)** high resolution TEM images of flake edges. By counting the dark fringes at the flake edges, the nanosheets were found to be ≤ 5 layers thick. TEM was accomplished in a JEM-2100F system (JEOL) working at an acceleration voltage of 200 kV

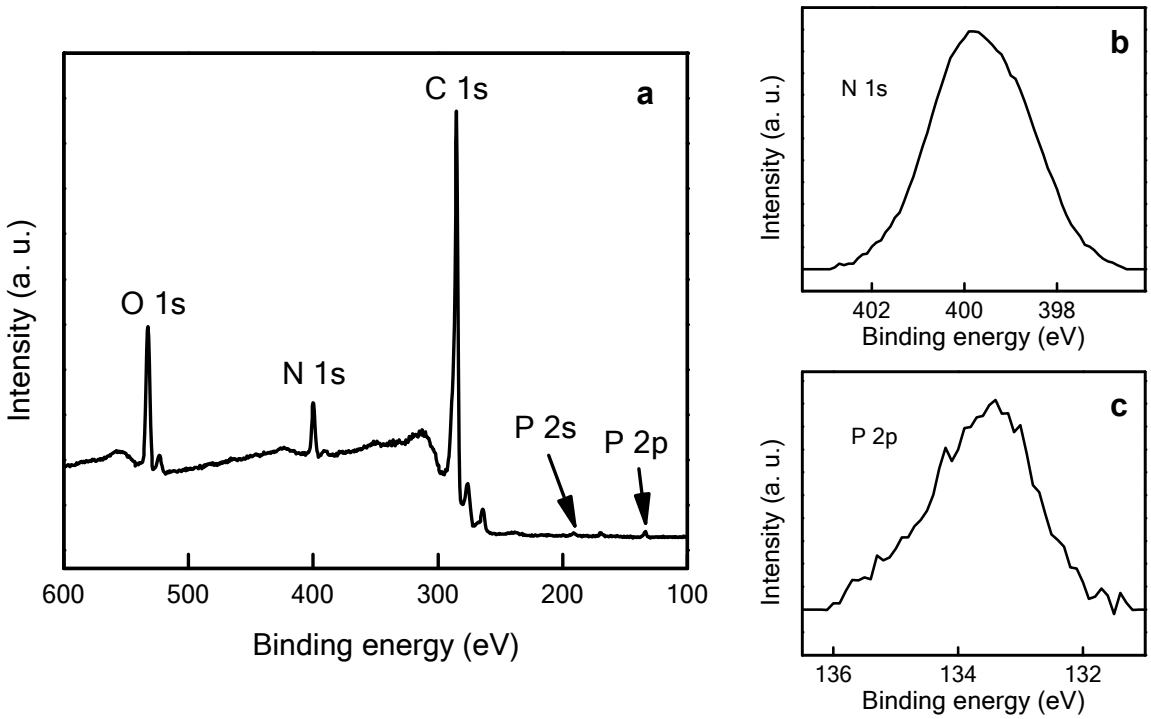

Figure S3. Additional XPS characterization of graphene nanosheets extracted by sonication in water from graphite anodically expanded using 0.1 M AMP: (a) survey spectra where the XPS bands have been labeled for clarity; background-subtracted, high resolution XPS spectra of **(b)** N1s and **(c)** P 2p core level bands. The graphene film analyzed by XPS was drop-cast from dispersion after seven washing cycles, each of them consisting of sedimentation and re-dispersion in pure water. Still, after such extensive washing, some AMP remained absorbed on its surface as reflected by its surface composition. Indeed, the P/C atomic ratio ~ 0.007, which leads to ~1 nucleotide molecule per each 7 nm^2 for a graphene monolayer. This value is just a lower limit, given that, as explained in the main text, most of the present nanosheets are few-layer flakes. Thus, the actual value should be ~1 nucleotide molecule per each 1–2 nm^2.

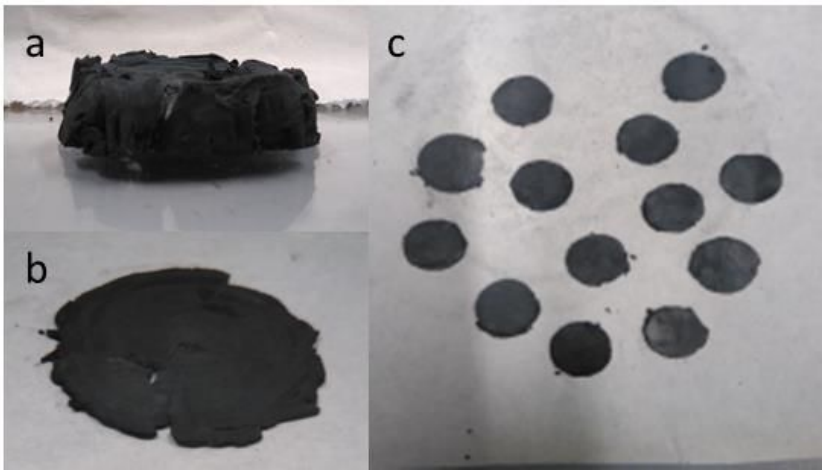

Figure S4. (a) Anodic graphene aerogel prepared using a 2 mg mL^{-1} dispersion derived from AMP. **(b)** Smashed aerogel from which (c) 0.95 cm^2 discs were cut out.

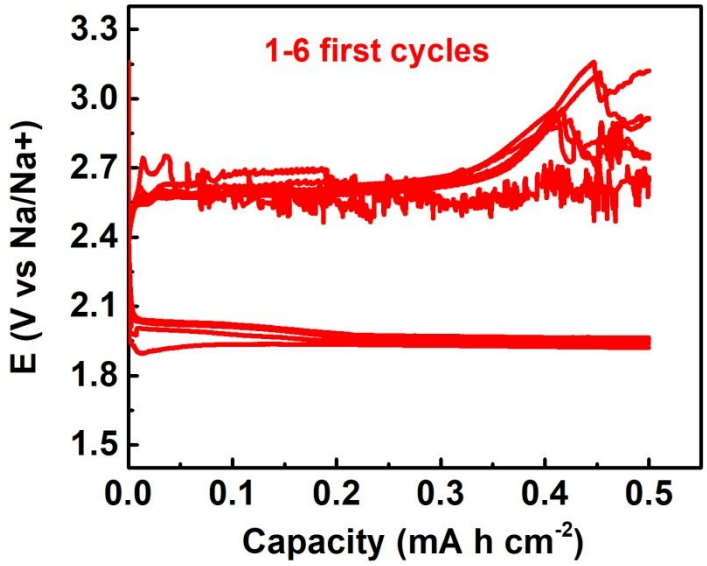

Figure S5. First cycles recorded during galvanostatic charge/discharge of graphene aerogel cathode at 0.2 mA cm^{-2} using 0.1 M $NaPF_6$ in DEGDME as the electrolyte. The observed voltage noise during the first cycles is ascribed to the formation of an electrically insulating, passivation layer on the cathode during discharge.

The cell used in this study was a modified Swagelok-type connected to a valve and a rapid gas connector, which was placed at the cathode side. A spring and a stainless steel mesh on top of the cathode to ensure the electronic conduction were placed. In order to replace the Ar inside the cell after assembling in the glove-box, the cells were purged and further pressurized with oxygen at 1 bar."

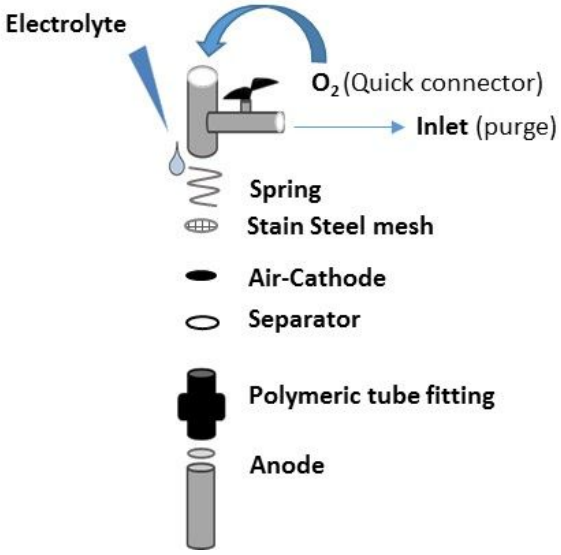

Figure S6. Schematic cell configuration of the Na-O_2 battery used in this work.

Table S1. Electrochemical performances of Na-air/O_2 batteries produced by this work and reported in literature.

		Discharge properties			Cycling performance			
Air-cathode [loading (mg) and area (cm^2)]	Electrolyte/ Environment	Capacity	Discharge product	Morphology	Voltage range (V)	Cycles	Overpotential (V)	Ref.
Graphene nanosheets [unknown]	0.25 $NaPF_6$ DME [1]	9268 mAh g^{-1} at 200 mA g^{-1}	Na_2O_2	Film	1.5-4	10 (300 mA g^{-1} to 1200 mAh g^{-1})	1.46-1.59	S1
Nitrogen doped graphene [0.3;0.71]	0.5 mol dm^{-3} $NaSO_3CF_3$ DEGDME [2]	6000 mAh g^{-1} or 3.63 mAh cm^{-2} at 75 mA g^{-1}	Na_2O_2	Small particles	1.8-3.6	3 (75 mA g^{-1} to 1150 mAh g^{-1})	0.6	S2
Graphene nanosheets with Pt nanoparticles [unknown]	1M $NaClO_4$:PC[3]	7574 mAh g^{-1} at 0.1 mA cm^{-2}	Na_2CO_3	Nanometric particles	2-3.5	10 (0.1 mA cm^{-2} to 100 mAh g^{-1})	1.3	S3
Ag-reduced graphene oxide [0.85 mg cm^{-2}]	1M $NaPF_6$ TEGDME[3]	566 mAh g^{-1} at 0.1 mA cm^{-2}	NaO_2, Na_2O_2 and Na_2O	Nanometric particles	1.5-4.5	30 (0.2 mA cm^{-2} to 0.125 mAh cm^{-2})	0.9	S4
Reduced graphene oxide [0.15;0.5]	0.25M $NaClO_4$ DME[3]	40000 mAh g^{-1} or 12 mAh cm^{-2} at 0.1 mA cm^{-2}	NaO_2	Cubic particles	1.8-2.8	17 (0.1 mA cm^{-2} to 1 mAh cm^{-2})	0.4	S5
Reduced graphene oxide aerogel [1.5-2.5;0.95]	0.1M $NaClO_4$ DME[3]	6.61 mAh cm^{-2} at 0.15-0.2 mA cm^{-2}	NaO_2	Cubic particles	1.8-3.2	40 (0.15 mA cm^{-2} to 0.5 mAh cm^{-2})	0.26	S6
3D N-doped graphene aerogel [1; 1.2]	0.3M $NaCF_3SO_3$ DEGDME[2]	10 905 mA h g_{carbon}^{-1} at 100 mA g_{carbon}^{-1}	Na_2O_2	Nanometric particles	2.0-4.0	100 (100 mA g−1 to 500 mA h g_{carbon}^{-1})	0.2	S7
This work [3-4;0.95]	0.1 M $NaPF_6$ DEGDME[3]	3.8 mAh cm^{-2} at 0.2 mA cm^{-2}	NaO_2	Cubic particles	1.8-3.2	50 (0.2 mA cm^{-2} to 0.5 mAh cm^{-2})	0.59-0.73	This work

[1] dried air
[2] 1 atm O_2
[3] O_2

Table S2. Areal and volumetric capacitance (C_A, C_V), energy (E_A, E_V) and power (P_A, P_V) values of a range of graphene-based electrodes determined with a two-electrode system. In general, the areas are those of the whole device, including the gaps between fingers. The thickness of the electrode material (t) is also indicated.

Material	T (μm)	I_A (μA cm^{-2})	C_A (mF cm^{-2})	E_A (μW h cm^{-2})	P_A (mW cm^{-2})	I_V (A cm^{-3})	C_V (F cm^{-3})	E_V (mW h cm^{-3})	P_v (W cm^{-3})	Ref.
reduced GO (rGO)	7.6	0.013	2.32	0.152	152	0.0168	3.05	0.2	200	S8
rGO	-	20	2.0	-	-	-	-	-	-	S9
N-doped rGO	10	20	3.4	0.3	0.2	0.02	3.4	0.3	0.2	S9
Graphene/ethylcellulose (EC) by LPE	0.04	1	0.07	0.01	0.16	0.25	17.8	2.47	40.3	S10
Graphene/EC by LPE	0.32	-	0.268	0.035	0.0045	-	8.38	1	0.01	S11
Graphene/EC by LPE	0.027	0.025	0.099	0.005	0.0001	0.009	36.7	~2	~0.04	S12
Electrochemically exfoliated graphene (EG)	0.5	-	0.8	-	-	-	16	-	-	S13
EG/PH1000 hybrid	2	-	5.4	-	-	-	27	-	-	S13
EG	0.75	-	0.7	0.075	0.0075	-	9.3	1	0.1	S14
EG	0.1	-	0.313	0.02	0.0004	-	31.3	~2	~0.04	S15
F-doped EG	0.7	0.014	14.2	3.92	1.47	0.2	110	56	21	S16
EG	0.4	-	0.441	-	-	-	1.16	-	-	S17
AMP-EG	0.3	5.4	0.27	0.03	0.003	0.2	8.5	1.2	0.1	This work

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