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Supplementary Information

Flat-shaped carbon-graphene microcomposites as electrodes for high energy supercapacitors

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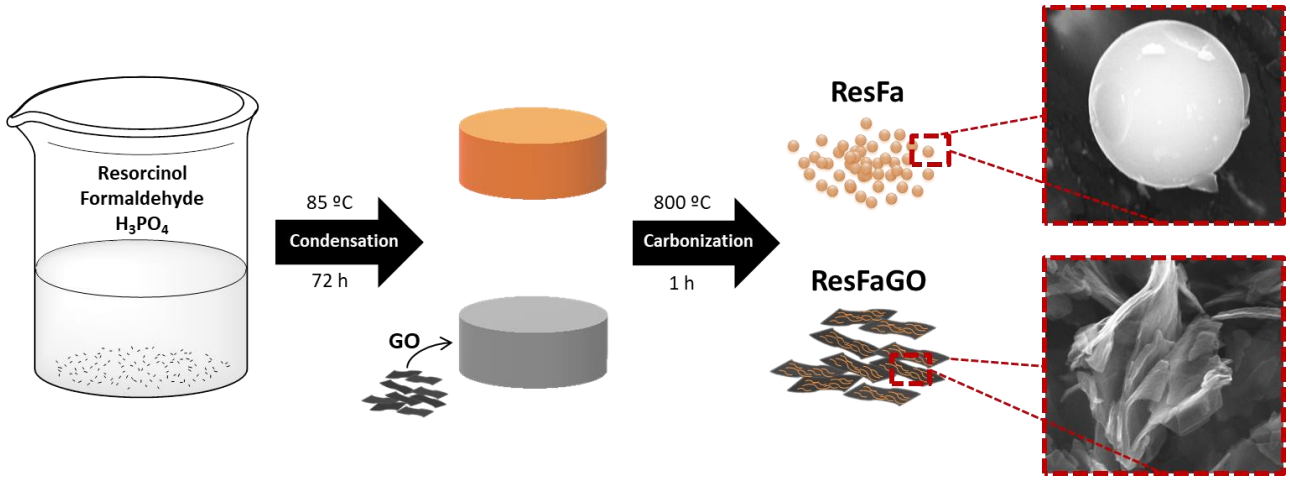

Scheme S1. Schematic route for the preparation of ResFa and ResFaGO samples.

Table S1. Chemical composition of the carbonaceous samples measured by Energy Dispersive X-ray spectroscopy (EDX).

Sample	C (wt. %)	O (wt. %)	P (wt. %)
ResFa	84.1	5.6	10.3
ResFaGO	95.6	2.4	2.0
ResFaGO-A	93.7	6.3	0

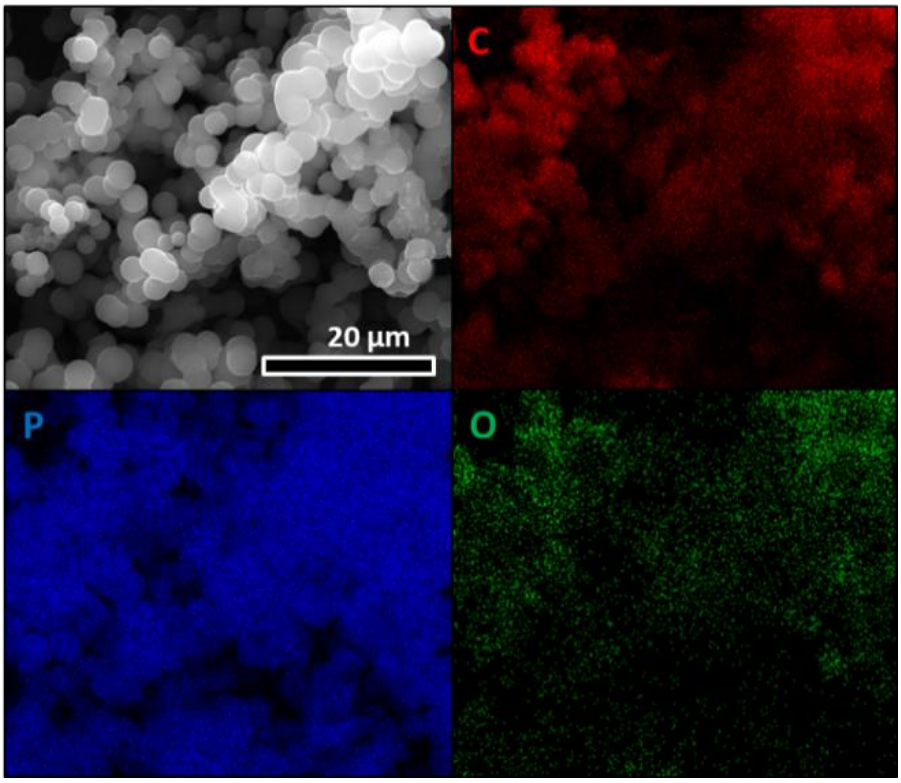

Figure S1. Elemental mapping showing the carbon (C, red), phosphorous (P, blue) and oxygen (O, green) distribution in the ResFa surface.

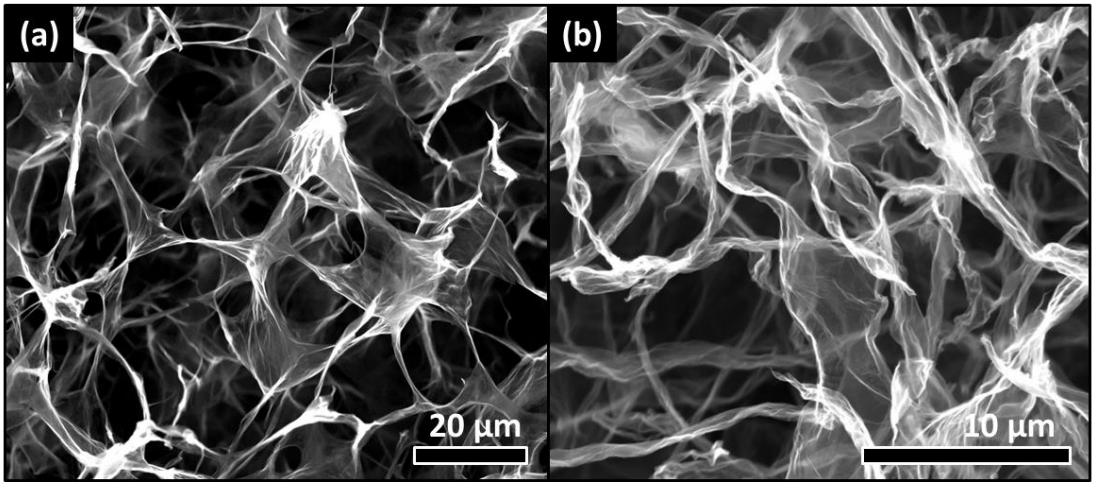

Figure S2. SEM images of (a) pristine graphene oxide and (b) thermally reduced graphene oxide at 800 ºC.

Nitrogen adsorption-desorption isotherms registered for the GO and rGO are depicted in Figure S3. Both graphene-based materials show a similar adsorption profile matching with type-II isotherms, typical of mesoporous materials, according to IUPAC classification. This characteristic porosity is related to the interparticle voids generated between the graphene sheets. The larger slope on the nitrogen uptake together with a marked hysteresis loop in rGO sample reveals the presence of narrower mesopores in the pyrolized material. BET SSA values of 21 and 76 $m^2 g^{-1}$ are obtained for GO and rGO respectively. The slight increase of the specific surface area observed in the rGO sample can be ascribed to the partial rearrangement and wrinkle of the graphene sheets during the thermal treatment due to the removal of oxygen surface functionalities during pyrolysis.

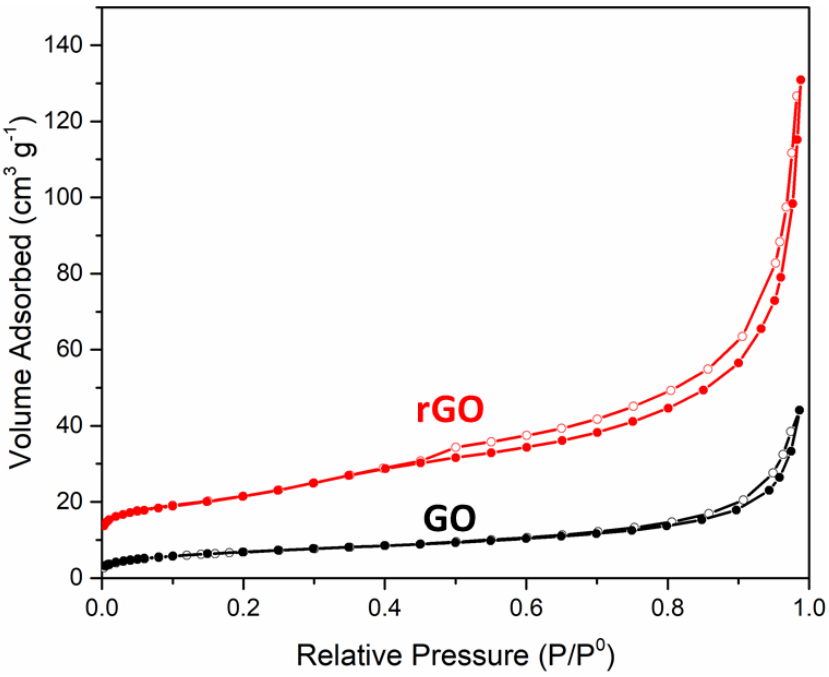

Figure S3. Nitrogen adsorption/desorption isotherms registered at -196 ºC of the pristine graphene oxide and (GO) thermally reduced graphene oxide at 800 ºC (rGO).

The surface chemistry of the ResFa sample was studied by X-Ray Photoelectron Spectroscopy (XPS) and deconvolution of the high-resolution core level spectra of P2p (128-144 eV region) (Figure S4). The P2p a spectrum was satisfactory deconvoluted by means of two energy stages, P2p3/2 and P2p1/2, which confirm the existence of phosphate groups. The fist peak centered at 132.9 eV is ascribed to the presence of phosphate groups while the second peak arising around 133.8 eV is associated with the existence of diphosphates and metaphosphates.

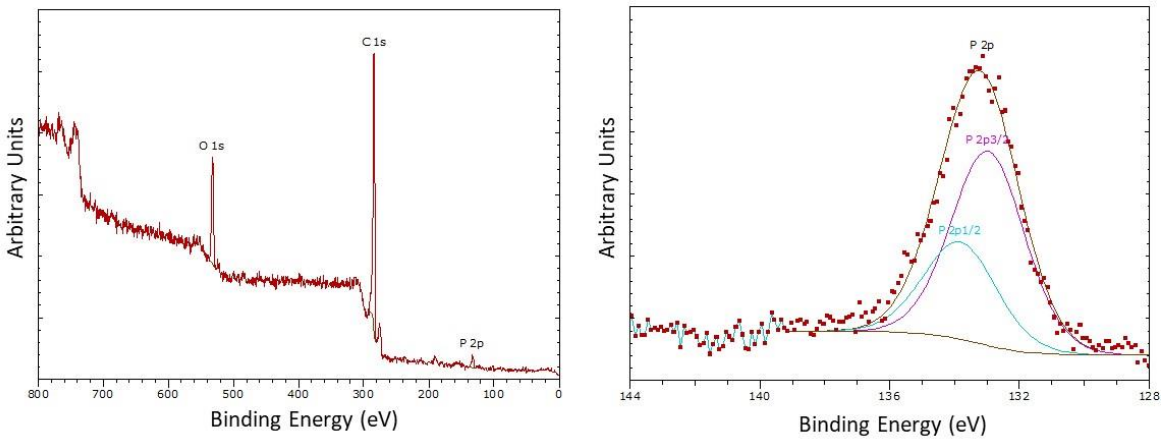

Figure S4. XPS survey spectra (a) and deconvolution analysis of P 2p peak (b) registered for the ResFa sample.

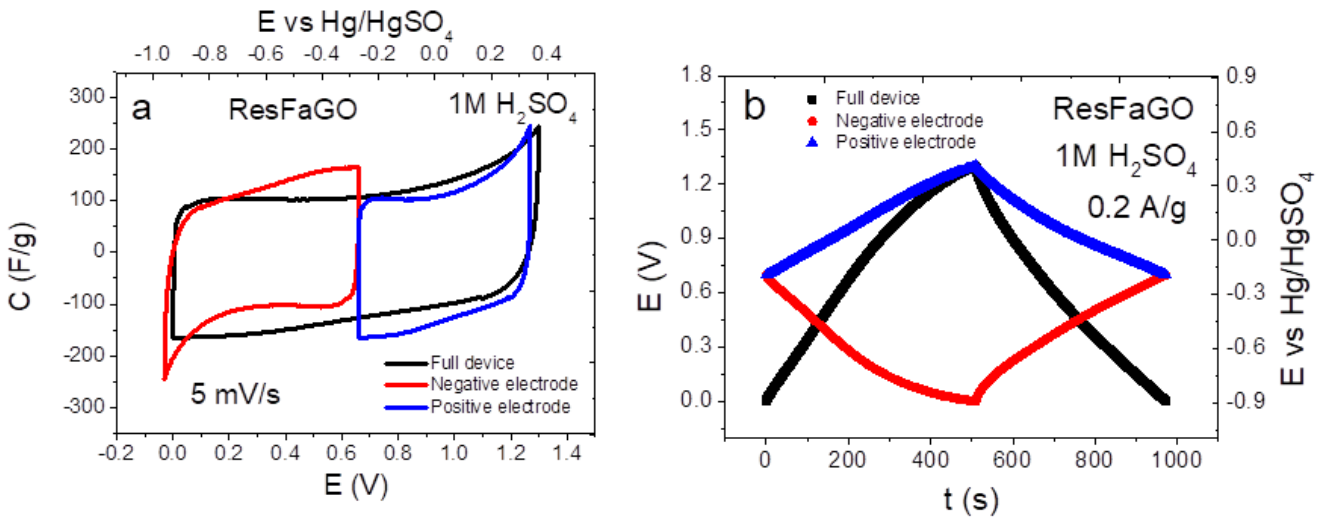

Figure S5. Individual contribution of both negative and positive electrodes to the full device of ResFaGO sample in the aqueous electrolyte 1M H_2SO_4 during cyclic voltammetry at 5 mV/s (a) and galvanostatic charge-discharge at 0.2 A g^{-1} (b).

Table S2. Performance of some representative porous materials as electrodes for supercapacitors in organic electrolyte.

Material	Activation	Electrolyte	Specific Capacitance ($F \cdot g^{-1}$)	Voltage window (V)	Energy density ($W \cdot h \cdot Kg^{-1}$)	Reference
PICACTIF Activated carbon (Ac)	Yes	1.5 M TEABF4/AN	100	2.3	17	[1]
Maxsorb, OPTI Activated carbons (Acs)	Yes	1 M TEABF4/ AN	110 100	2.5	---	[2]
Phenolic resins activated carbon (Ac)	No Yes	1 M TEABF4/ AN	6.9 89.5	2.5	---	[3]
Three-D activated carbon (Ac)	Yes	1 M TEABF4/ AN	119	2	16.52	[4]
Carbide derived carbon (CDC)	No	1.2 M TEMA	120	2.7	---	[5]
Multi-walled carbon nanotubes (MWNTs)	Yes	1.4 M TEABF4/ AN	65	2	---	[6]
Zeolite template carbon (ZTC)	Yes	1.5 M TEABF4/ AN	160	2.4	30	[7]
Zeolite template carbon (ZTC)	No	TEABF4/ AN	146	2.3	---	[8]
CMK-3 Order mesoporous carbon	No	1 M TEABF4/ PC	45	2	---	[9]
Carbon from graphene oxide-phenolic resins	No Yes	1.5 M TEABF4/ AN	61 105	2.7 2.6	15.4 25.5	This work

REFERENCES

1 P. L. Taberna, P. Simon and J. F. Fauvarque, *J. Electrochem. Soc.*, 2003, **150**, A292.

2 P. Azaïs, L. Duclaux, P. Florian, D. Massiot, M.-A. Lillo-Rodenas, A. Linares-Solano, J.-P. Peres, C. Jehoulet and F. Béguin, *J. Power Sources*, 2007, **171**, 1046–1053.

3 R. Heimböckel, S. Kraas, F. Hoffmann and M. Fröba, *Appl. Surf. Sci.*, 2018, **427**, 1055–1064.

4 W. Zhao, Y. Zhu, L. Zhang, Y. Xie and X. Ye, *J. Alloys Compd.*, 2019, **787**, 1–8.

5 M. Arulepp, J. Leis, M. Lätt, F. Miller, K. Rumma, E. Lust and A. F. Burke, *J. Power Sources*, 2006, **162**, 1460–1466.

6 E. Frackowiak, S. Delpeux, K. Jurewicz, K. Szostak, D. Cazorla-Amoros and F. Béguin, *Chem. Phys. Lett.*, 2002, **361**, 35–41.

7 H. Wang, Q. Gao, J. Hu and Z. Chen, *Carbon*, 2009, **47**, 2259–2268.

8 C. Portet, Z. Yang, Y. Korenblit, Y. Gogotsi, R. Mokaya and G. Yushin, *J. Electrochem. Soc.*, 2009, **156**, A1.

9 S. Inagaki, Y. Yokoo, T. Miki and Y. Kubota, *Microporous Mesoporous Mater.*, 2013, **179**, 136–143.