Electronic Supplementary Information (ESI)

Freestanding three-dimensional graphene foam gives rise to beneficial electrochemical signatures within non-aqueous media

Dale A. C. Brownson, Luiz C. S. Figueiredo-Filho[1], Xiaobo Ji[2], Maria Gómez-Mingot[3], Jesús Iniesta[3], Orlando Fatibello-Filho[1], Dimitrious K. Kampouris and Craig E. Banks*

Faculty of Science and Engineering, School of Science and the Environment, Division of Chemistry and Environmental Science, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, Lancs, UK.

[1]: Visiting student from: Departamento de Química, Universidade Federal de São Carlos, São Carlos - SP, Brazil, P.O. Box 676, 13560-970.

[2]: Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083,China.

[3]: Physical Chemistry Department and Institute of Electrochemistry, University of Alicante, 03690, San Vicente del Raspeig, Alicante, Spain.

*Corresponding author:
Email: c.banks@mmu.ac.uk; Tel: ++(0)1612471196; Fax: ++(0)1612476831
Website: www.craigbanksresearch.com

---

1. Freestanding 3D carbon foam: physical characterisation

Throughout the experimental (electrochemical) characterisation of our freestanding 3D graphene foam electrode we utilise an alternative (commercially available) freestanding 'carbon' foam for comparative purposes to allow the electronic properties and applicability of our new and

intriguing material to be correctly 'benchmarked'.

The alternative 3D foam is comprised of reticulated vitreous carbon (RVC), essentially meaning that it is a micro-porous glassy carbon electrode material and as such the characterisation in addition to the electrochemistry of glassy carbon materials are well known and widely reported throughout the literature. [1] The RVC foam structure is generally achieved by polymerisation of a resin combined with foaming agents, followed by carbonisation. The result is a low volume disordered glassy porous carbon with some crystallographic order, low electrical resistance and a continuous skeletal structure. [1]

SEM images of the freestanding 3D RVC foam are depicted in Fig. S3 where it is evident that the foam exhibits a similar architecture to the 3D graphene alternative, revealing a well-defined 3D macro-porous structure with an average pore diameter of *ca*. 400 μm (note that a correction factor is employed between the two foams to allow direct comparison of the voltammetry given that they exhibit different pore sizes – see Experimental section). [1] At a higher magnification it is evident that unlike at the 3D graphene, where wrinkles and ripples are evident from the synthesis process, the 3D carbon foam does not exhibit such micro-structural characteristics and instead exhibits a smooth continuous surface with less structural defects.

Raman spectroscopy of the 3D carbon foam (Fig. S4) reveals two characteristic bands: D (1321 cm^{-1}) and G (1593 cm^{-1}) and a wide G' band at *ca*. 2800 cm^{-1}; which as reported widely in the literature is consistent with glassy carbon (RVC). [2]

XPS was conducted on the 3D carbon foam which revealed it to exhibit a similar structural composition to graphene however with different percentage compositions in terms of the carbon and oxygen content. Analysis of the XPS de-convoluted spectra for the RVC foam reveals that of the 88.8 % composition of carbon (C1s), 69.2 % corresponded to 284.6 eV which is characteristic of graphitic groups from –C-C- and –C-H- bonds, whereas 15.6 % was at 286 eV and 4 % at 289 eV which correspond to –C=O and O=C-O respectively. The oxygen content (9.6 %) resulted from 7.2 % of O1s at 531.7 eV which correspond to C–OH groups, and 2.4 % at 533.3 eV which corresponds to groups such as -C=O, O=C-O or -C-O bonds. Unlike at the 3D graphene foam, impurities (sulphide) were present, making up a 1.6 % composition at 170 eV (corresponding to CS_2 bonds presumably) and of further note is that traces of N could occasionally/rarely be seen at 396 eV. Note that while the 3D graphene foam exhibits an oxygen

composition of *ca*. 5.0 %, the 3D carbon (RVC) alternative comprises of *ca*. 9.6 %, of which the highly oxygenated species of O=C are 4 % for the 3D carbon foam and 1 % for the 3D graphene.

Figure S1

XPS spectra of our freestanding 3D graphene foam. Overall spectrum (**A**) and de-convoluted C1s (**B**) and O1s (**C**) regions.

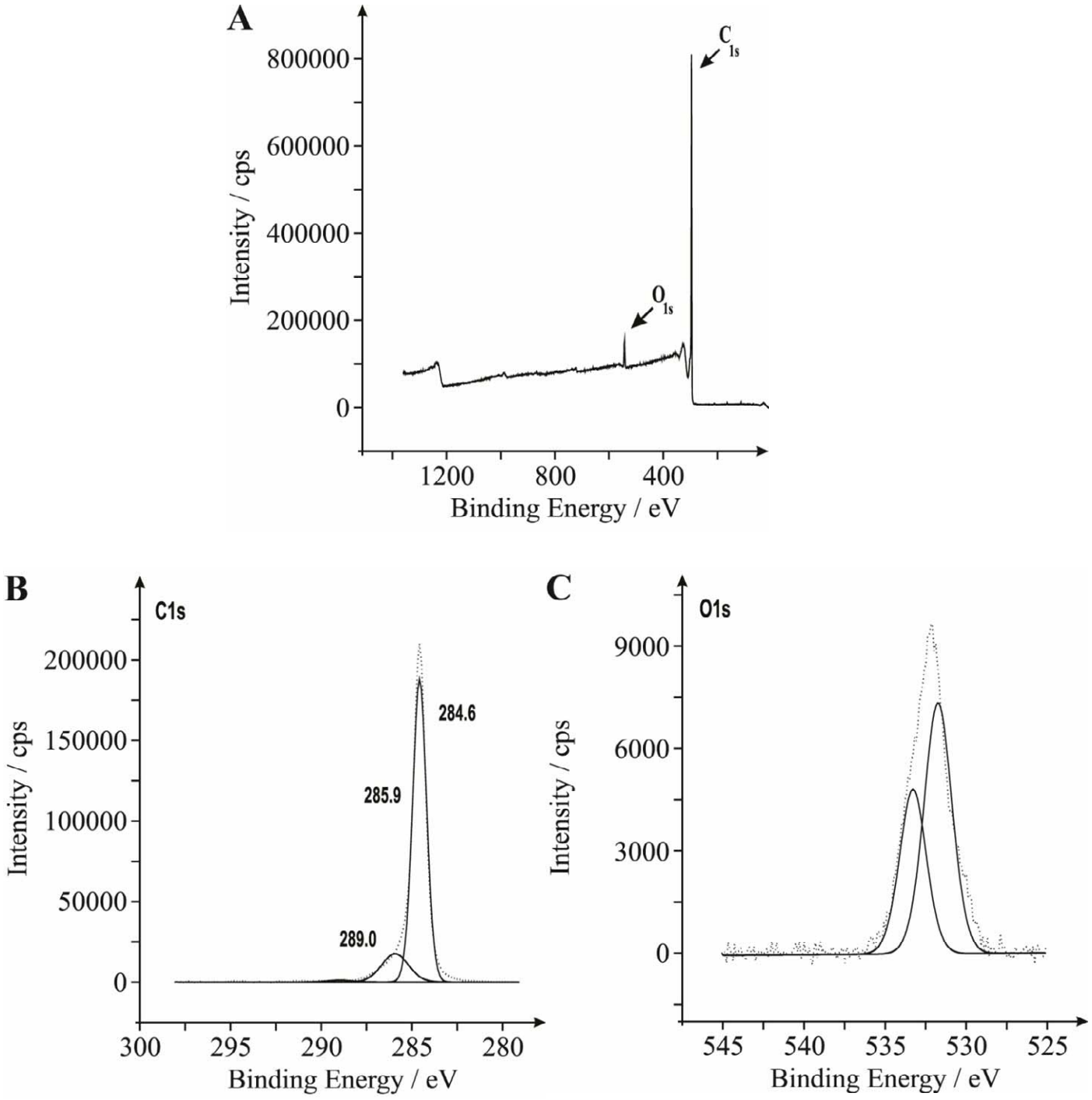


Figure S2

Optical images depicting the oleophilic capabilities of our freestanding 3D graphene foam: (**A**) a drop of 3-octanol (with added iodine to produce a colour contrast) is placed onto the surface of water; (**B**) the 3D graphene foam is positioned; (**C**) the 3D graphene is introduced to the 3-octanol/water where the 3-octanol is immediately and completely absorbed into the freestanding 3D graphene foam; (**D**) removal of the foam from the water surface, and with it, the complete removal of 3-octanol.

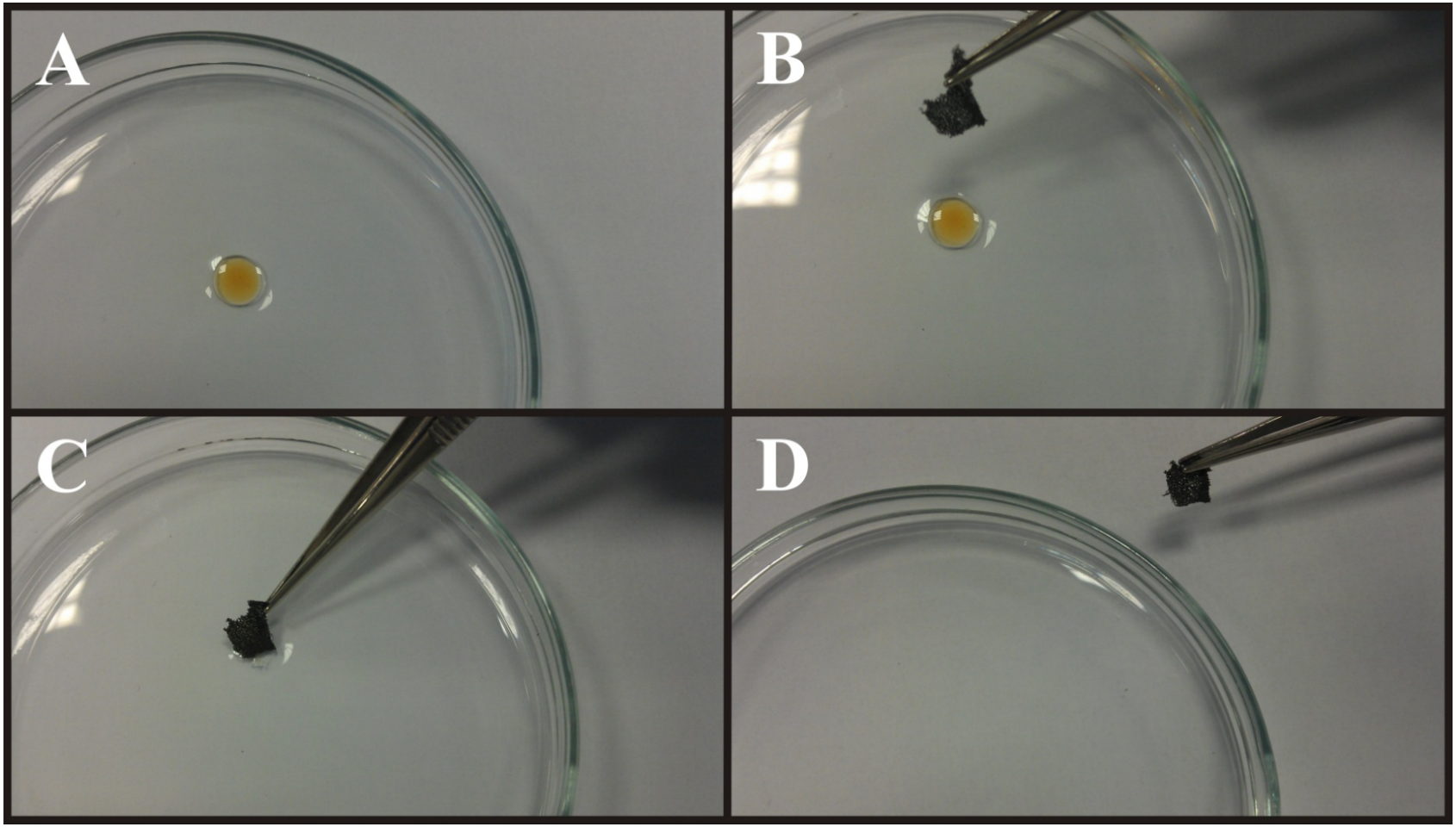


Figure S3

SEM image of the freestanding 3D Reticulated Vitreous Carbon (RVC) foam (**A**); and at a higher magnification (**B**).

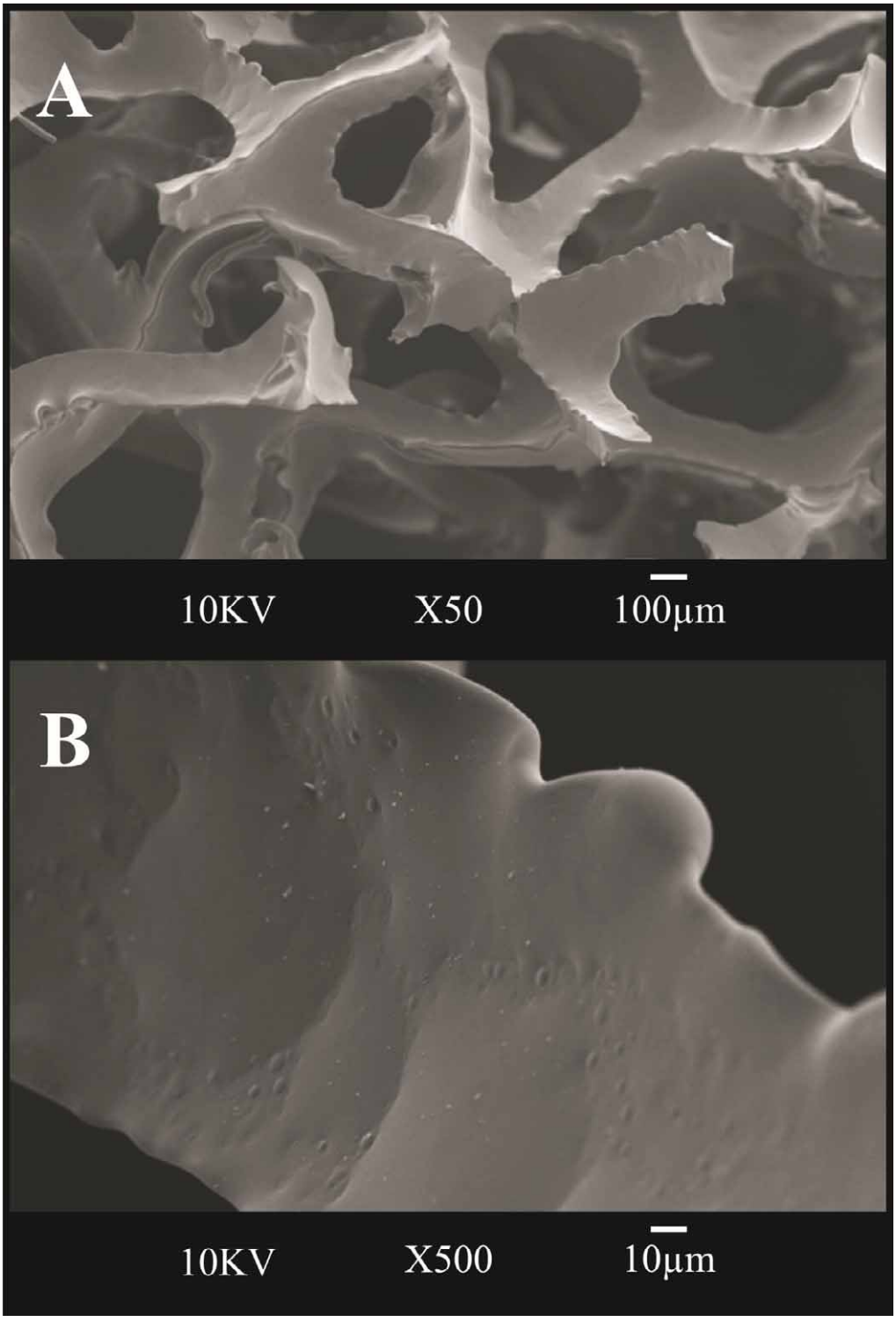
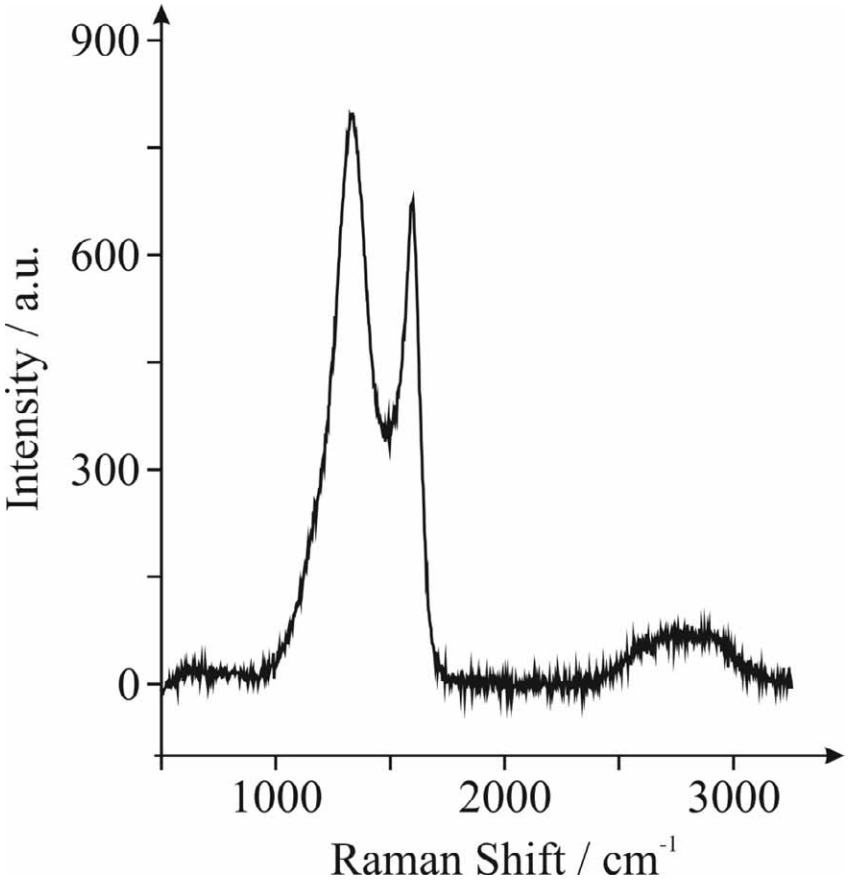


Figure S4

Raman spectra of the freestanding 3D carbon (RVC) foam.



References:

1. J. M. Friedrich, C. Ponce-de-Leon, G. W. Reade and F. C. Walsh, *J. Electroanal. Chem.*, 2004, **561**, 203.
2. Y. Wang, D. C. Alsmeyer and R. L. McCreery, *Chem. Mater.*, 1990, **2**, 557.