Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

HIGH DENSITY GRAPHENE-CARBON NANOSPHERES FILMS FOR CAPACITIVE ENERGY STORAGE

Noel Díez[a,b*], Mo Qiao[b], Juan Luis Gómez-Urbano[a], Cristina Botas[a], Daniel Carriazo[a,c*] and Maria Magdalena Titirici[b].

[a] *CIC EnergiGUNE, Parque Tecnológico de Álava, Albert Einstein 48, 01510 Miñano, Álava, Spain*

[b] *School of Engineering and Materials Science and Materials Research Institute, Queen Mary University of London, London, United Kingdom*

[c] *IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain*

*Corresponding author: noel@incar.csic.es; dcarriazo@cicenergigune.com

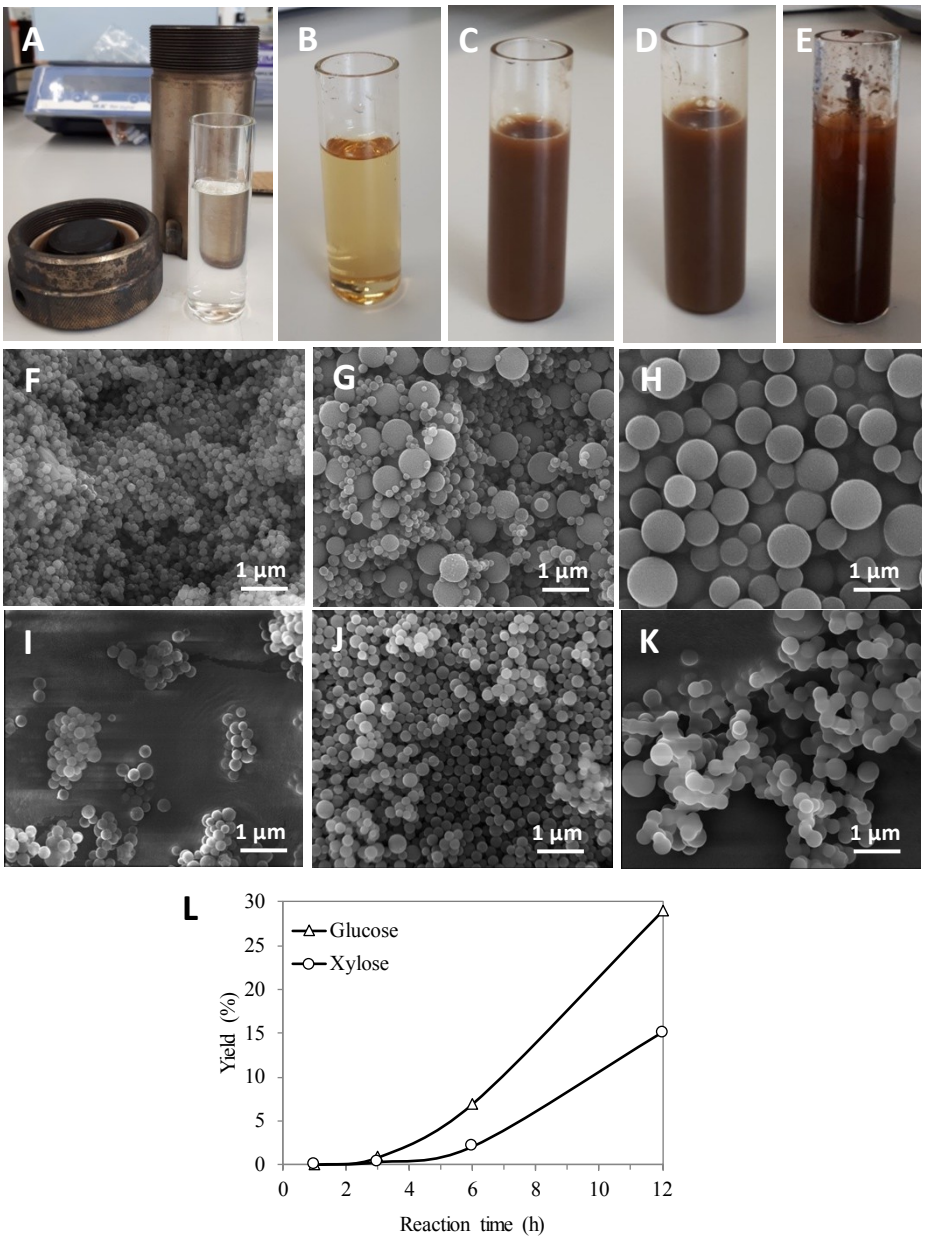

Figure S1. Digital images of (A) xylose solution and reaction products after (B) 1 h, (C) 3 h, (D) 6 h and (E) 12 h of hydrothermal treatment. FE-SEM images of the hydrochars obtained from xylose and glucose at different reaction times: xylose-3h (F), xylose-6h (G), xylose-12h (H), glucose-3h (I), glucose-6h (J) and glucose-12h (K). (L) Evolution of the hydrothermal reaction yields vs. reaction time with respect to the initial mass of the saccharide.

Supplementary Note 1: Synthesis of the sugar-derived carbon nanospheres.

It has been previously reported that hexose sugars decompose upon hydrothermal treatment giving rise to hydroxymethilfurfural as one of the main products, which will further condensate into a carbon-like material. On the contrary, Xylose derivatives dehydrate into furfural, which condensates into carbons with more aromatic structures.[1] After subjecting a xylose solution (Figure S1A) to hydrothermal treatment for 1 h, a yellowish solution was obtained (**Figure S1B**) and no solid product was recovered by centrifugation. After 3 and 6 h, a brown dispersion was obtained, and longer reaction times of 12 h led to well-distinguished solid and liquid fractions (**Figure S1C-E**). Glucose-based products (not shown) had the same appearance at the same reaction times. As can be seen in **Figure S1L**, the mass yield of each hydrothermal carbonization increased with the reaction time, from 1 wt.% (3h) to 29 wt.% (12 h) in the case of glucose and from 0.3 wt.% (3h) to 15 wt.% (12h) in the case of the xylose-derived hydrochar. The morphology and particle size of the different hydrochars were observed by FE-SEM. Carbon spheres obtained from xylose after 3 h of hydrothermal treatment had a very small and uniform size of ~ 100 nm (**Figure S1F**). However, these spheres were obtained in a very low yield of 0.3 %. At a reaction time of 6 h, spheres with a bimodal size distribution were obtained (**Figure S1G**). The majority of the spheres had a very small size of 60-120 nm, and a smaller number of them had larger a size of ~ 500 nm. When reaction time was increased to 12 h, a mixture of spheres with sizes between 500 nm and 1 micron was observed (**Figure S1H**). In the case of glucose, an increase of the size of the carbon spheres with the reaction time

was analogously observed. In this case, discreet carbon spheres with a size between 150 and 250 nm were obtained after 3 and 6 h of reaction (**Fig. S1I and J**). After 12 h of reaction, the carbon spheres merged and peanut-shaped particles or agglomerated clusters were obtained instead of independent spheres (**Fig. S1K**). Carbon nanospheres prepared from xylose and glucose under hydrothermal treatment for 6 h were selected for the formulation of the composites, since they combined a small sphere size with a reasonable reaction yield.

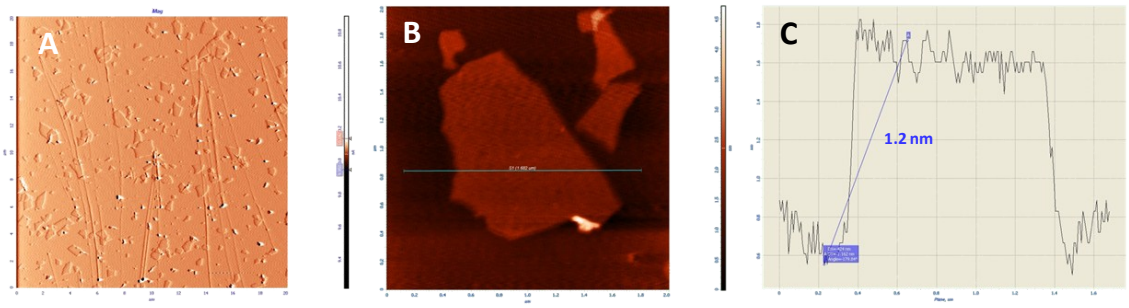

Figure S2. (A and B) AFM images and (C) height profile of the graphene oxide.

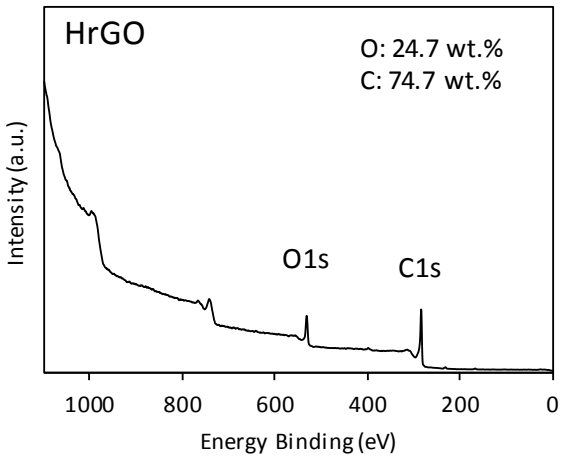

Figure S3. Survey XPS spectra and chemical composition of the HrGO film.

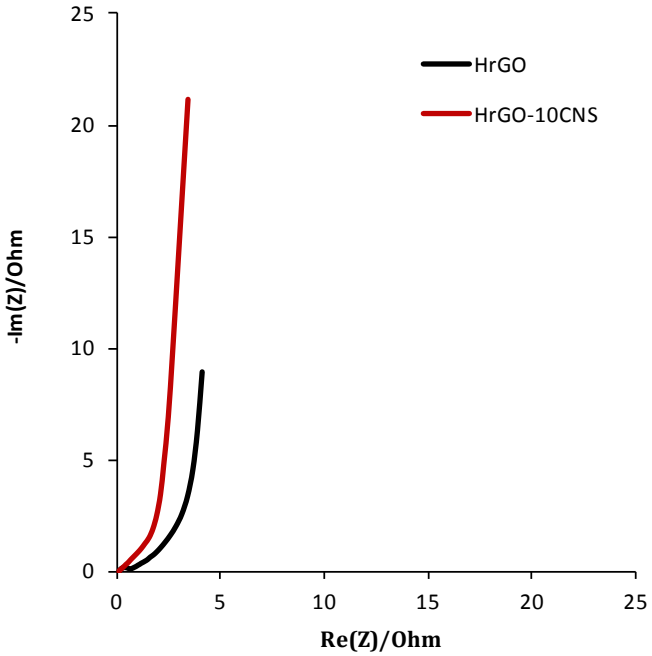

Figure S4. Nyquist impedance plot of symmetric supercapacitors built with HrGO and HrGO-10CNS films.

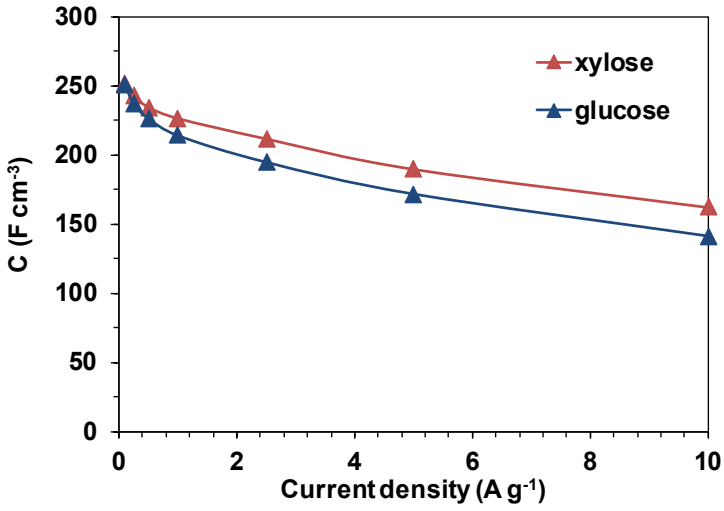

Figure S5. Evolution of the volumetric capacitance with the current density for HrGO-10CNS electrodes containing nanospheres derived from xylose and glucose.

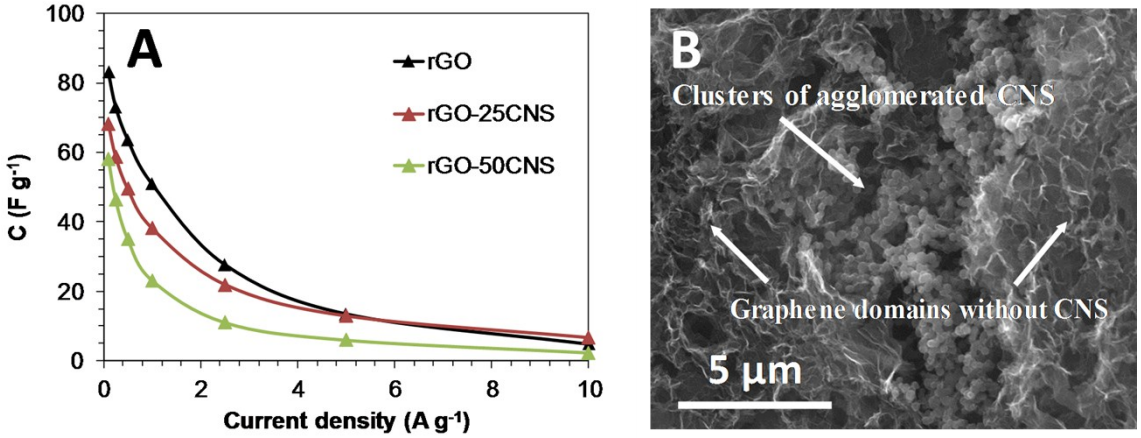

Figure S6. (A) Rate capability of the carbonized films containing a 25 and 50 wt.% of CNS. (B) SEM images of the rGO-25CNS film.

[1] M. M. Titirici and M. Antonietti, *Chemical Society Reviews*, 2010, **39**, 103-116