Supporting information

High voltage solid state symmetric supercapacitor based on graphene-polyoxometalate hybrid electrode with hydroquinone doped hybrid gel electrolyte

Deepak P. Dubal,[a] Jullieth Suarez-Guevara,[a] Dino Tonti,[b] Eduardo Enciso,[c] Pedro Gomez-Romero [a]***

[a]Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

[b]ICMAB (CSIC), Campus UAB E-08193 Bellaterra, Barcelona, Spain

[c]Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid (UCM) Campus Moncloa, Madrid, Spain

Supporting information S1

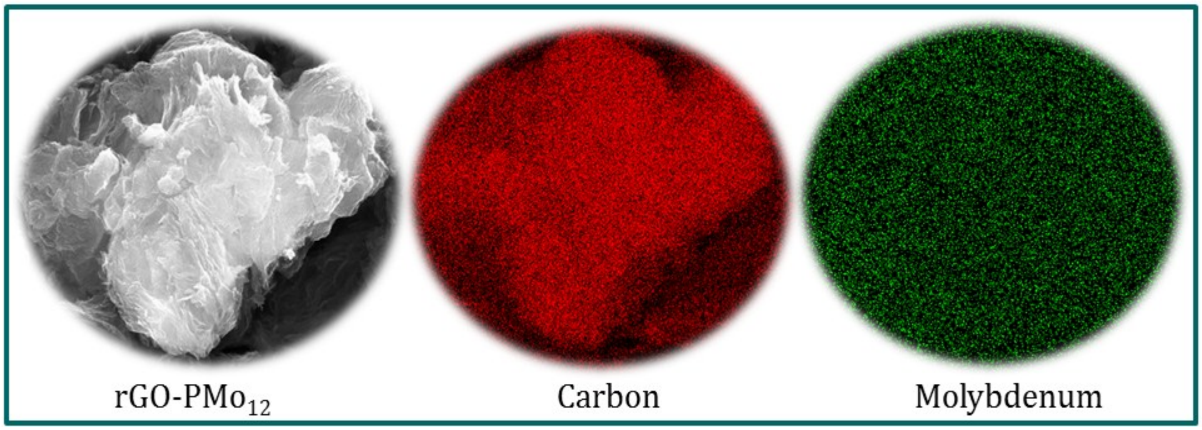

Figure S1 Scanning electron micrograph (SEM) with EDS mapping of rGO-PMo_{12} sample confirming the presence of carbon and molybdenum.

Supporting information S2

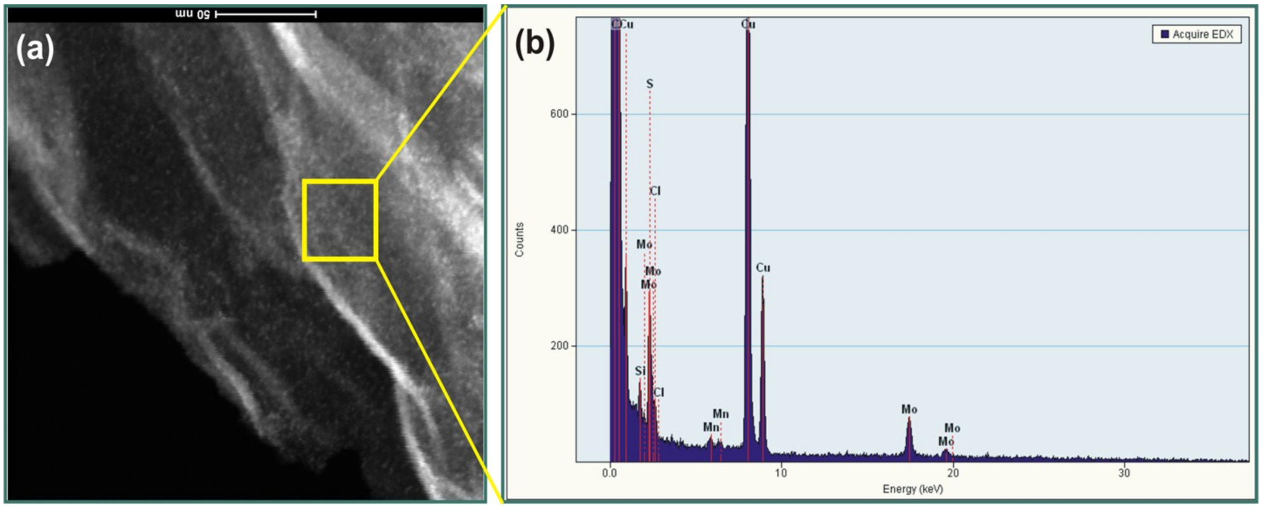

Figure S2 (a) Scanning transmission electron micrograph (STEM) with corresponding EDS spectrum of rGO-PMo_{12} hybrid material

Supporting information S3

Calculations:

The cell (device) capacitance (*C*) and volumetric capacitance of the symmetric devices were calculated from their CVs according to the following equation:

$$C_{cell} = \frac{Q}{\Delta V} \quad (1)$$

$$C_A = \frac{Q}{A \times \Delta V} \quad \text{and} \quad C_V = \frac{Q}{V \times \Delta V} \quad (2)$$

where, C_A and C_V are areal and volumetric capacitances, respectively. *Q* (C) is the average charge during the charging and discharging process, V is the volume (cm^3) of the whole device (The area and thickness of our symmetric cells is about 0.785 cm^2 (Area, $A=\pi r^2$, $3.14 \times (0.5)^2$) and 0.088 cm. Hence, the whole volume of device is about 0.069 cm^3, ΔV (V) is the voltage window. It is worth mentioning that the volumetric capacitances were calculated taking into account the volume of the device stack. This includes the active material, the flexible substrate and the separator with electrolyte.

Alternatively, the cell capacitance (C_{cell}), areal (C_A) and volumetric (C_V) capacitance of the electrode (C_V) was estimated from the slope of the discharge curve using the following equations:

$$C_{cell} = \frac{I \times \Delta t}{\Delta V} \quad (4)$$

$$C_A = \frac{I \times \Delta t}{A \times \Delta V} \quad \text{and} \quad C_V = \frac{I \times \Delta t}{V \times \Delta V} \quad (5)$$

where I is the applied current, V is the volume (cm^3) of the whole device (the whole volume of our device is about 0.069 cm^3), Δt is the discharging time, ΔV (V) is the voltage window.

Volumetric energy (E, Wh/cm^3) and power density (P, W/cm) of the devices were obtained from the following equations:

$$E = \frac{1}{2 \times 3600} C_V \Delta V^2 \tag{6}$$

$$P = \frac{3600 \times E}{\Delta t} \tag{7}$$

where E (Wh/cm^3) is the energy density, CV is the volumetric capacitance obtained from Equation (5) and ΔV (V) is the voltage window, P (W/cm^3) is the power density.

Supporting information S4

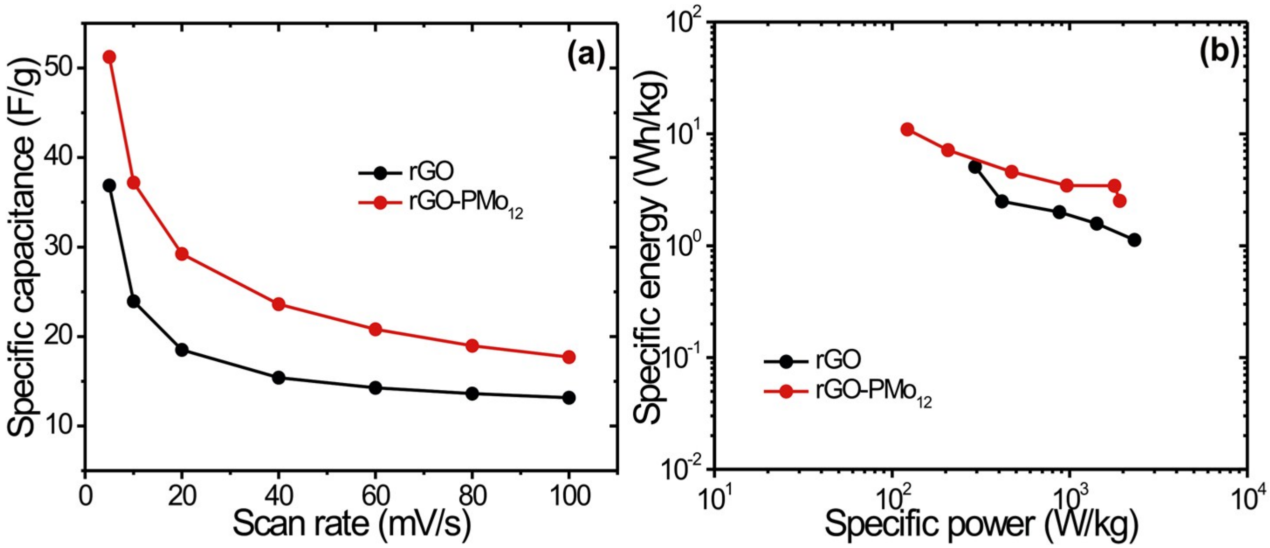

Figure S4 (a) Variation of specific capacitance with scan rate and (b) gravimetric ragone plot of rGO and rGO-PMo_{12} symmetric cells, respectively

Supporting information S5

Comparison on supercapacitive values of POM as well as metal oxide based electrodes

Electrode	Device	Electrolyte	Capacitance	Ref.
SWCNT-TBA-PV_2Mo_{10}	Symmetric	H_2SO_4	317 mF/cm^2	[1]
$H_3PMo_{12}O_{40}$/MWCNT	Symmetric	H_2SO_4	38 F/g	[2]
$H_3PMo_{12}O_{40}$/PPy//$H_3PW_{12}O_{40}$/PEDOT	Asymmetric	H_2SO_4	31 F/g	[3]
$H_3PMo_{12}O_{40}$/PAni	Symmetric	H_2SO_4	195 mF/cm^2	[4]
PAni/SiW_{12}	Symmetric	H_2SO_4	1.8 mF/cm^2	[5]
PAni/PW_{12}	Symmetric	H_2SO_4	15 mF/cm^2	[5]
MnO_2//Fe_2O_3	Asymmetric	Gel-electrolyte	1.21 F/cm^3	[6]
ZnO@MnO_2	Symmetric	Gel-electrolyte	0.325 F/cm^3	[7]
TiN	Symmetric	Gel-electrolyte	0.33 F/cm^3	[8]
Graphene	Symmetric	Gel-electrolyte	0.42 F/cm^3	[9]
ZnO@MnO_2//graphene	Asymmetric	Gel-electrolyte	0.52 F/cm^3	[10]
H-TiO_2@MnO_2//TiO_2@C	Asymmetric	Gel-electrolyte	0.70 F/cm^3	[11]
rGO-PMo_{12}	*Symmetric*	*Gel-electrolyte*	*3.18 F/cm^3 (278 mF/cm^2)*	*Present work*
rGO-PMo_{12} with HQ doped gel	*Symmetric*	*Gel-electrolyte*	*4.8 F/cm^3 (419 F/cm^2)*	*Present work*

References

[21] H. Y. Chen, R. Al-Oweini, J. Friedl, C. Y. Lee, L. Li, U. Kortz, U. Stimming, M. Srinivasan, *Nanoscale*, **2015**, 7, 7934-7941.

[2] M. Skunik, M. Chojak, I. A. Rutkowska, P. J. Kulesza, *Electrochim. Acta*, **2008**, 53, 3862-3869.

[3] G. M. Suppes, C. G. Cameron, M. S. Freund, *J. Electrochem. Soc.,* **2010**, 157,

A1030-A1034

[4] P. Gomez-Romero, M. Chojak, A. Cuentas-Gallegos, J. A. Asensio, P. J. Kulesza, N. Casan-Pastor, M. Lira-Cantu, *Electrochem. Commun.*, **2003**, 5, 149-153

[5] A. Cuentas-Gallegos, M. Lira-Cantu, N. Casan-Pastor, P. Gomez-Romero, *Adv. Funct. Mater.*, **2005**, 15, 1125-1133.

[6] X. Lu, Y. Zeng, M. Yu, T. Zhai, C. Liang, S. Xie, M. Balogun, Y. Tong, *Adv. Mater.* **2014**, *26*, 3148-3155.

[7] P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu,; T. Li, H. Jin, P. Liu, J. Zhou, C. P. Wong, Z. L. Wang, *ACS Nano* **2013**, 7, 2617-2626

[8] X. H. Lu, G. M. Wang, T. Zhai, M. H. Yu, S. L. Xie, Y. C. Ling, C. L. Liang, Y. X. Tong, Y. Li, *Nano Lett.* **2012**, 12, 5376-5381.

[9] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, 335, 1326-1330.

[10] W. Zilong, Z. Zhu, J. Qiu, S. Yang, *J. Mater. Chem. C,* **2014**, 2, 1331-1336.

[11] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong, Y. Li, *Adv. Mater.* **2013**, *25*, 267-272.

Supporting information S6

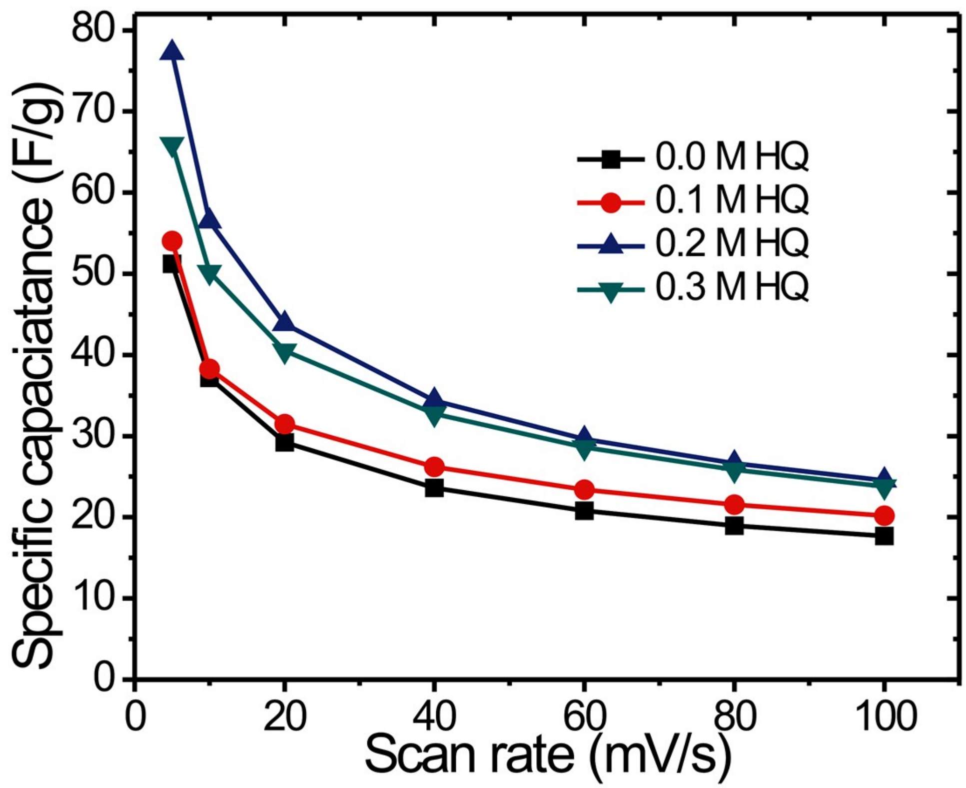

Figure S6 Variation of specific capacitance with scan rate for rGO-PMo_{12} symmetric cell at different concentrations of HQ doped gel-electrolyte.

Supporting information S7

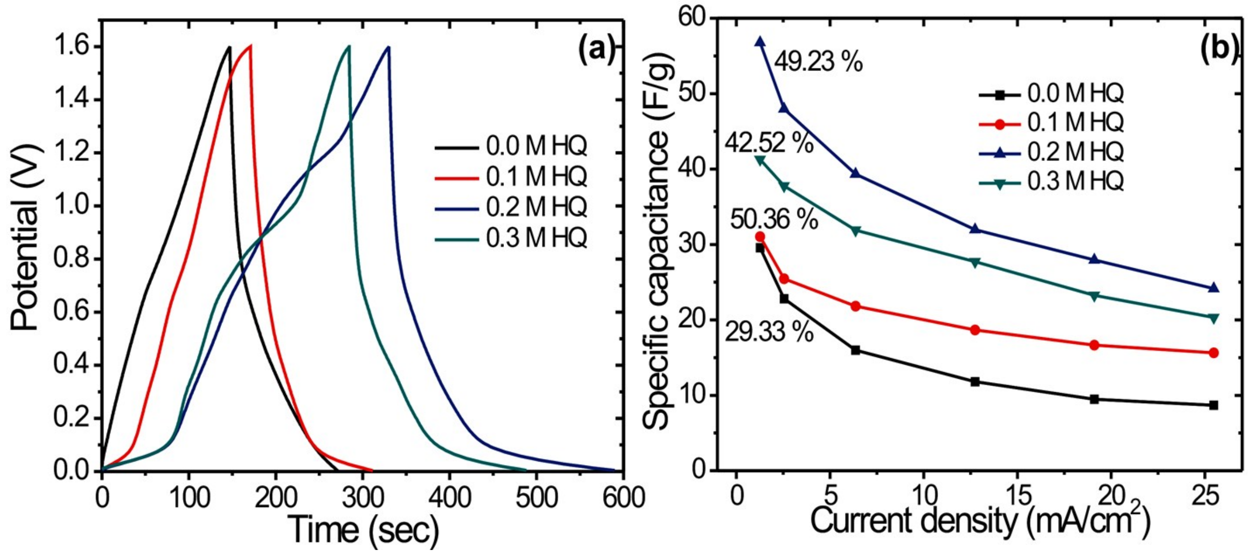

Figure S7 (a) Galvanostatic charge/discharge curves of rGO-PMo_{12} symmetric cell at different concentrations of HQ doped gel-electrolyte; (b) Variation of specific capacitance of rGO-PMo_{12} cell with current density at different concentrations of HQ doped gel-electrolyte.