

## Supporting Information

### AUTHORS:

Víctor Fernández-Jiménez<sup>1</sup>

Santiago de Bernardi-Martín<sup>4</sup>

Alejandra García-Gómez<sup>4</sup>

David López-Díaz<sup>1, 2, 3</sup>

M. Jesús Sánchez-Montero<sup>1, 2, 3</sup>

M. Mercedes Velázquez<sup>1, 2, 3</sup>

M. Dolores Merchán<sup>1, 2, 3\*</sup>

<sup>1</sup> *Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Salamanca, E37008, Salamanca, Spain.*

<sup>2</sup> *Grupo de Nanotecnología, Universidad de Salamanca, E37008, Salamanca, Spain.*

<sup>3</sup> *Laboratorio de Nanoelectrónica y Nanomateriales, USAL-NANOLAB, Universidad de Salamanca, E37008, Salamanca, Spain.*

<sup>4</sup> *Gnanomat S.L., Madrid, E28049 Spain.*

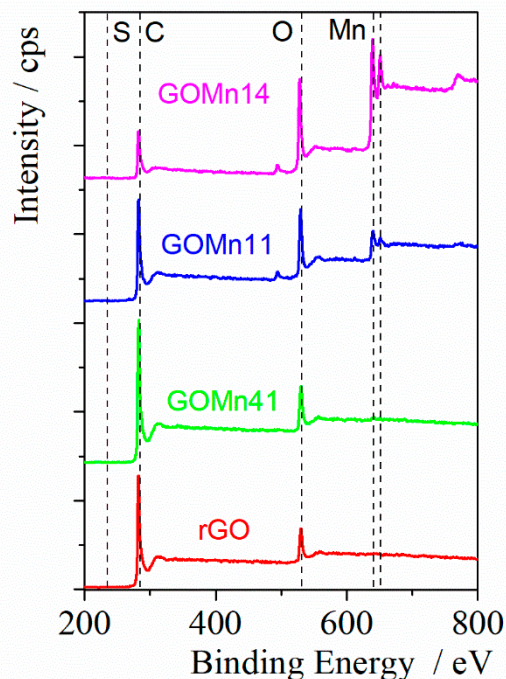
\* *Correspondence: [mdm@usal.es](mailto:mdm@usal.es); ORCID: 0000-0003-3573-3805*

**MANUSCRIPT TITLE:** The role of the manganese content on the properties of Mn<sub>3</sub>O<sub>4</sub> and reduced graphene oxide nanocomposites for supercapacitor electrodes

**NUMBER OF PAGES:** 4

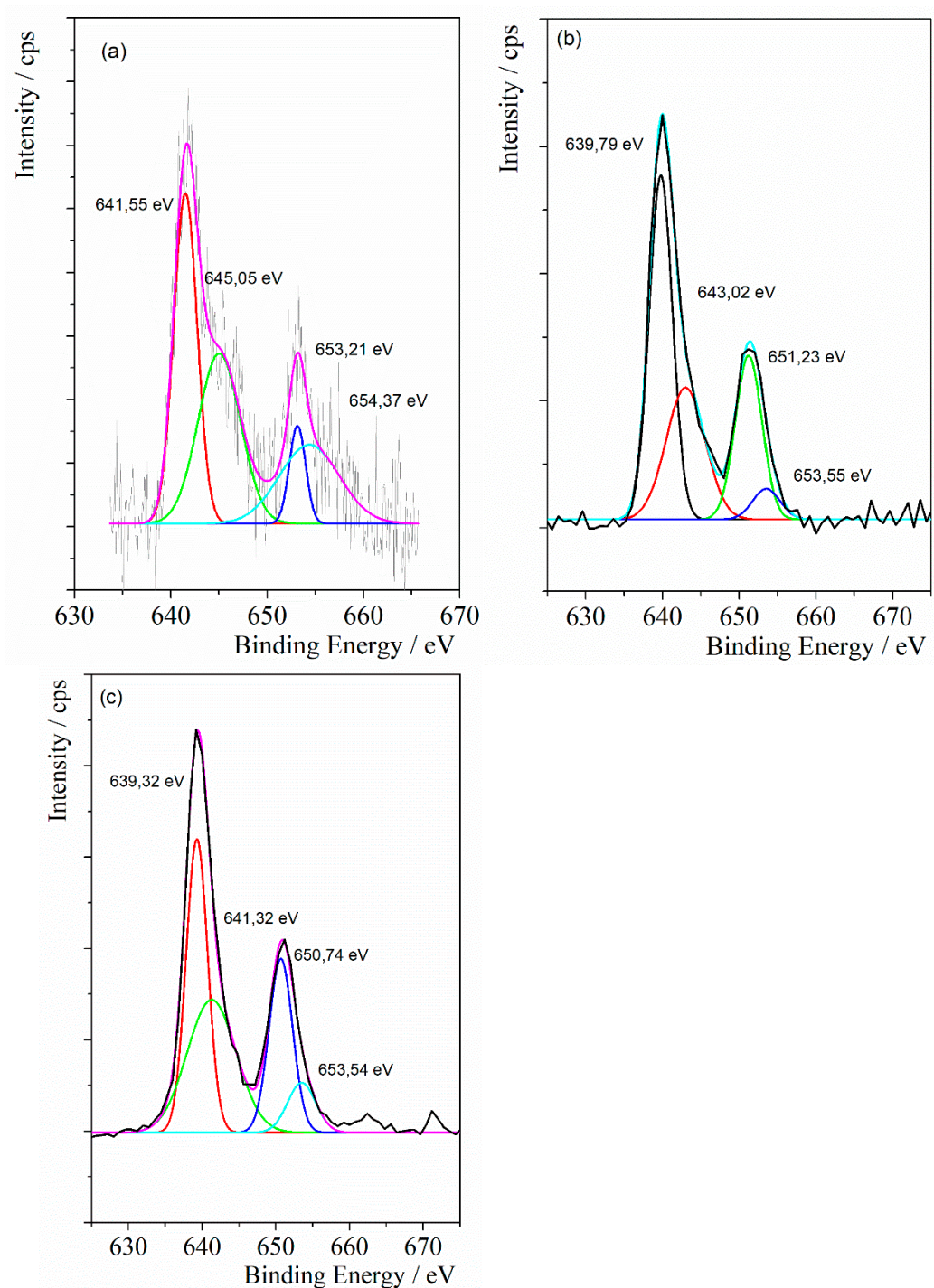
**NUMBER OF FIGURES:** 2

## Section 1. Characterization of $\text{Mn}_3\text{O}_4$ and reduced graphene oxide nanocomposites by XPS



**Figure S1.** XPS survey spectra.

The presence of C, O and Mn atoms was revealed by the survey spectra plotted in Figure 1a. Thus, bands at 285 eV and 530 eV, assigned to C1s and O1s, appear in all materials, while the two peaks centered at 642 and 653 eV, consistent with binding energies of Mn 2p<sup>3/2</sup> and Mn 2p<sup>1/2</sup>, respectively, appeared in hybrids, and its intensity increases with the percentage of Mn used in the synthesis. The presence of these two bands in the survey spectrum indicates the presence of  $\text{Mn}_3\text{O}_4$ , which perfectly matches the previously reported values for hausmannite [1,2]. Hausmannite contains both manganous and manganic ions [3,4]. Therefore, if the difference in the binding energies of manganous and manganic ions in hausmannite is large enough, the XPS spectrum will have a larger doublet separation of Mn 2p<sub>1/2</sub> and Mn 2p<sub>3/2</sub> spin-orbit levels than the simple oxides [1,2]. The XPS spectra of Mn 2p are analyzed in Figure S2 of the Supplementary Materials.



**Figure S2.** X-ray photoelectron spectra of Mn 2p core level of hybrids based on  $\text{Mn}_3\text{O}_4$  and reduced graphene oxide. (a) GOMn41, (b) GOMn11, (c) GOMn14.

## REFERENCES

1. Moses Ezhil Raj, A., et al., *XRD and XPS characterization of mixed valence Mn<sub>3</sub>O<sub>4</sub> hausmannite thin films prepared by chemical spray pyrolysis technique*. Applied Surface Science, **2010**, 256, 2920–2926.
2. Foord, J.S., R.B. Jackman, and G.C. Allen, *An X-ray photoelectron spectroscopic investigation of the oxidation of manganese*. Philosophical Magazine A, **1984**, 49, 657–663.
3. Oku, M., K. Hirokawa, and S. Ikeda, *X-ray photoelectron spectroscopy of manganese–oxygen systems*. Journal of Electron Spectroscopy and Related Phenomena, **1975**, 7, 465–473.
4. Di Castro, V. and G. Polzonetti, *XPS study of MnO oxidation*. Journal of Electron Spectroscopy and Related Phenomena, **1989**. 48, 117–123.