

## **Supplementary information**

**Stable Graphene-Polyoxometalate Nanomaterials**

**for Application in Hybrid Supercapacitors**

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## 1. Experimental Procedures

Graphene oxide (GO) was synthesized from natural graphite (powder <20 $\mu$ m particle size) by following a modified Hummers method [1]. Graphite flakes (5 g) were mixed with KNO<sub>3</sub> (6 g) and put into a solution of concentrated H<sub>2</sub>SO<sub>4</sub> (230 mL) stirred for 10 min at room temperature. 30 g of KMnO<sub>4</sub> was slowly added to the reaction mixture and stirred for 5h at 35 °C. Afterwards, 80 mL of distilled water were added dropwise. Finally, 8mL of H<sub>2</sub>O<sub>2</sub> (30 % v/v) and 200 mL of distilled water were incorporated. The resulting brown dispersion was dialyzed for 3 weeks until pH neutral. Exfoliation of GO was carried out by ultrasonication at 500 W for 30 min by utilizing 1 second pulses. GO density was 10 mg mL<sup>-1</sup>

For introducing phosphomolybdic acid (PMo<sub>12</sub>) in the GO matrix, the following methodology was utilized. In a 50 mL screw-capped Pyrex bottle, 5 mL of deionized water, 15 mL of aqueous exfoliated GO suspension and 10 mL of 10 mM aqueous solution of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·10H<sub>2</sub>O were added; this suspension was stirred for 10 min. The bottle was then tightly closed with a Teflon screw-cap and heated at 120 °C for 24h in an oven. After the hydrothermal treatment, the sample was filtered off, washed with deionized water and ethanol and dried at 50 °C in an oven overnight. The resultant material was labeled HT-RGO-PMo<sub>12</sub>.

For comparison purposes a blank experiment (no Polyoxometalate) was carried out. For this, an analogous hydrothermal reduction of GO suspension only was carried out. The final reduced material was labeled HT-RGO.

Thermogravimetric analysis was performed on a Q5000 IR in order to quantify the amount of polyoxometales introduced in the hybrid material. For this, a heating ramp of 10 °C min<sup>-1</sup> up to 900 °C under air flow (10 mL min<sup>-1</sup>) was used.

TEM-EDAX images were obtained with a field emission gun transmission electron microscope (*Tecnai G<sup>2</sup> F20 S-TWIN HR(S)TEM, FEI*) and EDAX measurements was used a super ultra-thin window (SUTW) X-ray detector with 136 eV. TEM grids with lacey carbon support films were used to prepare the samples.

RAMAN spectroscopy was carried out in a Horiba Jobin Yvon LAbRAM HR model, using 514 nm wavelength of an argon-ion laser.

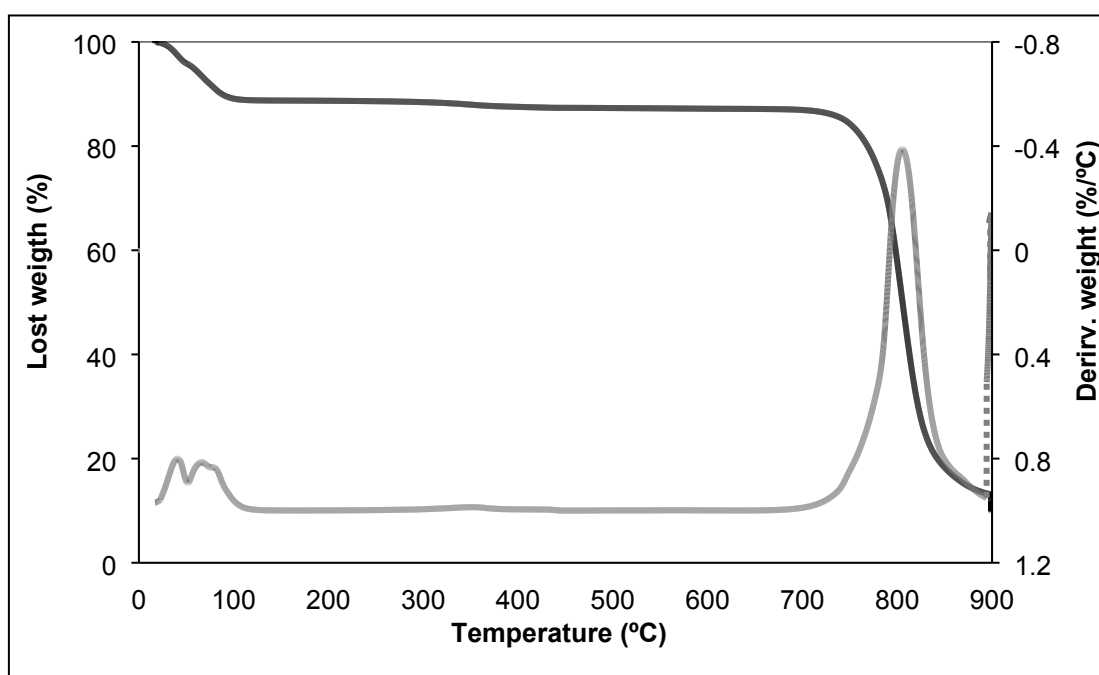
Elemental analysis was performed in order to quantify the amount of O in the final samples using Elemental Analyzer Flash-2000 C.E Instruments Thermo Fisher Scientific.

Electrochemical characterization of three and two-electrodes was carried out using on film-type electrodes (1 cm diameter) prepared by mixing 5 wt% of PTFE as a binder, 10 wt% of conductive additive (Csp, Timcal) and 85 wt% of activate material, and were tested using VPM3 Biologic Potentiostac. A 3-ways Teflon Swagelok® and 3 electrode conventional cells were used to characterize the electrode materials. Graphite roods was used as a current collector and Ag/AgCl (1 M KCl) and Pt were used as a reference and counter electrode, respectively. 1 M H<sub>2</sub>SO<sub>4</sub> was used as electrolyte. The specific capacitance on the system was calculated using the following expression  $C_e (Fg^{-1}): 2I/m (dV/dt)$  to the constant current discharge curve (discarding the ohmic drop), where  $I$  is

the current in amperes,  $(dV/dt)$  is the slope of the discharge curve and  $m$  is the mass of active material.

All materials used were purchased from Sigma-Aldrich and used without further purification.

**Figure S1.-** Thermogravimetric analysis corresponding to  $\text{H}_3\text{PMO}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$



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[1] W. S. Hummers, and R. E. Offermann, *J. Am. Chem. Soc.*, 1958, 80, 1339.