

## Electronic Supplementary Information for

### Green synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles embedded in a porous carbon matrix and its use as anode material for Li-ion batteries

Marcos Latorre-Sánchez, Ana Primo and Hermenegildo García\*

*Instituto Universitario de Tecnología Química, Univ. Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain. Fax: (+34) 96 3877809; E-mail: hgarcia@qim.upv.es*

#### Experimental Section

##### *Preparation of Fe<sub>3</sub>O<sub>4</sub>-C composite*

50 mL of a 10 g/L aqueous solution of alginic acid sodium salt (from Sigma-Aldrich) (pH 7.6) was added dropwise to 200 mL of a 50 g/L aqueous solution of FeCl<sub>3</sub> (pH 1.2). As soon as the drops of alginate solution enter into the FeCl<sub>3</sub> solution micrometric beads of this biopolymer containing Fe<sup>3+</sup> are formed and sediment at the bottom. These beads are left 24h in the FeCl<sub>3</sub> solution and then they are washed several times with milli-Q water and kept in 100mL of such water. This water was gradually replaced by ethanol. First, the beads were dispersed in a mixture of 90 mL of water-10 mL of ethanol for 20 min, then in 80 mL of water-20 mL ethanol mixture for the same time and so on until the beads are dispersed in pure ethanol. After this exchange, the alcogel beads were dried under supercritical CO<sub>2</sub> to remove the ethanol while maintaining its porous structure. These aerogel beads (Fe-*alg*) were then submitted to pyrolysis under argon atmosphere, first at 300°C, held at this temperature for 1 h, then at 500 °C and held for 2h to obtain the Fe<sub>3</sub>O<sub>4</sub>-Carbon (Fe<sub>3</sub>O<sub>4</sub>-C) composite.

##### *Preparation of Ca-*alg* beads*

The synthetic procedure is the same that the one described previously for the preparation of Fe-*alg* beads but in this case the alginate solution is added to a 35 g/L aqueous solution of CaCl<sub>2</sub> (pH 5.5). The Ca-*alg* beads are similar to the Fe-*alg* ones but

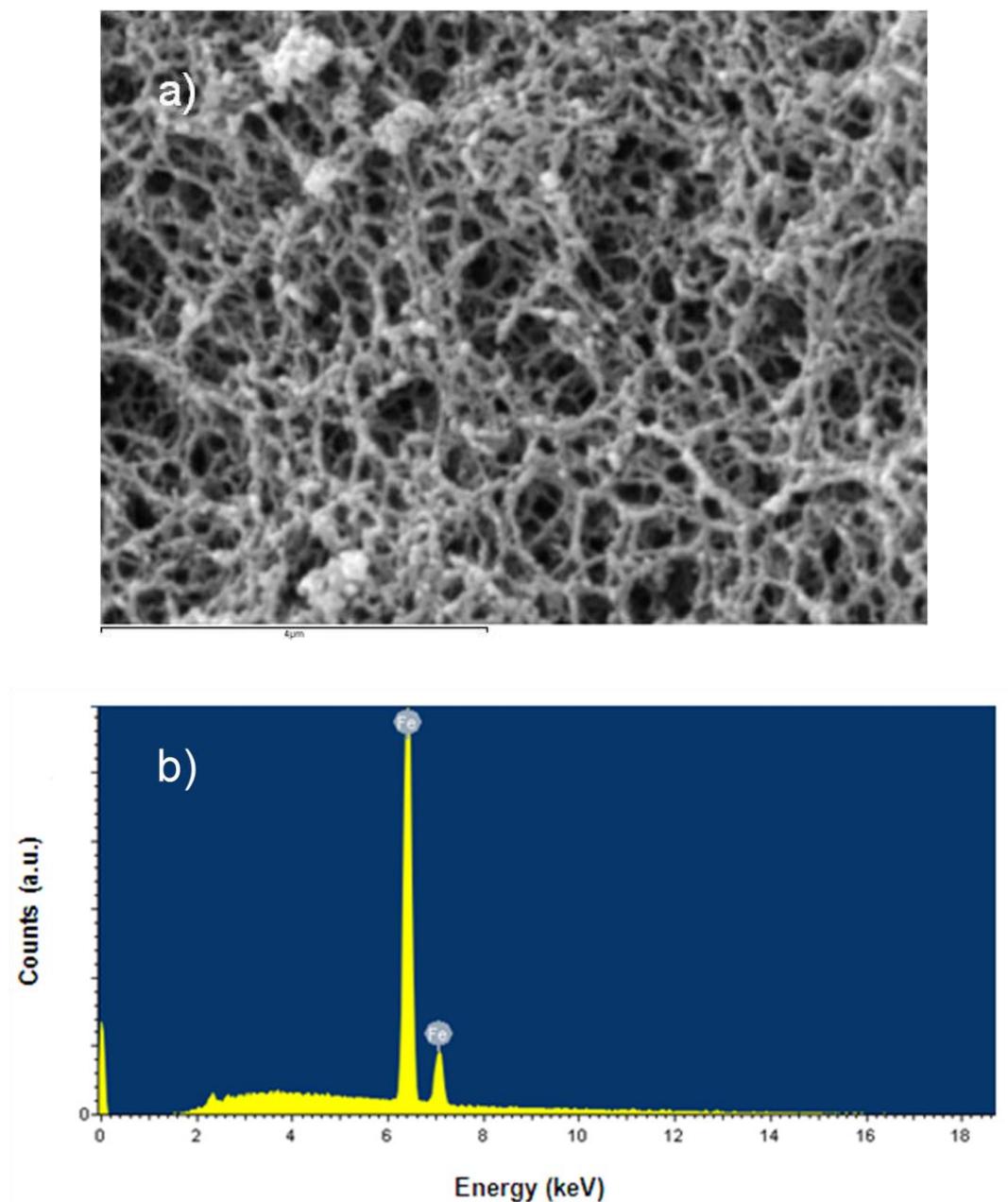
they are white instead of orange. The pyrolysis process is also the same that the one described above for Fe-alg beads.

### *Physical Characterization*

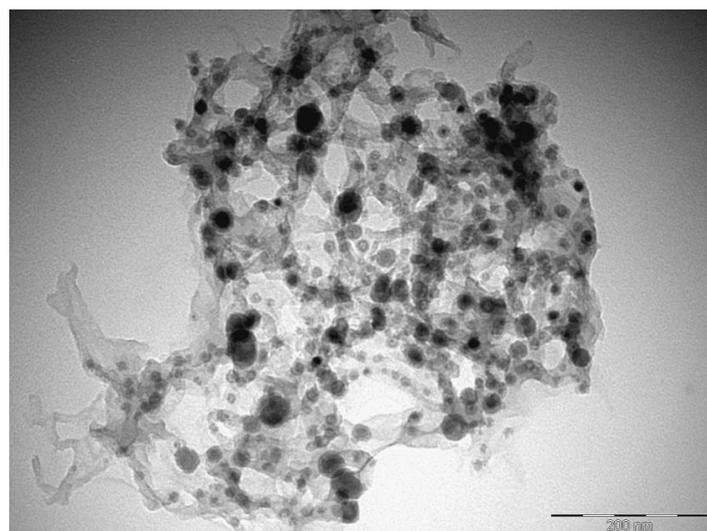
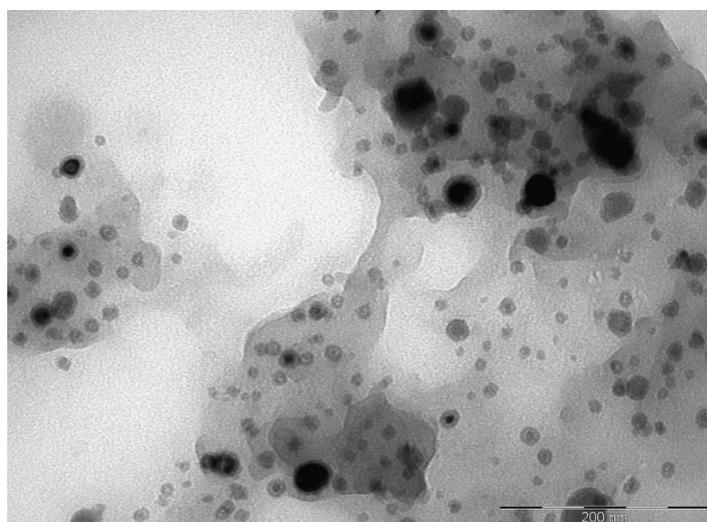
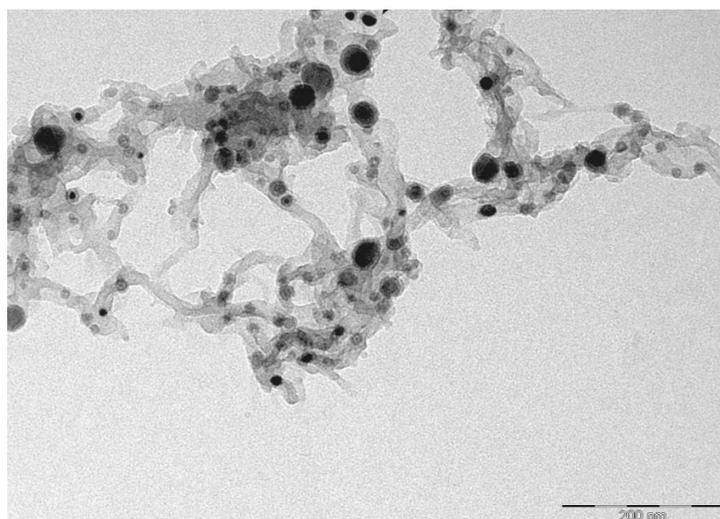
Transmission electron microscopy (TEM) images were done with a Philips CM300 FEG microscope operating at 100 kV. The scanning electron microscopy (SEM) images were carried out with a JEOL JSM-5410 electronic microscope operated at 20 kV and EDX analysis was conducted on an EDAX system from Oxford Instruments attached to this microscope. The Raman measurements (RenishawinVia Raman Microscope) were carried out at room temperature with the 514.5 nm line of an Ar ion laser as an excitation source. X-ray diffraction (XRD) patterns were obtained in a Philips X'Pertdiffractometer using the copper radiation ( $\text{Cu-K}\alpha = 1.541178 \text{ \AA}$ ). The thermogravimetric analysis (TGA) was done with a Mettler Toledo TGA/SDTA 851 apparatus in the 25-800 °C temperature range under 10 °C  $\text{min}^{-1}$  scan rate and an air flow of 30 mL  $\text{min}^{-1}$ . Induced coupled plasma (ICP) spectroscopy was carried out with a Varian 715-ES equipment. Surface areas were determined by Brunauer–Emmet–Teller (BET) analysis of nitrogen adsorption isotherms (Micromeritics ASAP-2420) carried out on outgassed samples.

### *Electrochemical measurements*

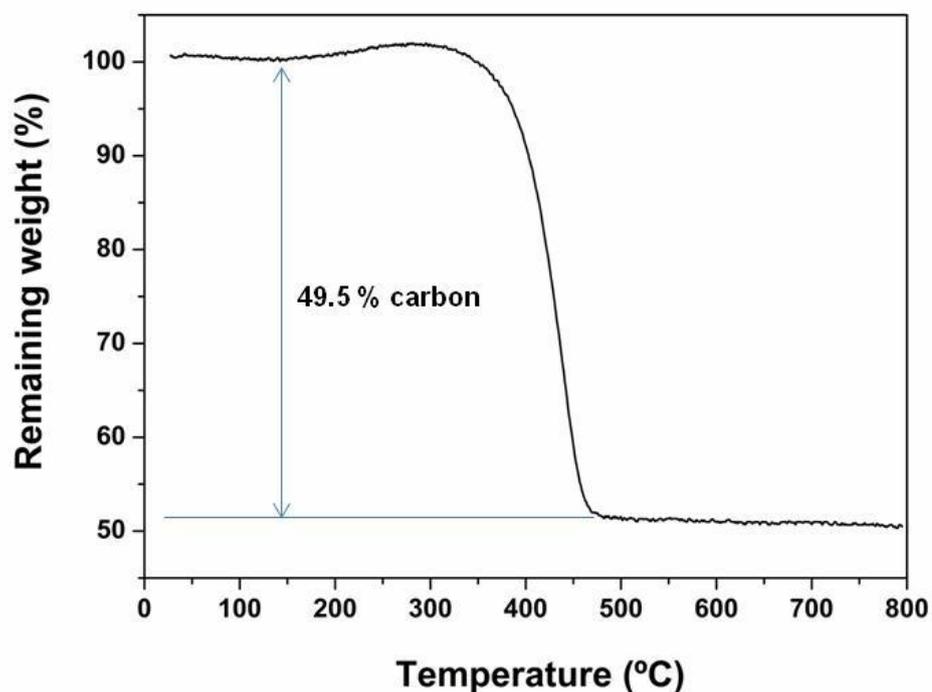
Electrochemical tests were carried out at room temperature in a home-made Swagelok type cell using Li foil as the counter electrode. A 1M solution of  $\text{LiPF}_6$  in a 1:1 (volume ratio) mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. A glass microfiber Whatman film was used as separator. The working electrodes were prepared from ball milling pastes of 70 wt% of the active material, 15 wt% of carbon black (Alfa Aesar) and 15 wt% of polyvinilidene difluoride (PVDF) binder in N-methyl-2-pyrrolidone solvent. The paste was coated onto a copper foil and then dried under vacuum at 120°C for 8h before electrochemical tests. The cells were assembled in a glove box filled with pure Ar. The cells were galvanostatically cycled in the potential range of 3-0.01 V (vs  $\text{Li}^+/\text{Li}$ ) at a current density of 350 mA  $\text{g}^{-1}$  using an Ametek Versastat 3 potentiostat/galvanostat. Cyclic voltagrams were recorded in the voltage range of 3-0V ( vs  $\text{Li}^+/\text{Li}$  ) at 0.5  $\text{mVs}^{-1}$ .



**Fig. S1** a) SEM image (scale bar: 4 μm) and b) EDX spectrum of the iron containing aerogel beads (Fe-alg) before pyrolysis

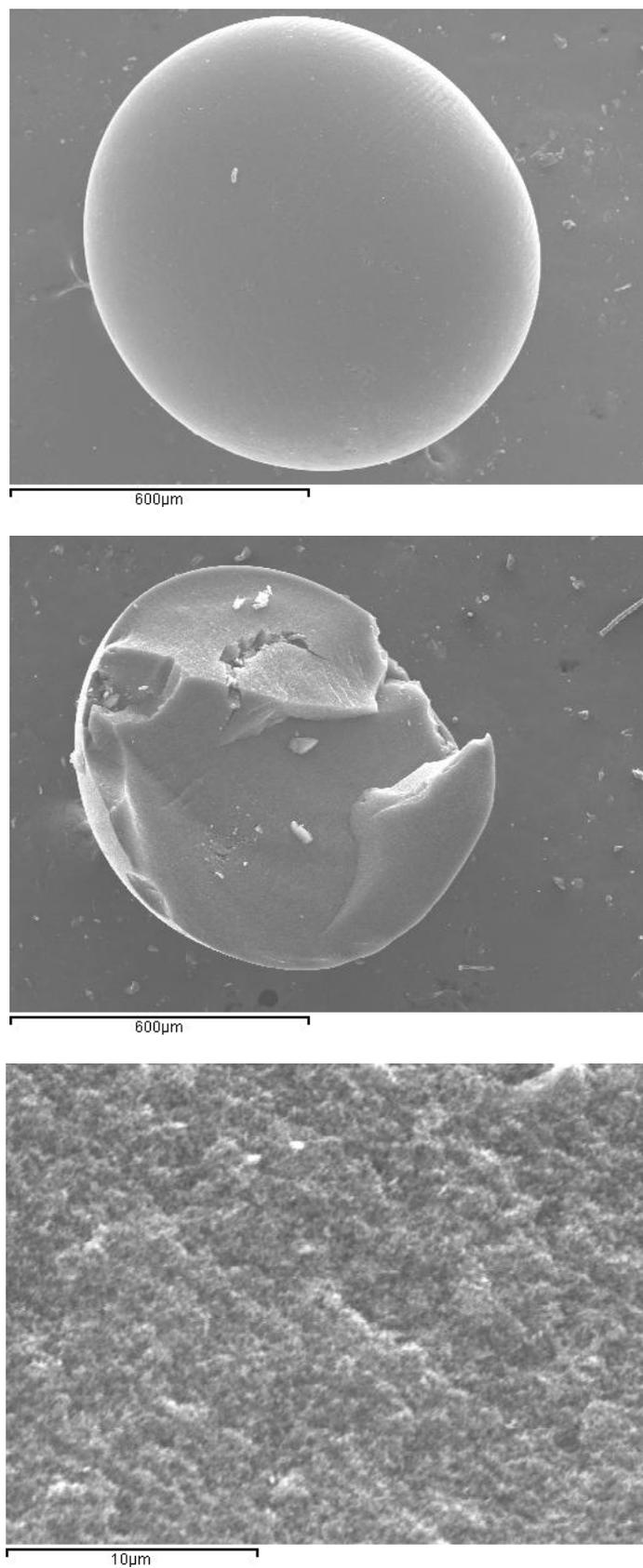


**Fig. S2** TEM images of the Fe<sub>3</sub>O<sub>4</sub>-C composite showing the Fe<sub>3</sub>O<sub>4</sub> nP and the carbon matrix

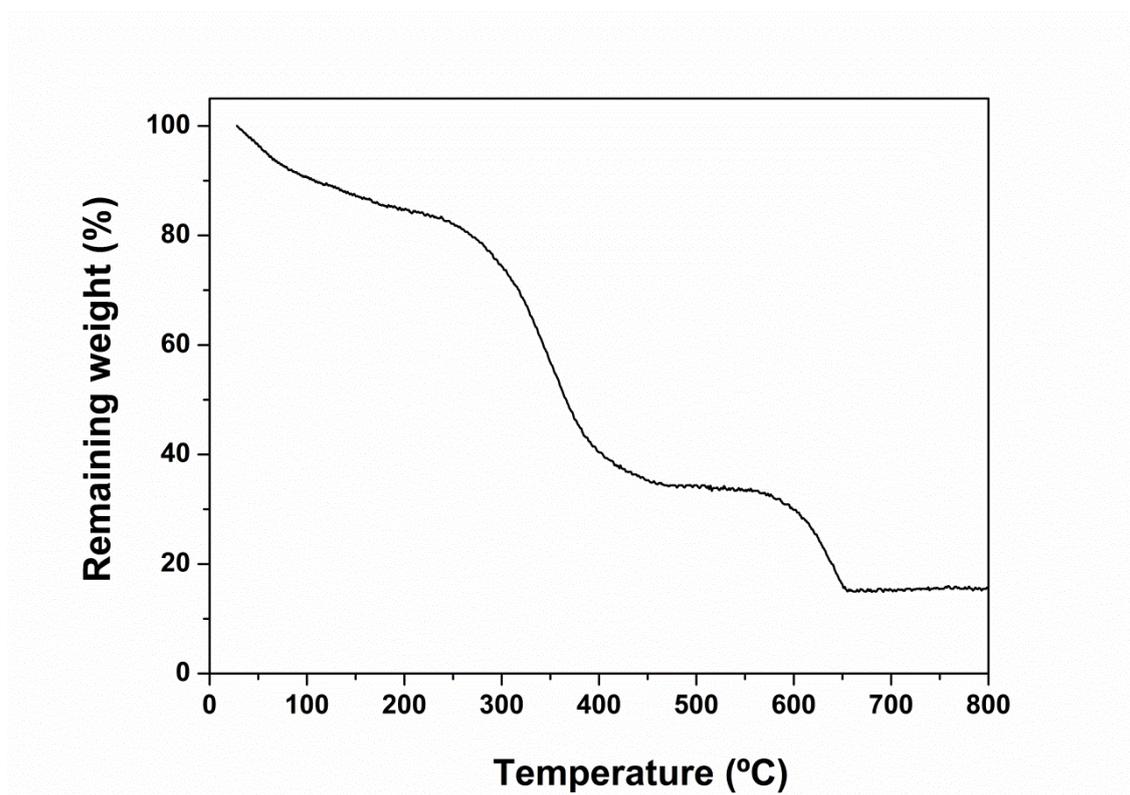


**Fig. S3** TGA profile of the Fe<sub>3</sub>O<sub>4</sub>-C composite up to 800°C in air.

The TGA profile displayed a small weight loss from room temperature to 150°C due to dehydration followed by a weight gain between 250°C and 300°C possibly due to the oxidation of Fe<sub>3</sub>O<sub>4</sub> to Fe<sub>2</sub>O<sub>3</sub>. The combustion of the carbon was complete at 450°C. From the weight loss between 150°C and 450°C the carbon content was calculated to be 49.5 w% and the balance (50.5 w%) was assumed to be Fe<sub>3</sub>O<sub>4</sub>.



**Fig. S4** SEM images of the Fe<sub>3</sub>O<sub>4</sub>-C composite beads showing its spherical shape and its porous texture.



**Fig. S5** TGA profile of the Ca-alg material up to 800°C in air.

The percentage of carbon calculated for the dried material (weight loss between 200 and 650°C) is around 80.4 w%.