Synthesis and Characterization of MoS_2 decorated Graphene Aerogels for Supercapacitor Electrodes

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In the past few years [1], considerable efforts have been devoted to the application of graphene in electrodes for electrochemical energy storage devices such as super-capacitors. The supercapacitors offer the advantage of fast discharge rates, high power densities, and long cycle lifetimes. They are based on two different charge storage mechanisms: the formation of a Helmholtz double layer at the electrode/electrolyte interface (non Faradic mechanism) and the generation of fast and highly reversible Faradic reactions such as surface and near - surface redox, intercalation and electro-sorption processes. Nanostructured carbon-based materials, in particular graphene and graphene-derived, have been largely studied and employed in the fabrication of electrodes for supercapacitors in electrical double layer configuration, due to excellent electrical conductivity, high mechanical strength, high specific surface area and easy accessibility by a liquid electrolyte. In these electrodes, in order to reach satisfying values of specific surface area and capacitance, a three-dimensional porous nanoarchitecture, e. g. aerogel matrix, is required. Moreover, with the aim to enhance the Faradic processes, transition metal oxides have been widely explored because of their ability to adopt a wide variety of oxidation states. More recently 2D transition metal dichalcogenides have attracted much attention also for promoting ions interlayer insertion, because of their rich intercalation chemistry and structural properties. [2].

In this work, we present a comparison between two nanocomposite graphene-based aerogels decorated with MoS_2 structures, successfully employed for the fabrication of supercapacitors electrodes. The incorporation of MoS_2 in graphene aerogels was obtained by two different approaches: *ex-situ* and *in-situ*. Concerning the *ex situ* hybrid synthesis, commercially available graphene-oxide (GO) and MoS_2 nanoflakes were dispersed in deionised water and submitted to a hydrothermal reduction. For the *in situ* nanocomposite generation, a dispersion of GO, phosphomolybdic acid as Mo precursor and L-cysteine as natural S precursor were mixed in deionised water and, after a pH adjustment at 6.5 value with NaOH, treated by hydrothermal reduction. The reduction reactions were carried out in an autoclave at 180°C for 12 hours and the resulting hydrogels were rapidly frozen by liquid nitrogen (nominal T= -198°C) and freeze dried (T= -50°C) under vacuum in order to quickly remove residing water without affecting 3-D structure shape and porosity of the expected graphene-based aerogels.

The graphene-MoS_2 aerogels have been characterized using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), micro-Raman Spectroscopy and N_2 adsorption/desorption at 77 K. The pristine graphene aerogel has a BET surface area of 1400 m^2/g, showing a pore size distribution ranging from micro- to macro-pores. FESEM micrographs (Fig 1) also evidence the porous nature of the aerogels and show that the morphology is not affected by the presence of both *ex-situ* MoS_2 flakes and *in-situ* MoS_2 nanosheets.

References

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Figure 2 reports the XPS HR Mo3d and S2s spectra of the 2 nanocomposites. In the *ex-situ* hybrid synthesis, the starting MoS_2 species (powder) are slightly affected by the hydrothermal process giving rise to the formation, as by-products, of traces of oxidized molybdenum (VI) compounds with oxygen. The *in-situ* synthesis is characterized by a high yield in terms of MoS_2 products with the presence of small amounts of reduced molybdenum (IV) compounds with oxygen.

The presence of MoS_2 crystalline structure is confirmed by XRD characterization. Despite the presence of stoichiometric MoS_2 species (EDX), in situ generated MoS_2-graphene nanocomposites do not show diffraction peaks of crystalline MoS_2 phase, so suggesting the intercalation of MoS_2 flakes among graphene sheets, preventing the assembly of MoS_2 layers in long range periodicity.

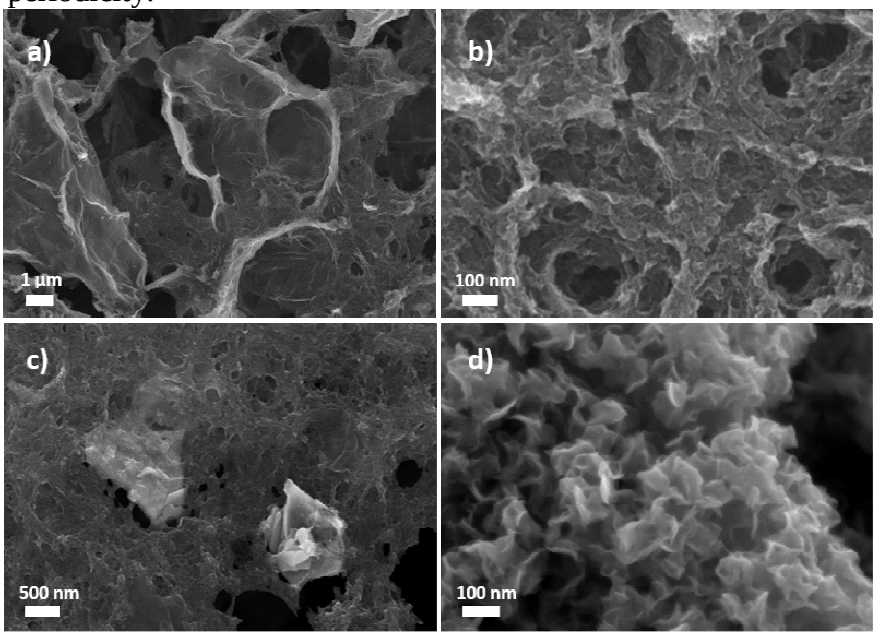

Figure 1: pure graphene aerogel a) and b); graphene aerogel decorated with MoS_2: c) *ex situ* hybrid synthesis and d) *in-situ* hybrid synthesis

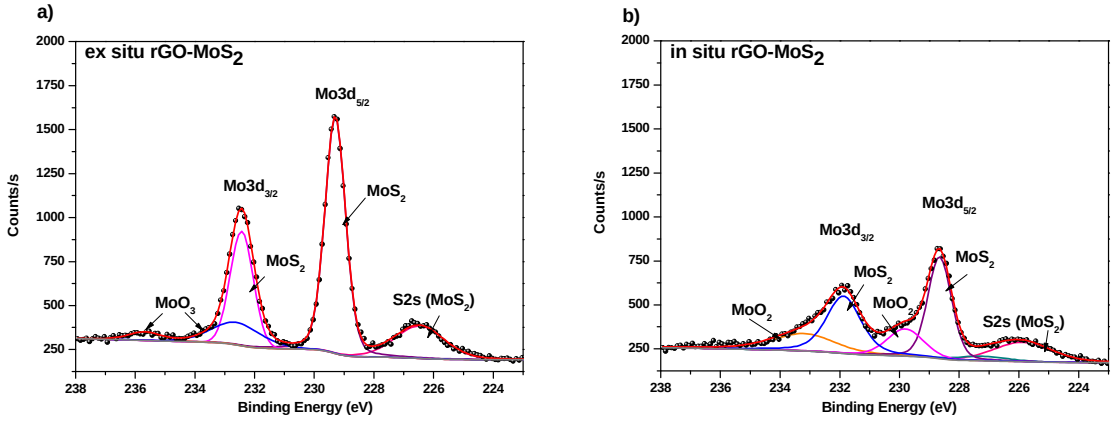

Figure 2: Mo3d and S2s HR spectrum of a) *ex-situ* MoS_2 nanocomposite and b) *in-situ* MoS_2 nanocomposite

The graphene-based aerogels decorated with MoS_2 nanostructures were tested in a double electrode symmetric cell showing that, due to the peculiar morphology and the homogeneous distribution of the 2D nanosheets in the 3D graphene nanoarchitecture, the specific capacitance and the energy density properties are enhanced. The material presents excellent characteristics, suitable for the fabrication of high performance supercapacitor electrodes.