Carbon Based Nanohybrid Materials (sp²-sp³) for Energy Applications

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Supercapacitors are considered potential devices to reach the compromise between high energy and high power density required for advanced green energy storage. The electrical conductivity, high surface area, and the orderly and tunable pore structure of carbon nanomaterials made them excellent candidates to improve the performance of current devices [1]. Carbon atoms are exceptionally good in forming strong covalent bonds in different hybridization states, sp, sp², sp³, producing a plethora of chemical compounds and carbon nanostructures. This versatility allows the formation of nanohybrids with enhanced properties for energy storage. In this work, we present the electron microscopy characterization of hybrid fullerite-graphene (sp²-sp³) nanohybrids (FG-1) with enhanced capacitive properties. Pure fullerite was synthesized by ultrasonication of fullerene (C₆₀) as a control system (F-1), while FG-1 was prepared with the addition of previously exfoliated few layer graphene (FLG) and C₆₀ [2]. FG-1 displayed a mixture of fullerenes, nano-onions, nano-diamonds and carbon dots when characterized by transmission microscopy (TEM), high-resolution TEM (HRTEM) and spectroscopic techniques. Figure 1 shows TEM images of as produced F-1 (a), fullerenes produced in the absence of graphene layers display a smooth surface (b) when compared with the FG-1 nanohybrids (c)-(g). HRTEM examination of FG-1 reveals the presence of nano-onions (d) and (e), nanodiamonds (f), and graphene dots (g) and (h). Fig. 1 (l, m, n) show phase images after different levels of background filtering where the distribution of Fe can be followed.

Defects and surface functionalities are considered important variables to improve capacitive processes in carbon materials. X-ray photospectroscopy (XPS) (h), and electron paramagnetic resonance (EPR) (i), were used to characterize the composition and type of defects available in synthesized materials and compared with HRTEM analysis. XPS demonstrates that FG-1 hybrids are mostly composed by carbon atoms, while and increased X-band EPR spectrum measured in the nanohybrid at room temperature (j) is composed of two components, a broader asymmetric one at lower fields and narrow symmetric at higher fields. Fitting the spectrum two a sum of Lorentzian and a Dyson lineshape leads to an excellent fit yielding g-factor values of g₁ = 2.0025 and g₂ = 2.0090, respectively. Whereas the former is very close to the electron free value expected for the more sp²-rich regions, the latter is more in the range expected for a polymer-like or diamond-like environments with a mixture of sp²- and sp³-hybridized states. The spectrum thus clearly shows nanostructural inhomogeneities of the nanohybrid observed by HRTEM analysis. In F-1 the broad Dyson-like line is completely absent (k). It is well known that supercapacitors performance is dependent on the electrode material and highly affected by the electrolyte, then, different aqueous and organic electrolytes were evaluated. A plausible mechanism based on the material porosity,
defects, functional groups and the electrolyte is proposed to explain the increased capacitance achieved by hybrids carbon nanomaterials (l) [4].

References

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Figure 1. TEM images of F-1 (a,b) and GF-1 (c,d). HRTEM images of GF-1, (e) displays curved nanostructures similar to nano-onions; (f) nano-diamonds are observed; (g,h) carbon dots. (i) The XPS confirms the carbon composition of F-1 and GF-1, the amount of oxygen is less than 2%. (j) X-band EPR spectrum measured in GF-1 at room temperature. Solid red line is a fit to a model comprising a narrow Lorentzian and a broader Dyson-like components. (k) Comparison of X-band EPR spectra measured in F-1 and GF-1 at room temperature. (l, m, n) Phase images of Fe containing Hybrid FG.