Abstract

Laser induced graphene microsupercapacitors: fabrication, characterization and integration.

The PhD has been devoted to the fabrication, testing, performance enhancement and application of laser induced graphene (LIG) micro-supercapacitors. LIG has been fabricated onto 125 μm thick polyimide sheets using a 10.6 μm wavelength, then the electrodes have been contacted with titanium grids and the device has been tested in Na_2SO_4 0.5M. Prior electrochemical characterization, physico-chemical measurements have been carried out using FESEM imaging and XPS, XRD and Raman spectroscopy. With the optimizing laser parameters, a sandwich configuration using two LIG electrodes with active area 0.5x1 cm^2 in Na_2SO_4 0.5M have been prepared. The device reached 9.8 mF cm^{-2} at 1 mV s^{-1}. At the same time, the different LIG supercapacitors have been employed as storage units in integrated
systems. This value is in line the average with respect to the current state of the art for LIG tested in aqueous electrolyte.[1] [2] Several approaches have been developed in order to improve the LIG performances. Zhang et al. [3] have decorated a LIG surface with ZnP flakes leading to a boost in pseudocapacitance and hydrophilicity. Again, Clerici et Al. [4] performed a similar decoration but using MoS_2, and successfully improved the performances. The performance improvement has been reached with two different methods. The first has been infiltration of activated carbons (AC), carbon black (CB) and PVDF solution through vacuum inside the porosities of LIG.
In addition, to increase the device surface area and hydrophilicity, immersion in nitric acid has been carried out before the AC infiltration. The initial geometry has been
an interdigitated one with 5 digits per electrode, and it has been able to reach 1 mF cm^{-2} at 5 mV s^{-1}. After the whole treatment the device has reached 20.4 mF cm^{-2}, assessing the improvement of the device performances. The presence of carbon black also helped the conductivity of the whole surface, and this has been appreciated
in the electrochemical impedance spectroscopy. The innovative path of this kind of improvement is that the increase of capacitance is only driven by the electrical double layer phenomena, instead of the much more exploited pseudocapacitive
boost. The second approach has focused on increasing the LIG electrodes pseudo capacitance in sandwich configuration by decorating it with manganese oxide through

electrodeposition. The manganese oxide decoration, and successive coupling with MXene-decorated LIG counter electrode, allowed to have 128 mF cm^{-2} device, which has been the highest value reached for LIG in this research. The single electrodes, decorated with the two pseudocapacitive materials, have been individually characterized through electrochemical and physico-chemical measurements. Many works have been developed regarding the study of manganese oxide decorations [5][6] but the novelty is the coupling with a likewise pseudocapacitive material, i.e., the MXene. Parallel to the improvement of performances, many research groups have tried to give LIG a green footprint by substituting polyimide with green substrates.[7][8] Herein, polyimide substrate has been substituted with a solution of lignin, chitosan, boric acid, glycerol and acetic acid. The mixture has been dried and graphenized through CO_2 laser. The obtained device, again with aqueous electrolyte, reached 9 mF cm^{-2}, which has been comparable to the polyimide LIG. Two other substrates have been tested: one based on microcrystalline cellulose extracted from olive leaves, and the other based on sulphonated polymer of intrinsic porosity (S-PIM1) on glass fiber. The obtained devices, however, showed less than 2 mF cm^{-2} capacitance. Finally, the supercapacitor has been coupled with other elements to create integrated device. First, it has been connected to a dye sensitized solar cell. This latter has been made flexible by using a titanium grid as photoanode and LIG as counter electrode. Then, the energy storage device has been integrated in a hydrogel-based strain sensor, to supply it. The three elements have been coupled together in a single integrated and flexible device for wearable applications. The solar cell supplies the sensor and charges the supercapacitor during daytime, while the supercapacitor acts as supply unit during nighttime or low indoor light.

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