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An industrial scalable approach for graphene/carbon nanotubes hybrid flexible supercapacitors

Flexible electronic devices are the forefront of research activity for their multiple uses. [1, 2] One of the major challenges in this research area is the fabrication of flexible energy storage systems (ESSs) since they can be used in wearable electronic applications such as medical devices, portable antennas, etc. [1, 2] Nowadays, batteries and conventional capacitors are prototypical ESSs but they suffer from some limitations. On the one hand, batteries have low power density, slow recharge time and limited cyclability [3]. On the other hand, conventional capacitors show high power density and life-cycles stability, but with the downside of lower energy density compared to batteries. The development of electrochemical double layer capacitors (EDLCs or supercapacitors) is bridging the gap between these two ESSs technologies. In fact, supercapacitors show higher energy density than conventional capacitors and higher charge/discharge rates, life – time and power density than batteries. [4] These performances are achieved thanks to the materials used in the electrodes for supercapacitors: high porous/specific surface area carbon based materials, *e.g.*, activated carbon (AC) [4]. However, AC suffers from a major drawback: its surface area is not entirely accessible to the ions of the electrolyte due to the presence of micro-pores that hinder the adsorption of ions. Moreover, AC based electrodes require the use of binder that wrap together the AC particles, but cause an increase in the electrical resistivity of the electrodes. [5] To overcome these drawbacks, many other carbon-based materials have been suggested as possible active material alternatives , including carbon nanotubes (CNTs) and graphene. [6] Nevertheless, electrodes fabricated by using either CNTs or graphene suffer from re-aggregation effects (such as the bundling of CNTs and the restacking of graphene flakes) which cause a reduction of the specific surface area and consequently of the electrochemical performance of the device. [7] To tackle these issues, hybrid compounds (graphene/CNTs mixtures) were proposed as possible solutions. [7] Herein, we introduce a scalable approach for the production of this type of devices. Our starting materials are commercial CNTs and graphite, dispersed in a solvent (N-methyl-2-pyrrolidon). The CNTs are de-bundled by means of ultrasonication techniques [8], while graphene is produced by wet-jet milling exfoliation of pristine graphite [9, 10]. The wet-jet milling is a high-yield (~ 100 %) procedure that allows the production of large quantities of graphene (> 20 g h^{-1}). [9, 10] These features are compatible with industrial requirements and avoid time-consuming solution-based processes. [11] By mixing the CNTs and graphene dispersions in a 1:1 weight ratio, the final functional ink is obtained and can be used for scalable manufacturing of supercapacitors through methods such as printing and vacuum filtration. [12] The as produced electrodes are flexible and self-standing (no binder is used) and the devices, fabricated without the need of any metal, show areal capacitances > 150 mF cm^{-2}.

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