Si-grown vertically aligned graphene nanosheets electrodes for high performance micro-supercapacitors using ionic liquid electrolytes

David Aradilla, Marc Delaunay, Saïd Sadki, Jean-Michel Gérard and **Gérard Bidan**

Univ. Grenoble Alpes, CEA/INAC, 17, rue des Martyrs, F-38000 Grenoble, France
gerard.bidan@cea.fr

Over the past years, the development of innovative technological applications in the field of micro-electronics, micro-medicine or nano-engineering, has sparked a great deal of attention in the research of high performance energy storage units. Recently, tremendous efforts have been devoted to develop novel **high-performance micro-supercapacitors (m-SCs) based on nanostructured material electrodes** with advanced architectures. From this perspective, new materials based on nanostructured silicon (e.g. silicon nanowires[1]), or nanostructured carbonaceous materials have attracted a special interest in the field of microsupercapacitor devices owing to their unique properties in terms of long cyclability and high power pulse.

Accordingly, in recent years micro-supercapacitors based on reduced graphene oxide (rGO) electrodes have been extensively investigated. However, the rGO morphology as horizontally stacked sheets parallel to the electrode surface does not allow easy diffusion of electrolyte ions. **The advent of vertically oriented graphene nanosheets (VOGNs) grown by plasma deposition allowed easy and fast access of ions to the electrode** [2] and made it possible to usher m-SCs into the high-frequency filtering arena with high ripple current [3].

This study reports the synthesis and application of VOGNs deposited on highly doped silicon substrates through an alternative and catalyst-free method based on electron cyclotron resonance-plasma enhanced chemical vapor deposition (ECR-CVD) technique. The graphene-based electrodes were employed in a symmetric micro-supercapacitor device using an aprotic ionic liquid ($PYR_{13}TFSI$) as electrolyte, which was used owing to its moderate viscosity and wide voltage stability window (4 V) [1]. A complete and detailed electrochemical characterization of the micro-device was evaluated by cyclic voltammetry, galvanostatic charge–discharge cycles and electrochemical impedance spectroscopy. Furthermore, an exhaustive morphological and structural characterization of the graphene electrodes was carried out by using scanning electron microscopy (fig. 1 A)), transmission electron microscopy and Raman spectroscopy.

The device was able to deliver an outstanding specific capacitance value of 2 mF cm^{-2}, (fig. 1 B)) **a power density value of 4 mW cm^{-2} and an energy density value of 4 mW h cm^{-2} operating at a large and stable cell voltage of 4 V** with a quasi-ideal capacitive behaviour. Moreover, the lifetime of the device exhibited a remarkable electrochemical stability retaining **80% of the initial capacitance after 150 000 galvanostatic charge–discharge cycles** (fig. 1C)) at a high current density of 1 mA cm^{-2}. These performances open the route for on-chip energy storage micro-units and their integration into miniaturized electronic devices [4].

References

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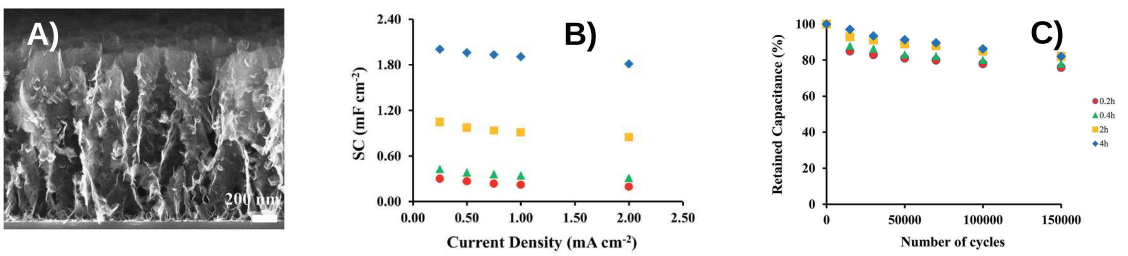

Figure 1: A), SEM images of the cross sectional view of VOGNs deposited using a deposition time of 0.4 h (2 µm thickness) on Si substrate; B), Specific capacitance as a function of current densities (0.25 - 2 mA cm^{-2}) and C) Lifetime testing of the devices performed using 150 000 complete charge–discharge cycles at a current density of 1 mA cm^{-2} between 0 and 4 V using different thicknesses of VOGNs (1 (red dot), 2 (green triangle), 6 (orange square) and 12 (blue diamond) µm respectively).