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Short communication

Layer-by-layer printing of laminated graphene-based interdigitated microelectrodes for flexible planar micro-supercapacitors

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ABSTRACT

Graphene-based planar micro-supercapacitors are layer-by-layer printed on flexible substrates using micro-extrusion technique. The laminated graphene films and polyvinyl alcohol-H_2SO_4 gel serve as the interdigitated micro-electrodes and electrolyte, respectively. The resultant solid-state micro-supercapacitors exhibit high capacitive performance, excellent flexibility and cycling stability. Such device promises potential applications in flexible electronics and lab-on-a-chip systems.

1. Introduction

Planar micro-supercapacitors (PMSCs) have attracted considerable efforts in recent years because of their amenability to be integrated with microelectronics and lab-on-a-chip devices [1]. In addition, their in-plane structure renders high power density because electrolyte ions are transported laterally between closely placed electrodes, without the necessity of any binder or separator [2,3]. PMSCs have been fabricated using photolithographic micro-fabrication and laser patterning [4,5]. These methods, however, are tedious, not cost-effective, and not compatible with flexible substrates. A screen-printed PMSC on a flexible substrate has been demonstrated [6]. But screen-printing requires pre-fabricated masks or stamps and substrate-specific in formulation. Current PMSCs usually require a layer of metallic current collector on the substrate [4]. This not only complicates the fabrication but also compromises the device flexibility. Furthermore, the practical applications of current PMSCs are often limited by the low specific capacitance [2].

Owing to its high specific surface area, excellent electrical conductivity, and exceptional mechanical properties, graphene is an ideal electrode material for PMSCs [7,8]. Thin-film graphene electrodes can be fabricated by vacuum-assisted infiltration, chemical vapor deposition, electrophoretic deposition, ink-jet printing, layer-by-layer deposition and spray deposition [9,10]. These methods, however, are not amenable for PMSC fabrication or require complicated procedures. The amphiphilic properties of graphene oxide (GO) sheets (thus high solubility in various solvents) make them suitable inks for printing processes [11,12]. In this work, we demonstrate a reduced-GO (rGO) based PMSC layer-by-layer printed on flexible substrate using the micro-extrusion printing technique. Micro-extrusion process involves extruding viscous ink through a deposition nozzle, with controlled speed and nozzle size as well as pre-programmed printing trajectory. In contrast to traditional micro-fabrication process and other printing techniques, micro-extrusion method enables programmable and convenient patterning (for both 2D and 3D architectures), high throughput printing on arbitrary substrates, and broad choices of printing materials (e.g., aqueous dispersions, metal or ceramic pastes, polymer melts, even live cells) [13,14]. The herein demonstrated graphene-based solid-state PMSC (free of metallic collector, binder, and separator) exhibits high specific volumetric capacitance (41.8 F/cm^3), cycling stability, and flexibility.

2. Experimental

The GO sheets were synthesized from graphite flake powders using a modified Hummers method [15]. The obtained GO aqueous solution was concentrated (to 20 mg/mL) by centrifugation. A self-built 3D micro-extrusion system was used to print graphene-based interdigitated electrodes. The printing system consists of a desktop XYZ motor (Technodigm, Model: DR3331T-EX), a temperature-controlled substrate holder (100 °C used here), and a high-precision displacement

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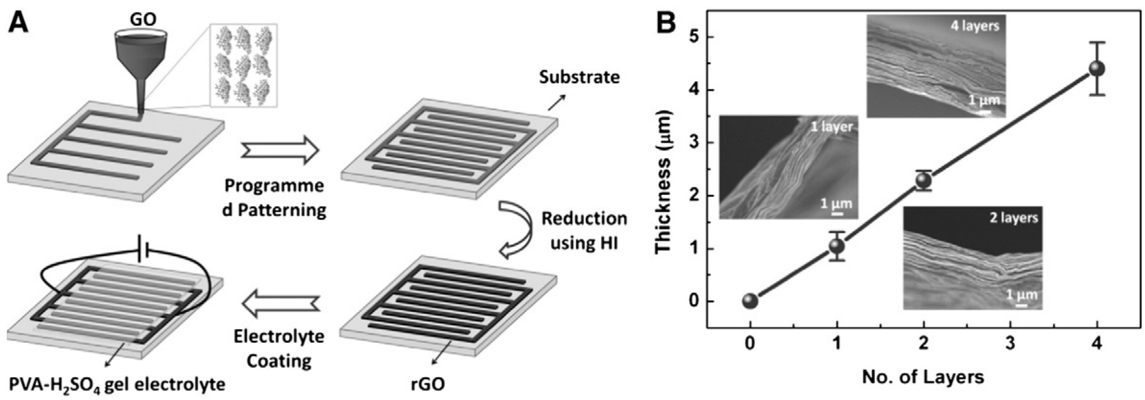

Fig. 1. (A) Schematic illustration of device fabrication. (B) The thickness of laminated rGO film is linearly proportional to the number of printing cycles. Error bars indicate the standard deviation ($n = 4$ samples).

pump (Technodigm, Model: PDP 1000). The printing head mounted on the precision XYZ motor (20 μm resolution) prints along the pre-programmed tracks with an adjustable speed (50 mm/s used). The printing head includes a piston, a syringe and a changeable micro-needle (inner diameter of 210 μm used). The displacement pump drives the piston with a controllable speed (0.001 mm/s) to extrude GO

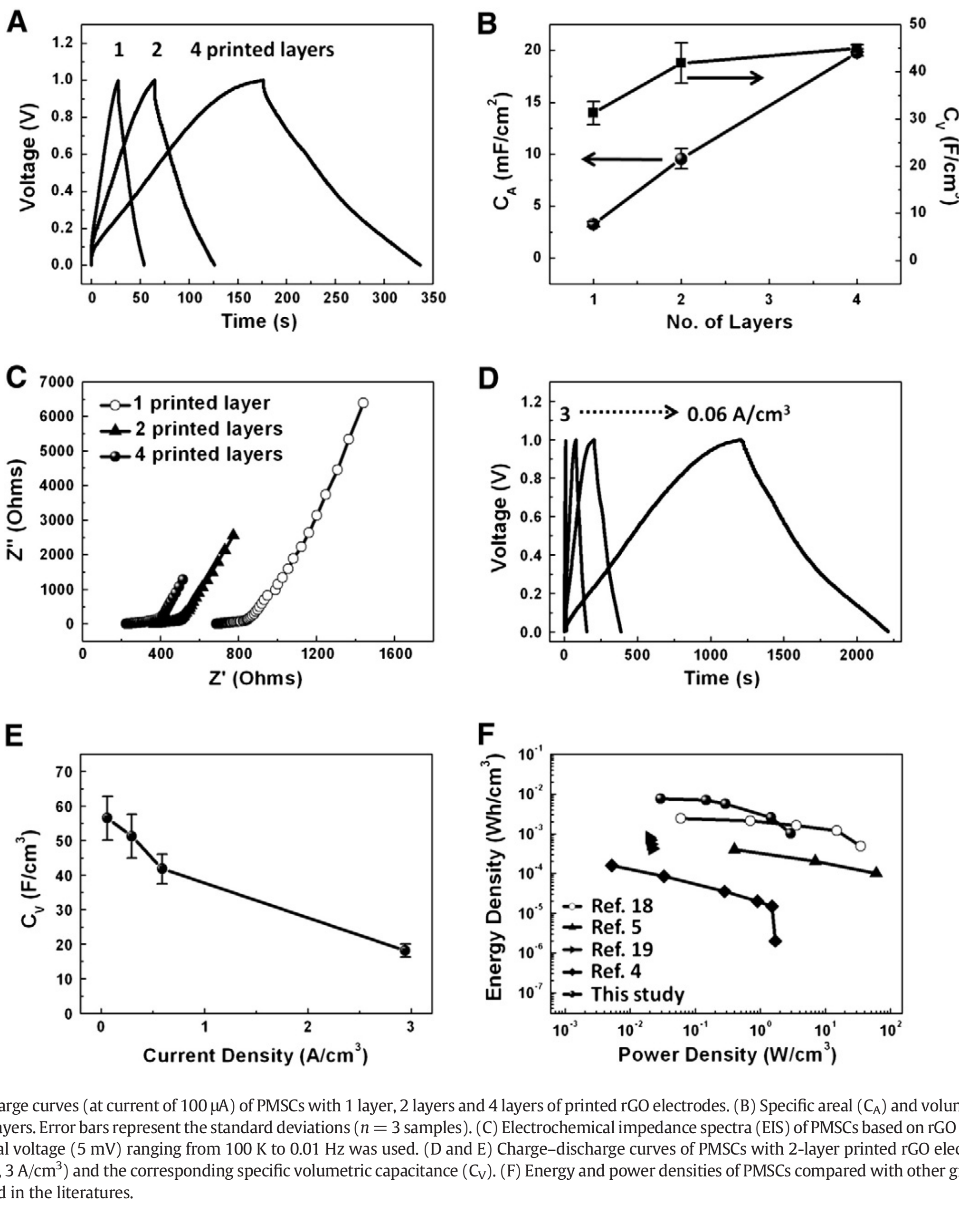

Fig. 2. (A) Charge–discharge curves (at current of 100 μA) of PMSCs with 1 layer, 2 layers and 4 layers of printed rGO electrodes. (B) Specific areal (C_A) and volumetric (C_V) capacitance vs. the number of printed-layers. Error bars represent the standard deviations ($n = 3$ samples). (C) Electrochemical impedance spectra (EIS) of PMSCs based on rGO electrodes with 1, 2, and 4 printed layers. Sinusoidal voltage (5 mV) ranging from 100 K to 0.01 Hz was used. (D and E) Charge–discharge curves of PMSCs with 2-layer printed rGO electrode at different current densities (0.06, 0.03, 0.6, 3 A/cm^3) and the corresponding specific volumetric capacitance (C_V). (F) Energy and power densities of PMSCs compared with other graphene-based solid-state supercapacitors reported in the literatures.