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All-solid-state micro-supercapacitors based on inkjet printed graphene electrodes

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ABSTRACT

All-solid-state graphene-based in-plane micro-supercapacitors are fabricated simply through reliable inkjet printing of pristine graphene in interdigitated structure on silicon wafers to serve as both electrodes and current collectors, and a following drop casting of polymer electrolytes (polyvinyl alcohol/H₃PO₄). Benefiting from the printing processing, attractive porous electrode microstructure with a large number of vertically orientated graphene flakes is observed. The devices exhibit commendable areal capacitance over 0.1 mF·cm⁻² and long cycle life over 1000 times. The simple and scalable fabrication technique for efficient micro-supercapacitors is promising for on-chip energy storage applications in emerging electronics.

The miniaturization of portable and autonomous electronic equipment, such as implantable medical devices and micro-robots, requires compact energy storage devices that can be integrated with other components directly on a chip.¹⁻³ Micro-supercapacitors (mSCs) are promising for such applications because of their high power density and long cycle life.⁴⁻¹⁰ In particular, as compared with the typical sandwich structure of conventional supercapacitors, the in-plane (usually interdigitated) structure of mSCs greatly facilitates direct on-chip fabrication and integration,¹ although the fabrication of mSCs necessitates certain patterning techniques, such as lithography and direct laser scribing.^{1,4-10} In the literature, a large number of mSCs have been fabricated with various electrode materials, including carbide-derived carbon,¹ carbon onions,¹⁰ graphene,^{4-7,9} MoS₂,¹¹ and conducting polymer.⁸ Among them, graphene is of the greatest research interest thanks to its large specific surface area, good electrical conductivity and excellent electrochemical stability. Niu *et al.*⁷ used lithography-patterned gold current collectors followed by electrophoretic deposition of reduced graphene oxide (RGO, 25 nm thick) electrodes to fabricate mSCs with areal capacitance around 0.46 mF/cm². Wu *et al.*⁹ fabricated mSCs of areal capacitance about 0.32 mF/cm² through spin-coating RGO films (15 nm thick), depositing patterned gold current collectors by sputtering (with assistance of masks) and finally etching the RGO films by oxygen plasma. These techniques, however, cannot prove cost efficiency because of the complicated processing, unavoidable mask-based patterning and considerable waste of graphene. Meanwhile, a direct patterning and cost-efficient technique, laser scribing, has been well developed for graphene-based mSCs. Gao *et al.*⁴ directly used laser to reduce graphene oxide paper and readily obtained a number of configurations for RGO-based mSCs. With the hydrated graphene oxide as the internal electrolytes, an areal capacitance of 0.59 mF/cm² was attained. El-Kady and Kaner⁵ further extended the technique and employed external polymer electrolytes and ionogel electrolytes to obtain areal capacitance over 2 mF/cm². This technique, however, has

to rely on pre-prepared graphene oxide films. It is not convenient for direct integration of the mSCs with other components on the same chip and still involves considerable material waste. In addition, its compatibility with on-chip integration still needs to be verified since by using the laser scribing technique under similar experimental conditions, another study² only obtained areal capacitance of less than $1 \mu\text{F}/\text{cm}^2$ for the RGO-based mSCs on silicon wafers. As another powerful and cost-efficient direct patterning technique, inkjet printing attracts significant interest in printed electronics because of the purely additive manufacturing, compatibility with versatile materials/substrates and low material waste.^{12,13} As a matter of fact, inkjet printing has been employed in the literature to print RGO electrodes for stacked supercapacitors^{14,15} although the following assembly processes make them not suitable for on-chip integration. In addition, some studies have even printed graphene-based interdigitated electrode structures.^{16,17} But possibly because of the inefficient inkjet printing techniques, the interdigitated structures have not been characterized as mSCs. We have recently developed an efficient inkjet printing technique for graphene¹⁸ and other 2D materials,^{19,20} and employed it to print graphene-based mSCs on flexible substrates. The devices achieve areal capacitance over $0.6 \text{ mF}/\text{cm}^2$ when Na_2SO_4 aqueous solutions serve as electrolytes.¹⁸ However, the use of liquid-phase electrolytes remains challenging for on-chip integration. Here we fabricate all-solid-state mSCs based on printed graphene electrodes and drop-cast polymer electrolytes, in no need of any extra assembly or package. The simple fabrication processing and good device performance prove efficiency for direct integration of energy storage devices into electronic chips.

As shown in Figs. 1(a)-1(c), the all-solid-state mSCs are fabricated on Si/SiO₂ substrates (SiO₂ is ~300 nm thick). Since at present most electronic circuits/systems are still produced on silicon wafers,^{2,3} Si/SiO₂ substrates are used in our technique to prove the feasibility of on-chip integration. Typically, the key components of supercapacitors comprise current

collectors, electrodes and electrolytes. To simplify the device structure and fabrication processing, we print graphene films through a Dimatix Material Printer (DMP 2800) in interdigitated structure to serve as both electrodes and current collectors for the mSCs. The graphene inks^{18–20} are formulated based on the solvent exchange technique²¹ with terpineol as the final main solvent and ethyl cellulose as the stabilizing polymer. In order to obtain sufficient electrode conductivity, the graphene inks are printed with 50 printing passes at an optimal drop spacing of 50 μm to ensure conformal patterns in high resolution [the gap between two fingers are only about 300 μm , Figs. 1(d)-1(f)]. For better pattern quality, we adopt a cycle-based processing. In sequence, each cycle consists of 5 printing passes, heating at 80 °C in air by hot plate for 10 min to evaporate the solvents and a second heating at 400 °C for ~1 hour to remove the stabilizing polymer. For each new cycle, precise alignment to the structure in the previous cycle is needed. Therefore, 10 cycles yield 50-printing-pass graphene electrodes, and there is no visible mismatch among different printing passes or cycles [Fig. 1(d)]. Benefitting from the cycle-based printing processing, nearly no polymer residue is visible in the scanning electron microscope (SEM) images in Figs. 1(g) and 1(h). In addition, the graphene electrodes exhibit porous morphology with many sharp graphene flakes vertically oriented, which may greatly increase the specific surface area and hence are very attractive for supercapacitor applications.^{22,23} After printing the graphene electrodes, we print two silver pads [Fig. 1(b)] as contacts for electrochemical characterization. Finally, 40 μL aqueous dispersion of mixed polyvinyl alcohol (PVA, 100 mg/ml) and H_3PO_4 (100 mg/ml) is drop cast by pipette onto each device as the polymer electrolyte. The PVA/ H_3PO_4 mixture has been identified as one of the best solid-state electrolyte for graphene-based supercapacitors.²⁴ After overnight drying of the electrolytes, the final all-solid-state mSCs are obtained [Fig. 1(c)] with no need of any extra assembly or package.

FIG. 1. Inkjet printing of graphene based mSCs. (a) Printed interdigitated graphene electrodes on Si/SiO₂ wafers. The fingers are 600 μm wide, 4.5 mm long and the inter-space is 300 μm. (b) Printed silver pads for electrochemical characterization. (c) Drop-cast PVA/H₃PO₄ as the solid electrolyte. (d-f) Microscopy of (d) as-printed, (e) dried and (f) annealed graphene patterns with 50 printing passes. Scale bars: 100 μm. (g,h) SEM images of the annealed graphene electrodes.

The electrochemical properties of the printed mSCs are characterized using a two-electrode configuration with Princeton Applied Research potentiostat/galvanostat (273A) and Biologic VMP2. Figure 2 shows the cyclic voltammograms (CV) of the printed mSCs. At a scan rate of 100 mV·s⁻¹ and a voltage window of 1 V, the CV curves exhibit excellent rectangularity [rounded parallelogram, Fig. 2(a)], indicating nearly ideal electrochemical double-layer

capacitive behavior.²⁵ In particular, the CV curves are very stable. After 8 scan cycles, there is no visible voltage shift (except a small shift in the first cycle). With increasing scan rate, the CV curves become increasingly biconvex (lens-shaped). However, even at a scan rate as high as $500 \text{ mV}\cdot\text{s}^{-1}$, the rectangularity is still acceptable [Fig. 2(b)]. Based on the CV curves, the areal capacitance C_s is calculated for different scan rates, as shown in Fig. 2(c). The low scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ gives a high C_s of $0.14 \text{ mF}\cdot\text{cm}^{-2}$, while at high scan rate of $500 \text{ mV}\cdot\text{s}^{-1}$, C_s decreases to about $40 \text{ }\mu\text{F}\cdot\text{cm}^{-2}$. However, because of the rough surface of our printed graphene electrodes [Figs. 1(g) and 1(h)], it is challenging to measure their thickness (for example, the signal-to-noise ratio in profilometer characterization is too low to identify reliable values for the graphene thickness), which prevents us from reporting volumetric capacitance for the printed mSCs. Nevertheless, the areal capacitance is comparable to that of most graphene-based mSCs fabricated through other techniques in the literature (typically $0.3\text{-}0.6 \text{ mF}/\text{cm}^2$),^{4,7,9} and has been competent for many on-chip integrated systems, (e.g, some demonstrated on-chip integrated systems^{2,3} only require areal capacitance around $1 \text{ }\mu\text{F}/\text{cm}^2$). This is very promising in consideration of the simplicity of printing fabrication. Furthermore, we also test the devices with PVA/H₂SO₄ as the electrolytes. Their C_s is a little higher than those with PVA/H₃PO₄, but the CV rectangularity is rather poor [Fig. 2(d)].

FIG. 2. Cyclic voltammetry of the printed mSCs. (a) CV curves scanned at 100 mV s^{-1} with 8 scanning cycles. (b) CV curves under different scan rates. (c) Areal capacitance calculated from the CV curves at different scan rates. (d) Comparison of CVs between mSCs with different acids in the solid electrolytes.

FIG. 3. EIS and galvanostatic charging/discharging of the printed mSCs. (a) Complex plane impedance and (b) phase angle against frequency for the mSCs. (c) Charging/discharging curves at different constant currents. (d) Relative specific capacitance (calculated from the charging curves) versus charging/discharging cycles at constant current of $4 \mu A$ ($\sim 8 \mu A/cm^2$).

Figure 3 shows the electrochemical impedance spectra (EIS) and galvanostatic charging/discharging curves. The EIS was characterized using a sinusoidal signal with the amplitude of 10 mV (d.c. voltage is 0 V) over a frequency range from 100 mHz to 100 kHz. The impedance plot [Fig. 3(a)] typically indicate three distinct regions, synchronous charging

region, asynchronous charging region and non-charging region, which may reflect the presence of multiple pore sizes and/or types in the printed graphene electrodes.²⁵ In the low-frequency (synchronous) region, the impedance plot exhibits an almost vertical straight line corresponding to ideal capacitive behavior. The synchronous region may result from the vertically oriented graphene flakes.²² The intermediate-frequency (asynchronous) region [the lower line with a slope near 45° in Fig. 3(a)] is dominated by the different types of pores²⁵ whose time constants are typically distributed over a wide range so that the devices are charging at different rates, i.e., asynchronously. The transition frequency between the two regions, f_{tr} , is about 0.5 Hz for our printed mSCs, comparable to most commercial supercapacitors.²⁶ At the high-frequency non-charging region, the well-defined arc might result from the shunt between the resistance and capacitance of the electrolyte while the graphene electrodes cannot charge in this region.²⁵ The high equivalent series resistance ~ 18 k Ω could be ascribed to the lack of metal current collectors. Likely for the same reason, the characteristic frequency, at which the phase angle is -45° [Fig. 3(b)], is about 0.5 Hz, much lower than other graphene-based supercapacitors. Nevertheless, the mSCs have good charging/discharging performance. At a constant current below 2 μ A (~ 4 μ A/cm²), the charging/ discharging curves exhibit perfect linearity [Fig. 3(c)], indicating ideal capacitive behavior. Even at higher current of 4 μ A (~ 8 μ A/cm²), the capacitance remains 90% after 1000 cycles [Fig. 3(d)]. This suggests that our present printed graphene-based mSCs are promising for integration into low-frequency electronic systems^{2,3} to serve as reliable energy storage components.

In conclusion, we have fabricated all-solid-state graphene-based on-chip-integratable micro-supercapacitors through a simple, yet efficient, inkjet printing technique. The devices exhibit commendable areal capacitance about 0.1 mF·cm⁻² and long cycle life over 1000 times, which are comparable to that of most graphene-based mSCs fabricated through other techniques and

have been competent for some integrated systems in the literature. The facile and scalable fabrication technique is anticipated to pave the way for on-chip integration of energy storage component in emerging electronics.

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