Selective Wetting-Induced Micro-Electrode Patterning for Flexible Micro-Supercapacitors

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Supercapacitors (SCs) are attracting significant interest as electrochemical energy storage devices owing to their high power density during rapid charging and discharging (within seconds), nearly infinite cycle life, high round trip efficiency, low cost, low self-discharging rates, and intrinsic safety.[1] SCs store energy as a build-up of charges in the electrical double layers (EDLs) formed at the electrolyte/electrode interface. Advantageously, energy is stored without the volumetric changes often observed in electrochemical energy storage materials during charging and discharging.[2] It is important to remember that the energy density of SCs are less than that of typical electrochemical energy storage systems, and thus they are most appropriate for applications where high cycle lives, round trip efficiencies, and high power densities are particularly important.[3]

Carbon-based materials have been widely explored as electrode materials for SCs due to their good electric conductivity and high specific surface area.[4] Recent advances in SCs have been motivated by a desire to both improve the power/energy delivery and ion/electron kinetics and to reduce total device volume, and microarchitecturing of the SC electrodes has proved to be particularly promising approach to achieve these goals.[5] Microarchitected components prepared for SCs include laser-scribed graphene,[6,7] carbide-derived carbon,[8] onion-like carbon,[9] reduced graphene oxide (rGO),[10,11] carbon nanotubes (CNTs),[12] rGO/CNT composites,[13,14] conducting polymers,[15] and activated carbon (AC).[16] In some cases, these components have been integrated to form compact on-chip micro-supercapacitors (mSCs) in a range of form factors,[8,17] however, it remains a challenge to fabricate flexible mSCs and to fabricate mSCs under the mild conditions required for integration with many materials and devices such as roll-up displays, electronic paper, and portable/wearable electronics.[18] Here we present a simple, reliable, and mild approach for fabricating solid-state flexible mSCs through selective wetting-induced micro-electrode patterning. The integrated devices consist of a poly(vinyl alcohol)/phosphoric acid (PVA/H₃PO₄) gel electrolyte and binder-free, interdigitated multi-walled carbon nanotubes (MWNTs) electrodes. The devices are highly flexible and exhibit high performance even under bending and good cycle stability. A comparative study with different micro-electrodes was performed to help to better understand the design tradeoffs inherent to these mSCs. This method is general, and should be applicable to patterning many SC electrode materials into a microarchitected arrangement, as long as the electrode components can be dispersed in a hydrophilic solvent.

Figure 1 outlines the mSC manufacturing process. Starting from a micro-patterned mold formed using a 120 µm-thick SU-8 negative photoresist on a silicon substrate through a conventional replica molding process (see Supporting Information).[19] poly(dimethylsiloxane) (PDMS) slabs with in-plane 10-, 14-, and 20-interdigitated finger-like micro-channels were constructed. The slabs have 100, 500, or 1000 µm spacing between adjacent micro-channels (all micro-channels have a width of 500 µm and height of 120 µm). Conventional microtransfer molding (µTM) for preparing the mSCs electrodes was first conducted on the micro-patterned PDMS,[20] but high quality micro-patterned MWNT-based electrodes were not formed, due to the inevitable wetting of the suspension throughout the PDMS as well as micro-channels when a 3 wt% aqueous suspension of MWNTs was used. To produce well-defined micro-patterns, the patterned side of the PDMS was exposed to an oxygen plasma, making it hydrophilic. The water contact angle of oxygen plasma-treated PDMS (75 W, 20 s) is 13°, which is smaller than the 80° water contact angle on untreated PDMS, enabling good wettability by the water-based MWNT suspension (Figure S1, Supporting Information). 10 µL of the aqueous MWNT suspension was then carefully micropipetted into two micro-channels perpendicular to the finger-like micro-channels. The solution then travelled along down the micro-channels, forming an interdigitated array of MWNT micro-electrodes after drying (Movie S1). Once the MWNT suspension in the micro-channels was partially dried at room temperature, the channels were refilled once more by the MWNT suspension. The second filling should be done before the channels are fully dried. Otherwise the hydrophilic channels become hydrophobic, which restricts the flow of solution. Filling the channels more than twice caused flooding across the channels, leading to short formation. After drying, by repeated sticking and peeling back Scotch Tape, excess MWNTs on the channels where the suspension was injected were completely removed (Figure S2). Before all experiments, using a multimeter, it was confirmed there was no electrical contact between the two isolated micro-channels. The solid-state flexible devices were finished by drop-casting a PVA/H₃PO₄ solution as a solid electrolyte onto the MWNT-patterned side of PDMS. Once the solvent dried, the MWNT micro-patterns were glued to the now solid PVA/H₃PO₄. Sufficient PVA/H₃PO₄ solution was used such that once this mixture solidified a continuous PVA/H₃PO₄...
film, containing the MWNT electrodes, could be peeled off the PDMS in one piece. The MWNT patterns on the PVA/H₃PO₄ film are well-defined, defect free, and robust, even to rubbing with fingers. The use of a polymer electrolyte enables formation of a compact micrometer-sized device without the complications of a liquid electrolyte. Here, the MWNT micro-channels serve as both the active electrodes and the current collector. No organic binders are included. The resulting micro-supercapacitors will henceforth be referred to as mSC-X where X denotes the interspace (in µm) between two isolated micro-electrodes. All the mSC designs are mechanically flexible and robust even to folding (Figure 1b and Figure S3).

Top and cross-sectional views of electrodes in mSCs are characterized through scanning electron microscopy (SEM) as shown in Figure 1c and 1d. The SEM images of mSC-100 indicate well-aligned ~500 µm wide channels uniformly filled with MWNTs, ~100 µm of interspace, and ~5 µm-thick electrodes. Other mSCs, mSC-500 and mSC-1000, prepared by the same procedure show the same channel width and height with interspaces of 500 µm for mSC-500 and 1000 µm for mSC-1000 (Figure S4). SEM-energy dispersive spectroscopy (EDS) mapping of phosphorous (yellow dots) reveals that the H₃PO₄-containing electrolyte penetrates deeply into the electrodes, as the phosphorous signals are present throughout the thickness of the electrodes (Figure 1d).

The electrochemical characterization of mSCs was performed by two-electrode cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. No redox reactions between the current collector and electrolyte are observed in the CV curve (Figure 2a). In the voltage window ranging from –0.4 to 0.4 V, the CV curve of mSC-100 exhibits a rectangular shape, demonstrating the effective formation of an EDL at the electrode/electrolyte interface and good charge propagation across the electrodes (Figure 2a).[21] The volumetric capacitance, calculated based on the total electrodes volume excluding the electrolyte, of mSC-100 is 5.5 F cm⁻³ at a scan rate of 10 mV s⁻¹, comparable to the value of other mSCs previously reported.[9,13,16] For mSC-500 and mSC-1000, the CV curves become distorted, and the cathodic/anodic current values decrease, indicative of a more resistive behavior. It is known that such performance drop is ascribed to the combination of a larger equivalent series resistance (ESR) of the electrodes and a slower ion diffusion.

Figure 1. (a) Schematic illustration for the fabrication of mSCs. The major steps of the fabrication process are: (i) fabrication of in-plane interdigitated finger-like SU-8 mold on a Si wafer via conventional photolithography, (ii) casting and curing of PDMS on the mold, (iii) peeling of the cured PDMS from the mold, (iv) injection of MWNT aqueous suspension along the micro-channels after oxygen plasma treatment of the patterned side of the PDMS, (v) drop-casting of PVA/H₃PO₄ solution, and (vi) peeling off the PVA/H₃PO₄ film after drying. (b) A photograph of the flexible mSC-100 device. (c) Top SEM image of the micro-electrodes and (d) cross-sectional SEM image of the electrolyte-filled MWNT layer and the overlying electrolyte layer of mSC-100 with the EDS elemental mapping of phosphorous shown as yellow dots. In the SEM image the overlying electrolyte layer is at the bottom.
within the electrolyte. Since the same electrodes were utilized for all the mSCs in this study, the decrease in capacitance with an increase in spacing between two electrodes must result from the longer ion diffusion path. For mSC-1000, which has the largest interspace among the devices, the capacitance drop is the most pronounced; its capacitance is four times smaller than that of mSC-100.

To further understand the capacitive features, GCD curves of mSCs were recorded at a constant current density of 0.017 A cm\(^{-3}\) (Figure 2b). The voltage–time responses of mSC-100 during charging/discharging show symmetric triangular-shaped GCD profiles with long duration time and small internal resistance (IR drop at beginning of discharge curve), which is a typical of an electric double layer capacitor. However, the duration time for charging/discharging gets smaller and charging curves become asymmetric with their corresponding discharge counterpart with the increase of interspace between electrodes, indicating poor capacitive behavior. As already mentioned, the IR drop is function of the interspace and can be attributed to the overall internal resistance. Minimizing the internal resistance is desirable, as internal resistances lead to lower performance and resistive heating during charging and discharging. The internal resistance calculated from the IR drop at the start of the discharge curve increases from 1.4 kΩ for mSC-100 to 23 kΩ for mSC-1000. This is consistent with CV results (Figure 2a) and previous studies that the mean ion diffusion path varies with the interspace between two electrodes. This finding is further corroborated by electrochemical impedance spectroscopy (EIS) (Figure S5). The intercept to the real axis of the Nyquist plots represents the ohmic resistance of electrolyte and the internal resistance of the electrode materials, and this value matches quite well with the internal resistance value computed from the IR drop of the GCD discharge curves. Information on ion diffusion in the mSCs is also obtained from the 45° Warburg region in the intermediate frequency of the Nyquist plot (Figure S5). mSC-100 exhibits a shorter Warburg region than mSC-500 and mSC-1000, reflecting faster diffusion of ions in mSC-100 due to the shorter mean ionic diffusion pathway between two micro-electrodes in that mSC.

Figure 2c shows the rate capability of mSCs measured by estimating the GCD profiles at current densities ranging from 0.005 to 0.05 A cm\(^{-3}\). The capacitance reduction and the increase of IR drop in the mSCs are clearly observed as the current is increased because charging/discharging processes are kinetically limited at high currents for which ions can not easily access the adsorption sites on electrode surface (Figure 2c and S6). The capacitance value of mSC-100 is ca. 5.0 F cm\(^{-3}\) at a discharge current of 0.009 A cm\(^{-3}\), which is larger than the 4.2 F cm\(^{-3}\) of mSC-1000 and 5 times larger than a conventional sandwich type SC at the same current density. The in-plane interdigitated microarchitecture in these mSCs can increase the fraction of electrodes and thus provide larger accessible surface area for EDL formation than that of sandwich type SC, resulting in a large charge storage capacity. The initial capacitance of mSC-100 remains as high as 3.6 F cm\(^{-3}\) even at a high discharge current of 0.05 A cm\(^{-3}\), corresponding to 67% retention. At this high discharge rate, the capacitance drops, however, become more significant as the interspace increases, with 56% and 42% retention of the initial capacitance values for mSC-500 and mSC-1000, respectively.

The mSCs are robust to mechanical stresses and cycling, and can even provide a sufficient current to light a light-emitting-diode (LED). The robustness of the mSC device to mechanical stresses was examined by performing CV measurement of bent samples and after bending cycles (Figure 3a). The CV curves of the mSC-100 at 60°, 90°, and 120° bend angles (8.2, 5.4, and 3.8 mm of bend radii, respectively) and after 100 bending cycles (with a radius of curvature of 5.4 mm) remain almost unchanged. After 10,000 GCD cycles at a constant current of 0.035 A cm\(^{-3}\), mSC-100 retained 98% of initial capacitance value and its coulombic efficiency remains intact, demonstrating a good cycle life (Figure 3b). Even 4 months later, the CV curve of mSC-100 is similar to when it was first prepared (Figure S7).

Tandem mSCs were configured in series and in parallel (Figure S8). These configurations provide either an increased operating voltage window (series configuration) or an increased capacitive current (parallel configuration). The tandem serial mSC-100s were operated over a 1.6 V window (twice that of a single mSC-100), and as expected, there was a degradation in the current output due to added resistance, as confirmed by CV and GCD. The tandem parallel mSC-100s provided twice the output current of a single mSC-100, while maintaining a steady
flexibility and long-term cycle durability as well as a reliable high power output, suggesting it could be a promising candidate for high power on-chip energy storage applications. The electrode fabrication method demonstrated here is based on the flow of a MWNT suspension in a polar, hydrophilic solvent (water in this study) along hydrophilic-treated micro-channels. We suspect this approach could be applied to pattern various other functional materials (e.g. other carbon materials, polymers, and metal oxide nanoparticles) as long as they disperse well in hydrophilic solvents.

**Experimental Section**

*Micro-supercapacitor (mSC) Fabrication*: Micro-patterned PDMS having 10-, 14-, and 20-interdigitated 500 µm wide and 120 µm high finger-like channels were fabricated by replica molding. Detailed information is provided in the Supporting Information. The patterned side of the PDMS was treated by oxygen plasma (75 W, 20 s) to make it hydrophilic, and then the micro-channels in the PDMS were filled with 10 µL of MWNT suspension (3 wt% in water, Nanostructure & Amorphous Materials, Inc.) by injecting the suspension into the channels perpendicular to the finger-like channels using an adjustable micropipette. Before the water in the suspension completely dried, injection of the MWNT suspension (10 µL) was repeated. The MWNT suspension in the PDMS channels was then dried at 60 °C for 12 h. Over-coated MWNTs were removed by repeated sticking and peeling back Scotch Tape to ensure a reproducible performance and avoid electrical shorts. The PVA/H₃PO₄ electrolyte solution was prepared as follows. 1.0 g of PVA (Mₙ ∼ 95 000 g mol⁻¹, 95% hydrolyzed, Aldrich) was dissolved in 15 mL of deionized water at 90 °C with vigorous stirring until the solution became transparent. After cooling to room temperature, 0.8 g of H₃PO₄ (85 wt% aqueous solution, Aldrich) was added into the solution and stirred for 12 h at room temperature forming a homogeneous solution. The PVA/H₃PO₄ solution was cast onto the MWNT-patterned side of PDMS and then dried at 60 °C for 12 h. The dried PVA/H₃PO₄ film was peeled off the PDMS substrate, taking the patterned MWNTs electrodes with it. For better electric contact with probes of the measurement analyzer, the electrode edges of the mSCs were extended using an adhesive copper tape with help of silver paint.

**Characterization and Measurements**: Oxygen plasma treatment was performed in a March GCM-200. The microstructures were imaged using a Hitachi S-4700 SEM. Electrochemical characterization, including CV, GCD, and EIS, was performed using a VMP3 multichannel potentiostat (Bio-Logic, USA) in the two-electrode mode at room temperature, 0.8 g of H₃PO₄ (85 wt% aqueous solution, Aldrich) was added into the solution and stirred for 12 h at room temperature forming a homogeneous solution. The PVA/H₃PO₄ solution was cast onto the MWNT-patterned side of PDMS and then dried at 60 °C for 12 h. The dried PVA/H₃PO₄ film was peeled off the PDMS substrate, taking the patterned MWNTs electrodes with it. For better electric contact with probes of the measurement analyzer, the electrode edges of the mSCs were extended using an adhesive copper tape with help of silver paint.

**Supporting Information**

Supporting information is available from the Wiley Online Library or from the author.

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