ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Air-Stable, High-Performance, Flexible Microsupercapacitor with Patterned Ionogel Electrolyte

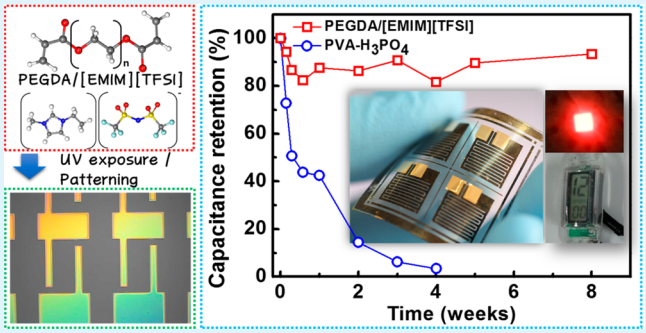
Daeil Kim,[†] Geumbee Lee,[‡] Doyeon Kim,[‡] and Jeong Sook Ha*[,†,‡]

[†]Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea

[‡]KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 136-701, Republic of Korea

Supporting Information

ABSTRACT: We describe the fabrication of air-stable, high-performance, planar microsupercapacitors (MSCs) on a flexible poly(ethylene terephthalate) substrate with patterned ionogel electrolyte, i.e., poly(ethylene glycol) diacrylate/1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and electrodes of spray-coated multiwalled carbon nanotubes. The flexible MSC showed good cyclability, retaining ~80% of initial capacitance after 30 000 cycles, and good mechanical stability down to a bending diameter of 3 mm under compressive stress; 95% of the initial capacitance was retained after 1000 bending cycles. The MSC had high electrochemical stability with retaining 90% of its initial capacitance for 8 weeks in air. Furthermore, vertical stacking of MSCs with patterned solid film of ionogel electrolyte could increase the areal capacitance dramatically. This flexible MSC has potential applications as an energy-storage device in micro/nanoelectronics, without encapsulation for air stability.



KEYWORDS: *flexible microsupercapacitor, ionogel electrolyte, air stable, patterned electrolyte, all-solid-state*

1. INTRODUCTION

The increasing demand for wearable and bioimplantable micro/nanoelectronic devices has accelerated research on the novel design and fabrication of flexible/stretchable electronics.[1−4] Energy-storage devices that can be integrated into flexible/stretchable electronics have also been investigated intensively.[5,6] The fabrication of various operational flexible/stretchable micro/nanoelectronics with on-chip integrated energy-storage devices requires the development of patterning techniques for all the electronic components and the use of high-performance materials, including the electrodes and electrolytes.

Among energy-storage devices, supercapacitors have the advantages, compared with conventional batteries, of high power densities, fast charging and discharging rates, long cycling lifetimes, and superior safety.[7] Planar all-solid-state microsupercapacitors (MSCs) with micrometer-scale spaces between the electrodes can be easily integrated into the circuits of micro/nanoelectronic devices.[6,8,9] As is the case of a complementary metal−oxide−semiconductor (CMOS) device, patterning of electrolyte is critical to vertically stack the multiple MSCs for high density; if the insulating electrolyte is not patternable but covering the whole MSC, it is not easy to electrically connect the MSCs vertically to stack them. Therefore, it is important to pattern the electrolyte as well as the electrodes for the facile and efficient integration of MSCs.

Ionogel electrolytes, which consist of polymer backbones and aqueous- or organic-solvent-based ionic salts, have been widely investigated for use as energy-storage devices in supercapacitors, Li-ion batteries and fuel cells, field-effect transistor electronic devices, and solar cells.[10−18] Ionogel electrolytes have the advantages of high ionic conductivities, flexibility/stretchability, nonvolatility, nonleakage, and high potential windows; therefore, they are suitable for use in flexible and stretchable electronics.[10,17,19] In particular, it has been reported that poly(ethylene glycol) diacrylate (PEGDA), which is a nondegradable and hydrophilic polymer, in an ionogel electrolyte can be patterned on any substrate, using a photolithographic process.[20,21] Patterned PEGDA films were therefore widely used in microfluidic devices, transistors, sensors, and optical communications.[21−27]

Recently, several groups have demonstrated the use of PEGDA-based ionogel electrolytes with ionic liquids such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) as a gate insulator in organic transistors, because they have low switching voltages, high on-currents, and high capacitances and are easily patterned.[28−30]

Here, we report on the fabrication of planar MSCs on a flexible PET substrate with patterned ionogel electrolyte and electrodes of spray-coated multiwalled carbon nanotubes (MWNTs). The PEGDA/[EMIM][TFSI] electrolyte was patterned down to 10 μm, using a photolithographic process.

Received: November 7, 2014
Accepted: February 9, 2015
Published: February 9, 2015

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608−4615

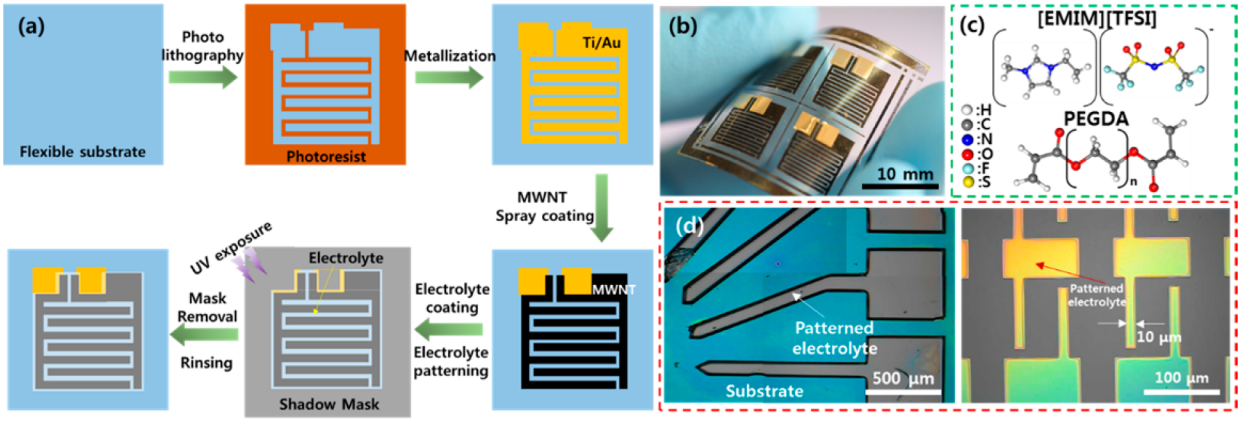


Figure 1. (a) Schematic diagram of fabricating flexible MSC with patterned solid electrolyte on a PET substrate; (b) photographic image of fabricated flexible MSCs on a PET substrate; (c) molecular structures of [EMIM][TFSI] and PEGDA; (d) optical microscopy images of various electrolyte patterns.

The flexible MSC gave a good electrochemical performance, with a stack capacitance of 5.3 F/cm^3 at a scan rate of 10 mV/s, an energy density of 2.9 mWh/cm^3 at a power density of 0.05 W/cm^3, and a power density of 21.0 W/cm^3 at an energy density of 0.17 mWh/cm^3 at a high potential window of 0 to 2 V. The flexible MSC had good cyclability, and retained ~80% of its initial capacitance after 30 000 cycles. It was also electrochemically stable under bending down to a bending diameter of 3 mm under compressive stress, and retained 95% of its initial capacitance after 1000 bending cycles. Furthermore, the flexible MSC had highly stable electrochemical properties under ambient conditions: after 8 weeks in air, about 90% of the initial capacitance was retained. These results are important, because flexible MSCs with the commonly used solid electrolyte poly(vinyl alcohol) (PVA)/H_3PO_4 show significant decreases in the initial capacitance, down to 3%, after 4 weeks in air. The air stability of the flexible MSC with a patterned ionogel electrolyte was confirmed by the absence of changes in photographic images of the flexible MSC surface with time on exposure to ambient air. Furthermore, it was possible to vertically stack the multiple MSCs, increasing the areal capacitance owing to the use of patterned solid state ionogel electrolyte.

2. MATERIALS AND METHODS

2.1. Synthesis of PEGDA/[EMIM][TFSI] and PVA/H_3PO_4 Electrolytes. PEGDA (M_w = 575; Sigma-Aldrich), 2-hydroxy-2-methylpropiophenone (HOMPP; Sigma-Aldrich), and the ionic liquid [EMIM][TFSI] (Sigma-Aldrich) were used as purchased. [EMIM]-[TFSI], the PEGDA, and HOMPP [ultraviolet (UV) cross-linking initiator] were mixed at ratios of 88:8:4 (w/w), and the mixed solution was stirred, using a Voltex-2 Genie (Scientific Industries) stirrer, for 30 min.[28] For comparative electrochemical performance measurements, a PVA/H_3PO_4 gel electrolyte was synthesized by mixing PVA (15 g; M_w 89 000–98 000, Aldrich) with H_3PO_4 (15 mL, Aldrich) in deionized (DI) water (150 mL) at 150 °C, until a clear solution was obtained.

2.2. Fabrication of MSC with Patterned Ionogel. To fabricate the current collector, a two-layer photoresist film, consisting of a lift-off resist (LOR, K1 solution) layer and an AZ5214 (Microchemicals) layer spin-coated (10 s at 500 rpm and 60 s at 2000 rpm) on a flexible PET substrate, was patterned using a photolithography technique. After deposition of a Ti (5 nm)/Au (50 nm) film by electron-beam evaporation, the photoresist was removed with acetone, using a lift-off process, and the LOR was then removed by dipping in the developer (AZ300, Microchemicals) for 10 s. Functionalized MWNT (MWNT-COOH) solution in DI water (1.0 mg/mL) was spray-coated in the vertical direction onto the patterned Ti/Au collector with a photoresist pattern, while heating the substrate at 100 °C. The spray coating used 6 mL of the MWNT solution. After fabrication of the MWNT electrodes, the photoresist was removed using the same process as that used for metallization.[6] The mixed ionogel electrolyte was drop-cast onto the entire flexible MSC. A shadow mask was placed on the MSC, followed by irradiation with UV light (365 nm, 80 mW/cm^2) for 40 s. The shadow mask was removed, and the flexible MSC with the unexposed ionogel was rinsed with chloroform for 5 s and DI water for 10 s. Finally, the flexible MSC was dried by gentle blowing with N_2 gas.

To fabricate a vertically aligned stack of multiple MSCs, holes with a diameter of 2 mm are punched on the electrodes of an individual MSC and the MSCs are stacked vertically. After the vertical assembly, Ecoflex (Ecoflex 0030, Smooth On) is used as an adhesive and the electrodes are electrically connected with liquid metal of Galinstan (68.5% Ga, 21.5% In, and 10% Sn; Rotometals).

2.3. Characterization of MSC with Patterned Ionogel. CV curves, galvanostatic charge–discharge curves, and Nyquist plots were obtained using an electrochemical analyzer (Compact Stat, Ivium Technologies). Electrochemical performances were evaluated in a normal air environment (T = 27 °C, relative humidity = 50%), and the flexible MSCs were stored in ambient air. Optical microscopy images of the ionogel electrolyte film were obtained using a PSM-1000 (MS Tech) instrument, and photographic images were obtained using an EOS 7D (Canon) camera.

3. RESULTS AND DISCUSSION

Figure 1a shows a schematic diagram of fabricating the MSC with a patterned ionogel electrolyte. The flexible MSC was fabricated using photolithography to produce the MSC pattern, electron-beam evaporation to produce the current collector, and spray-coating with functionalized MWNTs to produce the electrodes. After drop-casting the electrolyte onto the spray-coated MWNT electrodes, the electrolyte was patterned by irradiation with UV light. Details of the fabrication process are given in the Materials and Methods section. The fabricated flexible MSC with MWNT electrodes and a patterned electrolyte on a PET substrate is shown in Figure 1b. Figure 1c shows the molecular structures of the ionic liquid [EMIM][TFSI] and the UV cross-linkable polymer PEGDA. [EMIM][TFSI], in which [EMIM] and [TFSI] are the cation and anion, respectively, has a high potential window of ~4 V and room-temperature ionic conductivity of 9.4 × 10^{-3} S/cm.[17]

The PEGDA pattern was obtained using a photolithographic process. UV irradiation (365 nm, 80 mW/cm^2) generates free

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608–4615

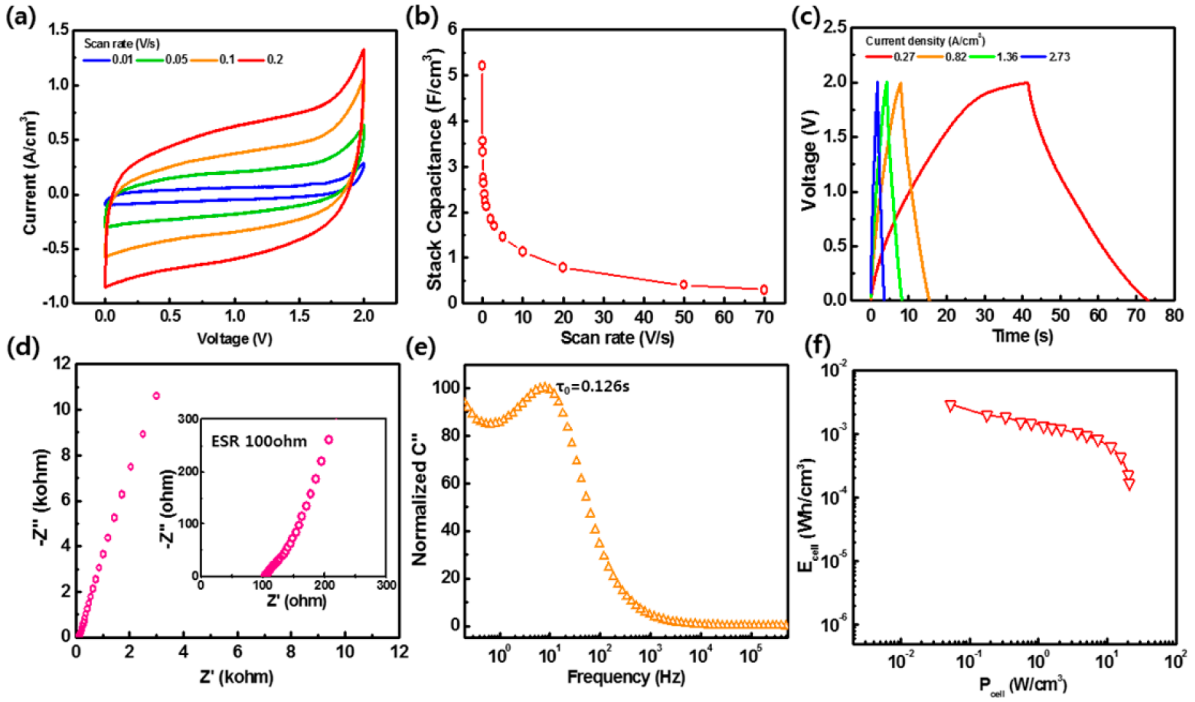


Figure 2. (a) Cyclic voltammetry curves obtained at various scan rates from 0.01 to 0.2 V/s; (b) stack capacitances of flexible MSC obtained at various scan rates; (c) galvanostatic charge−discharge curves obtained at current densities from 0.27 to 2.73 A/cm^3; (d) Nyquist plots measured between 0.1 and 10 kHz (the inset shows magnified plots in the high-frequency region); (e) normalized C'' ($C'' = Z'/\omega|Z|^2$, ω is the angular frequency) vs frequency; (f) Ragone plots of MSCs.

radicals from HOMPP, and these initiate solidification of the acrylate end groups on the PEG derivatives.[28] This solidification process was used to form various PEGDA/[EMIM][TFSI] ionogel electrolyte patterns with sizes down to 10 μm, as shown in Figure 1d. Cross-sectional scanning electron microscopy (SEM) images of a 20 μm wide pattern of the electrolyte on a SiO_2/Si substrate are shown in Figure S1a and b (Supporting Information). A cross-sectional SEM image of the MSC with MWNT electrodes and a patterned electrolyte is shown in Figure S1c (Supporting Information). These images clearly show that the microstructure is successfully formed by patterning the electrolyte and that the patterns are uniformly fabricated on the PET substrate.

The electrochemical properties of the fabricated flexible MSC were investigated to evaluate the basic characteristics of the patterned ionogel electrolyte. Figure 2a shows CV curves of the flexible MSC obtained at various scan rates between 0.01 and 0.2 V/s. Furthermore, the CV curves at high scan rates between 1.0 and 70 V/s are also shown in Figure S2 (Supporting Information). The flexible MSC shows excellent rectangular curves in the voltage range between 0 and 2 V, indicating that the MSC with a patterned ionogel electrolyte gives a very stable electrochemical performance. The stack capacitances of the flexible MSC can be estimated from the CV curves, using eq 1.[6]

$$C_{\text{stack}} = \frac{\int_{V_i}^{V_f} I(V)\,\mathrm{d}V}{2S(V_f - V_i)V} \quad (1)$$

Here, I, S, and V are the current, scan rate, and total volume of the MSC, respectively; V_i and V_f are the initial and final potential, respectively. The total area of the flexible MSC was estimated to be 0.733 cm^2, as shown in Figure S3 (Supporting Information). The flexible MSC has interdigitated electrodes with an interspace of 150 μm and a width of 500 μm. The thicknesses of the flexible MSC electrode and current collector are about 500 and 55 nm, respectively (Figure S4, Supporting Information). In this case of MSC, the surface of the MSC is defined from the whole projected surface area including the gap between the electrodes, and the thickness is also defined from the current collector to the active material.[8,31]

Figure 2b shows the changes in the calculated stack capacitance with changes in the scan rate between 0.01 and 70 V/s. The flexible MSC has a stack capacitance of 5.3 F/cm^3 at a scan rate of 0.01 V/s, which is similar to the values reported recently. Braun et al. reported a stack capacitance of 5.5 F/cm^3 at 0.01 V/s for a planar MSC with an MWNT electrode and PVA/H_3PO_4 electrolyte,[32] and Hsia et al. reported a stack capacitance of 86 mF/cm^3 at 0.1 V/s for a vertically aligned carbon nanotube (VACNT) electrode and [EMI][TFSI] ionogel electrolyte.[33] Figure 2c shows galvanostatic charge−discharge curves obtained at current densities between 0.27 and 2.73 A/cm^3. The charge−discharge curves are triangular and indicate a high Coulombic efficiency of ~100% at a current density of 2.73 A/cm^3. The flexible MSC also shows stable performances at various potential windows, namely, 0−0.8, 1.0, 1.5, and 2.0 V in the CV curves and 0.8, 1.0, 1.2, 1.6, 1.8, and 2.0 V in the charge−discharge curves (Figure S5, Supporting Information). The flexible MSC has a small equivalent series resistance value, i.e., 100 Ω, as shown in Figure 2d. It is also worth noting that a rapid frequency response by the flexible MSC is confirmed by the short relaxation time constant (τ_0) of 0.126 s, where τ_0 is the reciprocal of the frequency (f_0) at the peak in the normalized capacitance (C'') versus frequency plot (Figure 2e).

The time constant, τ_0, is the transition point at which the behavior of the electrochemical capacitor changes from

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608−4615

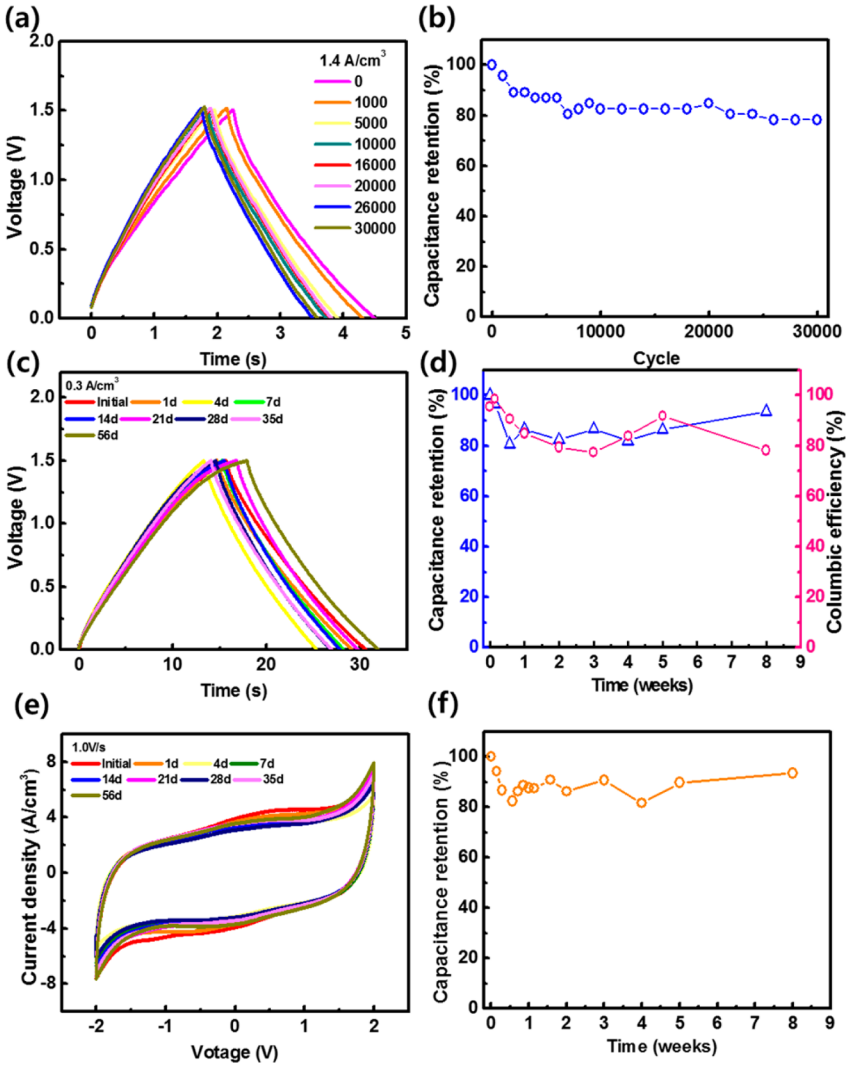


Figure 3. Cyclic stability (a, b) and air stability (c–f) of flexible MSC with PEGDA/[EMIM][TFSI] ionogel electrolyte. Changes in (a) galvanostatic charge–discharge curves and (b) capacitance retention at a current density of 1.4 A/cm^3 up to 30 000 cycles, respectively. Changes in (c) CV curves, (d) capacitance, (e) galvanostatic charge–discharge curves, and (f) Coulombic efficiencies with time in air for up to 8 weeks.

capacitive to resistive, and corresponds to the point of maximum energy dissipation. Figure 2f shows the Ragone plot of the MSC. The energy (E_{cell}) and power density (P_{cell}) were estimated using eqs 2 and 3, respectively

$$E_{cell} = \frac{C_{stack} \cdot (\Delta V)^2}{7200} \quad (2)$$

$$P_{cell} = \frac{E_{cell} \times 3600}{\Delta t} \quad (3)$$

where ΔV is the range of the operating potential and Δt is the discharge time. The flexible MSC has an energy density of 2.9 mWh/cm^3 at a power density of 0.05 W/cm^3 and a power density of 21.0 W/cm^3 at an energy density of 0.17 mWh/cm^3, respectively.

It is important to achieve long cycling durability and long-term air stability of the flexible MSC, in addition to a good electrochemical performance.[34] Figure 3a shows that the flexible MSC exhibits excellent cycling stability; ~80% of the initial capacitance is retained after 30 000 cycles at a current density of 1.4 A/cm^3 (Figure 3b). Figure 3c shows the changes in the CV curves of a flexible MSC kept in an air environment at 27 °C and a relative humidity of 50%. There is no noticeable shape change in the CV curves up to 8 weeks. Furthermore, the flexible MSC retained 90% of the initial capacitance, even after 8 weeks in air, as seen in Figure 3d. Figure 3e shows typical galvanostatic charge–discharge curves with increasing time under ambient air. The capacitance and Coulombic efficiency remained at 90 and 80%, respectively, of the initial values after 8 weeks (Figure 3f). The triangular shape did not change with time kept in air.

Figure 4a shows photographic images of the MSC on a PET substrate under convex bending down to a bending diameter (D) of 3.0 mm. The CV curves under various bending conditions, from flat to D = 3 mm, at a scan rate of 1 V/s, are shown in Figure 4b. Regardless of the bending diameter, the CV curves have ideal rectangular shapes, without any noticeable deterioration. The fabricated MSC with a patterned ionogel electrolyte also shows stable performance on repeated deformation, and up to 90% of the capacitance was retained after 1000 bending cycles, from D = 16 to 5 mm, as shown in Figure 4c.

The CV curves in the inset of Figure 4c also show ideal rectangular shapes, regardless of the number of bending cycles.

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608–4615

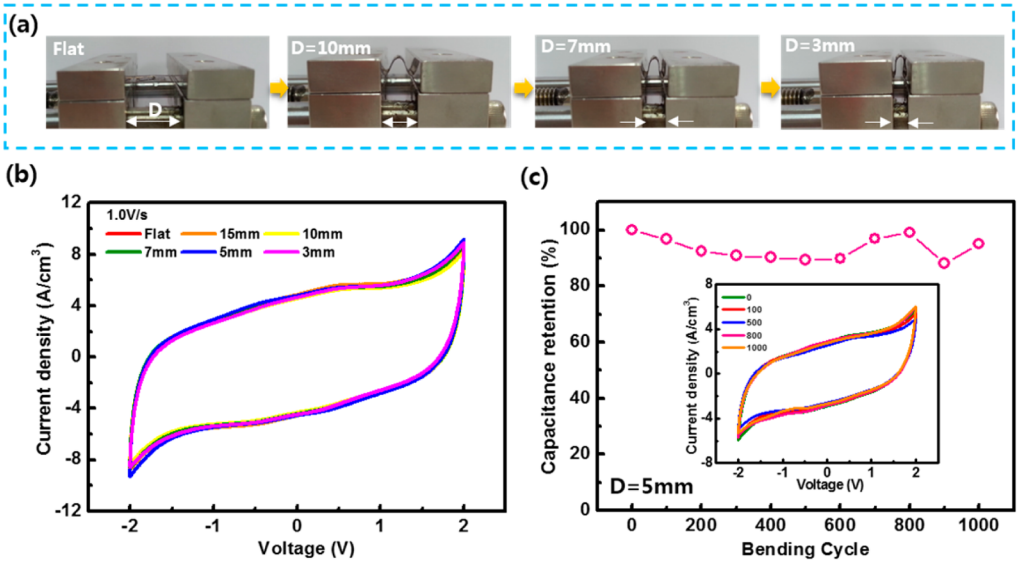


Figure 4. (a) Photographs showing convex bending of flexible MSC with changes in bending diameter (D); (b) CV curves obtained under convex bending at different D values; (c) changes in capacitance with repetition of bending deformation at D = 5.0 mm. The inset shows changes in CV curves during 1000 bending cycles.

The SEM images of Figure S6 (Supporting Information) taken from the Ti/Au electrode, the MWNT film on the Ti/Au electrode, and the patterned ionogel electrolyte with the MWNT electrode and Ti/Au current collector did not show any defect or crack during the bending, confirming the mechanical stability of our MSC as we expected from the electrochemical properties. These results imply that this flexible MSC can be used as an energy storage device in flexible portable devices.

Next, the air stabilities of flexible MSCs with patterned ionogel electrolyte and the conventional solid electrolyte PVA/H_3PO_4 were compared. In both MSCs, the same electrode pattern and electrode material, i.e., a spray-coated MWNT-COOH film, were used. The flexible MSC with PVA/H_3PO_4 has stable electrochemical properties, as shown in Figure S7 (Supporting Information). Parts a and b of Figure 5 show photographic images of MSCs with a patterned PEGDA/[EMIM][TFSI] electrolyte and with PVA/H_3PO_4, respectively, during storage in air for 14 days. It can be seen that the MSC with the PEGDA/[EMIM][TFSI] electrolyte shows no noticeable damage, whereas that with PVA/H_3PO_4 has a white circle on the surface. This might be attributed to the evaporation of water in the PVA/H_3PO_4 electrolyte, causing dryness on the surface. Figure 5c shows the capacitance retention properties of the two MSCs with time in a normal ambient air environment for 8 weeks. The MSC with PVA/H_3PO_4 shows fast degradation, and the initial capacitance decreases to ~75%, even after 1 day, and ultimately to ~3% after 4 weeks. However, the MSC with a patterned ionogel electrolyte retains ~90% of its initial capacitance even after 8 weeks. The CV curves of both MSCs are shown in Figure S8 (Supporting Information). The curves for the flexible MSC with PEGDA/[EMIM][TFSI] maintain their initial shape, whereas that with PVA/H_3PO_4 shows significantly degraded CV curves.

This implies that the electrolyte based on an acidic solution in DI water cannot maintain its performance for a long time in ambient air, probably because of evaporation of water. The evaporation of water may cause a decrease in the ionic mobility in the MSC. However, the patterned electrolyte based on an ionic liquid and PEGDA polymer does not change in ambient air for a long time. As a result, the flexible MSC with PEGDA/

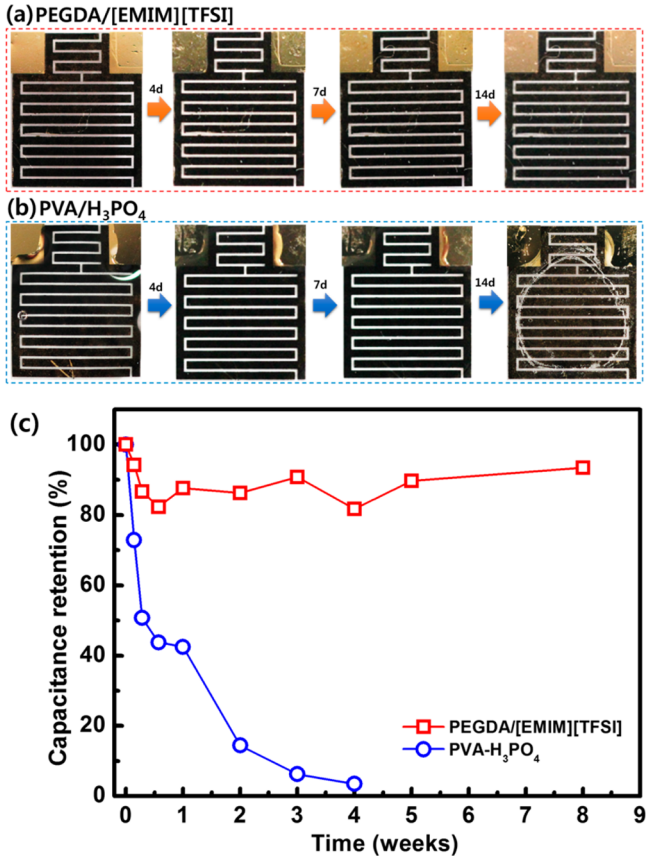


Figure 5. Time-dependent optical images of electrolyte films in normal ambient air environment for 2 weeks. (a) PEGDA/[EMIM][TFSI] film and (b) PVA/H_3PO_4 film. (c) Normalized capacitance retentions of flexible MSCs with PEGDA/[EMIM][TFSI] (red squares) and PVA/H_3PO_4 (blue circles). The capacitance is estimated from the CV curves measured at a scan rate of 1.0 V/s.

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608−4615

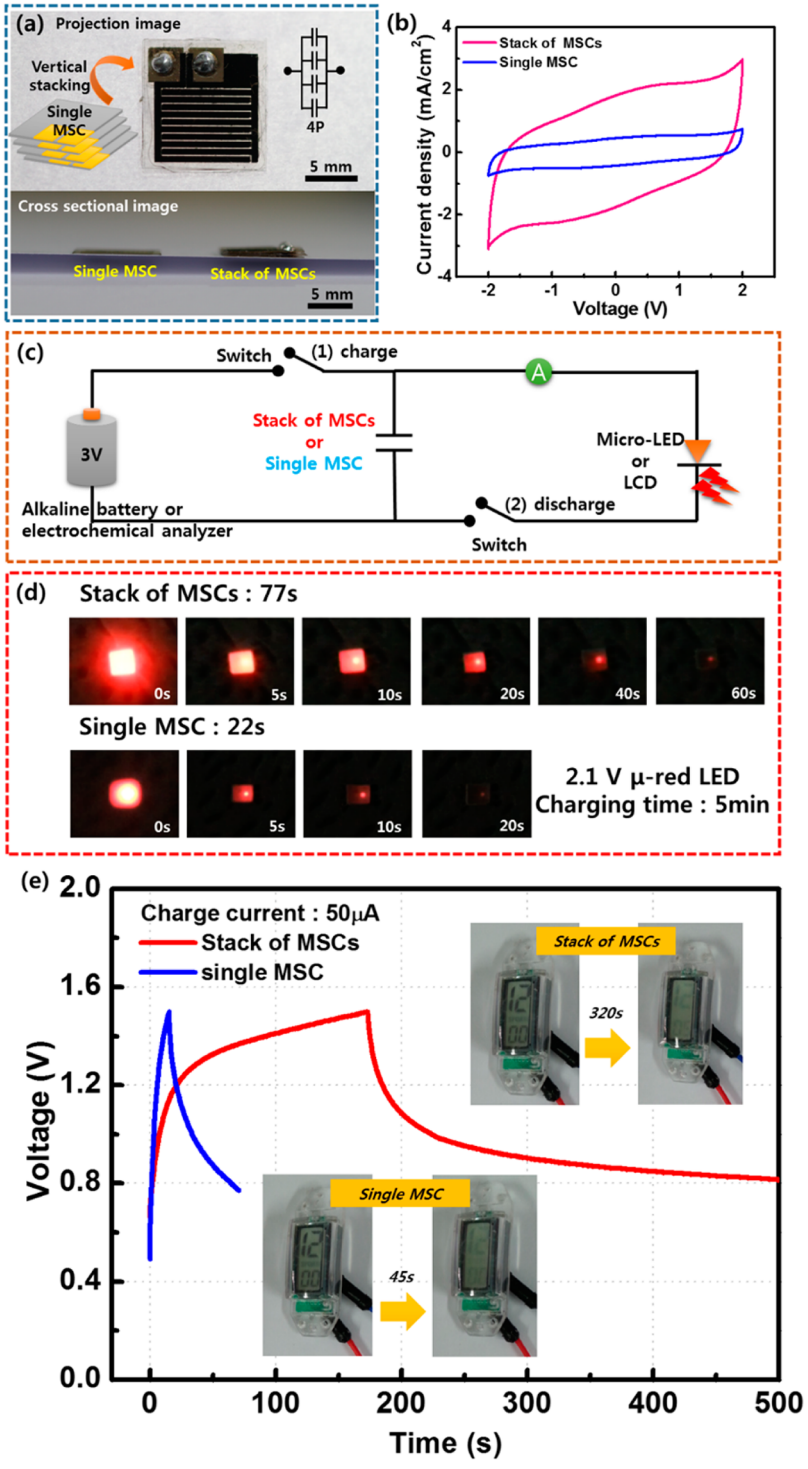


Figure 6. (a) (top) From the left, scheme of stacking MSCs, optical image of a stack of 4 MSCs, and a circuit of 4 parallel stacked MSCs. (bottom) Cross-sectional images of a single MSC (left) and a stack of 4 MSCs (right). (b) CV curves of the stack of 4 MSCs (red) and a single MSC (blue) taken at a scan rate of 1 V/s. (c) Schematic circuit diagram of operating a μ-LED and a LCD with MSCs and switches. (d) Time dependent optical images of a μ-LED lit by a stack of 4 MSCs and a single MSC. Here, the charging of MSC was done by using a 3 V battery. (e) Charge/discharge curves of a stack of 4 MSCs (red) and a single MSC (blue) for operation of a LCD, respectively. The inset images are for operation of the LCD with the stack of 4 MSCs (top right) and a single MSC (bottom left), respectively. Here, the charging of MSC was done by using our electrochemical analyzer.

[EMIM][TFSI] has excellent long-term electrochemical properties, without any noticeable deterioration in performance. These results demonstrate that flexible MSCs with PEGDA/[EMIM][TFSI] electrolytes are suitable for use as high-performance energy-storage devices in on-chip integrated electronics, without any encapsulation process.

Since the flexible MSC with patterned ionogel electrolyte is in perfectly all-solid-state, it is easy to fabricate a vertically aligned stack of multiple MSCs for increasing the areal

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608−4615

capacitance as well as the total capacitance. Figure 6a shows optical images taken from a stack of 4 MSCs connected in parallel. It is clearly shown that the 4 MSCs are vertically aligned perfectly. As a result, the total thickness of the stack of 4 MSCs is estimated to be 750 μm by using a Vernier caliper, which is about 4 times thicker than that of a single MSC (180 μm) shown in the SEM image of Figure S1c (Supporting Information). The CV curves taken from a single MSC and a stack of 4 MSCs at a scan rate of 1.0 V/s are compared in Figure 6b. Both the total and areal capacitance values increased 4 times with vertical stacking, as expected.

Figure 6c shows the circuit diagram for operating a red μ-light-emitting diode (LED) or a liquid crystal display (LCD) connected to a MSC (stack of MSCs); the LED and LCD require 2.1 and 0.8 V for turn-on, respectively. Switch (1) is first closed for charging the MSC and the stack of MSCs with a 3 V alkaline battery at a constant voltage or with the electrochemical analyzer at a constant current. Switch (2) is then closed for operation of the μ-LED and the LCD by discharging the MSC and the stack of MSCs. Figure 6d compares operation of the red μ-LED using the flexible MSC and a stack of 4 MSCs with a patterned ionogel electrolyte. Since the MSC is charged with a 3 V battery, the red μ-LED is lit by just a single MSC or a stack of 4 MSCs connected in parallel. However, the μ-LED was not lit by the MSC with a PVA/H_3PO_4 electrolyte due to an insufficient output voltage of 0.8 V. The μ-LED was lit for 22 and 77 s with a single MSC and the stack of 4 MSCs, respectively, due to increased capacitance by stacking MSCs in parallel. In addition, a LCD panel is operated by using the MSCs. Figure 6e shows the charge/discharge curves taken from the single MSC and the stack of 4 MSCs. The operation time for the LCD is estimated to be 320 s with the stack of MSCs, which is 7 times longer than that of a single MSC. These results clearly demonstrate that flexible MSCs with patterned ionogel electrolytes have many potential applications, e.g., as small energy-storage devices in flexible/stretchable micro/nanoelectronics and bioimplantable systems.[35]

4. CONCLUSION

We demonstrate air-stable, high-performance, flexible MSCs with patterned ionogel electrolyte of PEGDA/[EMIM][TFSI]. The fabricated flexible MSC shows good electrochemical performances with a stack capacitance of 5.3 F/cm^3 at a scan rate of 10 mV/s, an energy density of 2.9 mWh/cm^3 at a power density of 0.05W/cm^3, and a power density of 21.0 W/cm^3 at an energy density of 0.17 mWh/cm^3. In particular, the flexible MSC has highly stable electrochemical properties in a normal environment to retain 90% of the initial capacitance for 8 weeks. The MSC also shows good cycling properties and mechanical stability upon repeated bending. Furthermore, all-solid-state MSCs with patterned electrolyte can be vertically stacked, increasing the total capacitance per unit area. This report describes a new all-solid-state flexible MSC which can be used in various flexible/stretchable micro/nanoelectronic devices.

■ ASSOCIATED CONTENT

Supporting Information

Cross-sectional SEM images of patterned electrolyte and MSC; cyclic voltammetry curves obtained at various scan rates from 1.0 to 70 V/s; dimensions of interdigitated electrodes of MSC; cross-sectional SEM image of MWNT film; CV curves and galvanostatic charge−discharge curves of MSCs with various potential windows; optical and SEM images of MSC under bending with a bending distance of 5 mm; CV curves of MSC with PVA/H_3PO_4 electrolyte at scan rates of 0.5 and 1.0 V/s; time-dependent CV curves of MSCs with two different electrolytes, measured for 3 weeks. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jeongsha@korea.ac.kr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a National Research Foundation of Korea (NRF) grant, funded by the Korean government (MEST) (Grant No. NRF-2013R1A2A1A01016165). We also thank the KU-KIST Graduate School of Korea University, Korea.

■ REFERENCES

(1) Kim, D.-H.; Viventi, J.; Amsden, J. J.; Xiao, J.; Vigeland, L.; Kim, Y.-S.; Blanco, J. A.; Panilaitis, B.; Frechette, E. S.; Contreras, D.; Kaplan, D. L.; Omenetto, F. G.; Huang, Y.; Hwang, K.-C.; Zakin, M. R.; Litt, B.; Rogers, J. A. Dissolvable Films of Silk Fibroin for Ultrathin Conformal Bio-Integrated Electronics. *Nat. Mater.* **2010**, *9*, 511−517.

(2) Kim, R.-H.; Kim, D.-H.; Xiao, J.; Kim, B. H.; Park, S.-I.; Panilaitis, B.; Ghaffari, R.; Yao, J.; Li, M.; Liu, Z.; Malyarchuk, V.; Kim, D. G.; Le, A.-P.; Nuzzo, R. G.; Kaplan, D. L.; Omenetto, F. G.; Huang, Y.; Kang, Z.; Rogers, J. A. Waterproof AlInGaP Optoelectronics on Stretchable Substrates with Applications in Biomedicine and Robotics. *Nat. Mater.* **2010**, *9*, 929−937.

(3) Shin, G.; Bae, M. Y.; Lee, H. J.; Hong, S. K.; Yoon, C. H.; Zi, G.; Rogers, J. A.; Ha, J. S. SnO_2 Nanowire Logic Devices on Deformable Nonplanar Substrates. *ACS Nano* **2011**, *5*, 10009−10016.

(4) Xu, S.; Zhang, Y.; Jia, L.; Mathewson, K. E.; Jang, K.-I.; Kim, J.; Fu, H.; Huang, X.; Chava, P.; Wang, R.; Bhole, S.; Wang, L.; Na, Y. J.; Guan, Y.; Flavin, M.; Han, Z.; Huang, Y.; Rogers, J. A. Soft Microfluidic Assemblies of Sensors, Circuits, and Radios for the Skin. *Science* **2014**, *344*, 70−74.

(5) Xu, S.; Zhang, Y.; Cho, J.; Lee, J.; Huang, X.; Jia, L.; Fan, J. A.; Su, Y.; Su, J.; Zhang, H.; Cheng, H.; Lu, B.; Yu, C.; Chuang, C.; Kim, T.-i.; Song, T.; Shigeta, K.; Kang, S.; Dagdeviren, C.; Petrov, I.; Braun, P. V.; Huang, Y.; Paik, U.; Rogers, J. A. Stretchable Batteries with Self-Similar Serpentine Interconnections and Integrated Wireless Recharging Systems. *Nat. Commun.* **2013**, *4*, 1543.

(6) Kim, D.; Shin, G.; Kang, Y. J.; Kim, W.; Ha, J. S. Fabrication of a Stretchable Solid-State Micro-Supercapacitor Array. *ACS Nano* **2013**, *7*, 7975−7982.

(7) Conway, B. E. Transition from "Supercapacitor" to "Battery" Behavior in Electrochemical Energy Storage. *J. Electrochem. Soc.* **1991**, *138*, 1539−1548.

(8) El-Kady, M. F.; Kaner, R. B. Scalable Fabrication of High-Power Graphene Micro-Supercapacitors for Flexible and On-Chip Energy Storage. *Nat. Commun.* **2013**, *4*, 1475.

(9) Wu, Z.-S.; Parvez1, K.; Feng, X.; Müllen, K. Graphene-Based In-Plane Micro-Supercapacitors with High Power and Energy Densities. *Nat. Commun.* **2013**, *4*, 2487.

(10) Pandey, G. P.; Hashmi, S. A. Ionic Liquid 1-Ethyl-3-methylimidazolium Tetracyanoborate-Based Gel Polymer Electrolyte for Electrochemical Capacitors. *J. Mater. Chem. A* **2013**, *1*, 3372−3378.

(11) Pandey, G. P.; Hashmi, S. A.; Kumar, Y. Performance Studies of Activated Charcoal Based Electrical Double Layer Capacitors with Ionic Liquid Gel Polymer Electrolytes. *Energy Fuels* **2010**, *24*, 6644−6652.

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608−4615

(12) Yang, C.; Ju, J. B.; Lee, J. K.; Cho, W. I.; Cho, B. W. Electrochemical Performances of Electric Double Layer Capacitor with UV-cured Gel Polymer Electrolyte based on Poly[(ethylene glycol)-diacrylate]−Poly(vinylidene fluoride) Blend. *Electrochim. Acta* **2005**, *50*, 1813−1819.
(13) Liew, C.; Ramesh, S.; Arof, A. K. A Novel Approach on Ionic Liquid-based Poly(vinyl alcohol) Proton Conductive Polymer Electrolytes for Fuel Cell Applications. *Int. J. Hydrogen Energy* **2014**, *39*, 2917−2928.
(14) Lee, J.; Panzer, M. J.; He, Y.; Lodge, T. P.; Frisbie, C. D. Ion Gel Gated Polymer Thin-Film Transistors. *J. Am. Chem. Soc.* **2007**, *129*, 4532−4533.
(15) Lee, J.; Kaake, L. G.; Cho, J. H.; Zhu, X.-Y.; Lodge, T. P.; Frisbie, C. D. Ion Gel-Gated Polymer Thin-Film Transistors: Operating Mechanism and Characterization of Gate Dielectric Capacitance, Switching Speed, and Stability. *J. Phys. Chem. C* **2009**, *113*, 8972−8981.
(16) Cho, J. H.; Lee, J.; Xia, Y.; Kim, B.; He, Y.; Renin, M. J.; Lodge, T. P.; Frisbie, C. D. Printable Ion-Gel Gate Dielectrics for Low-Voltage Polymer Thin-Film Transistors on Plastic. *Nat. Mater.* **2008**, *7*, 900−906.
(17) Cho, J. H.; Lee, J.; He, Y.; Kim, B.; Lodge, T. P.; Frisbie, C. D. High-Capacitance Ion Gel Gate Dielectrics with Faster Polarization Response Times for Organic Thin Film Transistors. *Adv. Mater.* **2008**, *20*, 686−690.
(18) Bideau, J. L.; Viau, L.; Vioux, A. Ionogels, Ionic Liquid Based Hybrid Materials. *Chem. Soc. Rev.* **2011**, *40*, 907−925.
(19) Saricilar, S.; Antiohos, D.; Shu, K.; Whitten, P. G.; Wagner, K.; Wang, C.; Wallace, G. G. High Strain Stretchable Solid Electrolytes. *Electrochem. Commun.* **2013**, *32*, 47−50.
(20) Revzin, A.; Russell, R. J.; Yadavalli, V. K.; Koh, W.-G.; Deister, C.; Hile, D. D.; Mellott, M. B.; Pishko, M. V. Fabrication of Poly(ethylene glycol) Hydrogel Microstructures Using Photolithography. *Langmuir* **2001**, *17*, 5440−5447.
(21) Castro, D.; Ingram, P.; Kodzius, R.; Conchouso, D.; Yoon, E.; Foulds, I. G. Characterization of Solid UV Cross-Linked PEGDA for Biological Applications. *Micro Electro Mech. Syst. (MEMS)* **2013**, *20*−*24*, 457−460.
(22) Nemir, S.; Hayenga, H. N.; West, J. L. PEGDA Hydrogels with Patterned Elasticity: Novel Tools for the Study of Cell Response to Substrate Rigidity. *Biotechnol. Bioeng.* **2010**, *105*, 636−644.
(23) Zhu, J. Bioactive Modification of Poly (ethylene glycol) Hydrogels for Tissue Engineering. *Biomaterials* **2010**, *31*, 4639−4656.
(24) Sun, Q.; Kim, D. H.; Park, S. S.; Lee, N. Y.; Zhang, Y.; Lee, J. H.; Cho, K.; Cho, J. H. Transparent, Low-Power Pressure Sensor Matrix based on Coplanar-Gate Graphene Transistors. *Adv. Mater.* **2014**, *26*, 4735−4740.
(25) Attia, R.; Pregibon, D. C.; Doyle, P. S.; Viovy, J. L.; Bartolo, D. Soft Microflow Sensors. *Lab Chip* **2009**, *9*, 1213−1218.
(26) Choi, M.; Choi, J. W.; Kim, S.; Nizamoglu, S.; Hahn, S. K.; Yun, S. H. Light-Guiding Hydrogels for Cell-Based Sensing and Optogenetic Synthesis *in vivo*. *Nat. Photonics* **2013**, *7*, 987−994.
(27) Chan-Park, M. B.; Yan, Y.; Neo, W. K.; Zhou, W.; Zhang, J.; Yue, C. Y. Fabrication of High Aspect Ratio Poly (ethylene glycol)-Containing Microstructures by UV Embossing. *Langmuir* **2003**, *19*, 4371−4380.
(28) Lee, S. W.; Lee, H. J.; Choi, J. H.; Koh, W. G.; Myoung, J. M.; Hur, J. H.; Park, J. J.; Cho, J. H.; Jeong, U. Periodic Array of Polyelectrolyte-Gated Organic Transistors from Electrospun Poly(3-hexylthiophene) Nanofibers. *Nano Lett.* **2010**, *10*, 347−351.
(29) Lee, S. K.; Kabir, S. H.; Sharma, B. K.; Kim, B. J.; Cho, J. H.; Ahn, J. H. Photo-Patternable Ion Gel-Gated Graphene Transistors and Inverters on Plastic. *Nanotechnology* **2014**, *25*, 014002.
(30) Choi, J.-H.; Lee, S. W.; Kar, J. P.; Das, S. N.; Jeon, J.; Moon, K. J.; Lee, T. I.; Jeong, U.; Myoung, J.-M. Random Network Transistor Arrays of Embedded ZnO Nanorods in Ion-Gel Gate Dielectric. *J. Mater. Chem.* **2010**, *20*, 7393−7397.
(31) Pech, D.; Brunet, M.; Durou, H.; Huang, P.; Mochalin, V.; Gogotsi, Y.; Taberna, P.-L.; Simon, P. Ultrahigh-Power Micrometre-Sized Supercapacitors Based on Onion-like Carbon. *Nat. Nanotechnol.* **2010**, *5*, 651−654.
(32) Kim, S.-K.; Koo, H.-J.; Lee, A.; Braun, P. V. Selective Wetting-Induced Micro-Electrode Patterning for Flexible Micro-Supercapacitors. *Adv. Mater.* **2014**, *26*, 5108−5112.
(33) Hsia, B.; Marschewski, J.; Wang, S.; In, J. B.; Carraro, C.; Poulikakos, D.; Grigoropoulos, C. P.; Maboudian, R. Highly Flexible, All Solid-State Micro-Supercapacitors from Vertically Aligned Carbon Nanotubes. *Nanotechnology* **2014**, *25*, 055401.
(34) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-Liquid Materials for the Electrochemical Challenges of the Future. *Nat. Mater.* **2009**, *8*, 621−629.
(35) Hong, S. Y.; Yoon, J.; Jin, S. W.; Lim, Y.; Lee, S. J.; Zi, G.; Ha, J. S. High-Density, Stretchable, All-Solid-State Microsupercapacitor Arrays. *ACS Nano* **2014**, *8*, 8844−8855.

DOI: 10.1021/am5077843
ACS Appl. Mater. Interfaces 2015, 7, 4608−4615