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A printed highly stretchable supercapacitor by a combination of carbon ink and polymer network

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ABSTRACT

A supercapacitor requires two electronic conductors with large surface areas, separated by an ionic conductor. Here we demonstrate a method to print a highly stretchable supercapacitor. We formulate an ink by mixing graphene flakes and carbon nanotubes with an organic solvent, and use the ink to print two interdigitated electronic conductors on the surface of a dielectric elastomer. We then submerge the printed electronic conductors in an aqueous solution of monomer, photoinitiator, crosslinker, and salt. The organic solvent and water form a binary solvent in which the ions are mobile. Upon UV irradiation, a polymer network forms. In each printed electrode, the graphene flakes and carbon nanotubes form a percolating network, which interpenetrates the polymer network. The electronic and ionic conductors form large interfacial areas. When the supercapacitor is stretched, the graphene flakes and carbon nanotubes slide relative to one another, and the polymer network deforms by entropic elasticity. The polymer network traps individual graphene flakes and carbon nanotubes, so that repeated stretch neither breaks the percolating network nor shorts the two electrodes. The supercapacitor maintains 88% the initial capacitance after 1600 cycles of stretch to five times its initial dimension. The interpenetration of a covalent network of elastic polymer chains and a percolating network of conductive particles is generally applicable for making stretchable ionotronic devices.

1. Introduction

Supercapacitors commonly use porous conductors, such as active carbons, carbon nanotubes, and graphene flakes [1,2]. These electronic conductors, once immersed in ionic conductors, guarantee large interfacial areas of electric double layers (EDL), but their brittleness limits stretchability [3,4]. Many researchers have attempted to fabricate stretchable conductors for supercapacitors [5]. Examples include serpentines [6,7], kirigamis [8,9], meshes [10,11], and corrugated structures [12,13]. However, the materials themselves are brittle, and easily fracture at sites of stress concentration. Stretchable conductors also include elastomers embedded with metal particles, but the elastomers reduce the performance of supercapacitors [14,15].

Recently, hydrogels are used to function as ionic conductors in stretchable devices [16–18]. A hydrogel is a polymer network containing water. Hydrogels have been developed with excellent biocompatibility, ionic conductivity, stretchability, and toughness [19–21]. Hydrogels embedded with carbon particles have been fabricated as stretchable electronic conductors [22–24].

Here we describe an approach to printing highly stretchable supercapacitors (Fig. 1). We prepare an ink consisting of graphene flakes (reduced graphene oxides, rGOs), carbon nanotubes (CNTs), diethylene glycol, and manganese chloride. The last two ingredients, diethylene glycol and manganese chloride, are included to control the rheology of the ink, such that the ink is printable and the prints retain their shapes for a long enough time for subsequent fabrication steps. The ionized divalent manganese cations serve as a crosslinker at the surface of the graphene, causing gelation, and the interaction improves the mechanical properties and stability of the graphene [25,26]. We use the ink to print interdigitated electrodes with two pads on the surface of a dielectric elastomer (Fig. 1a). The printed electrodes are

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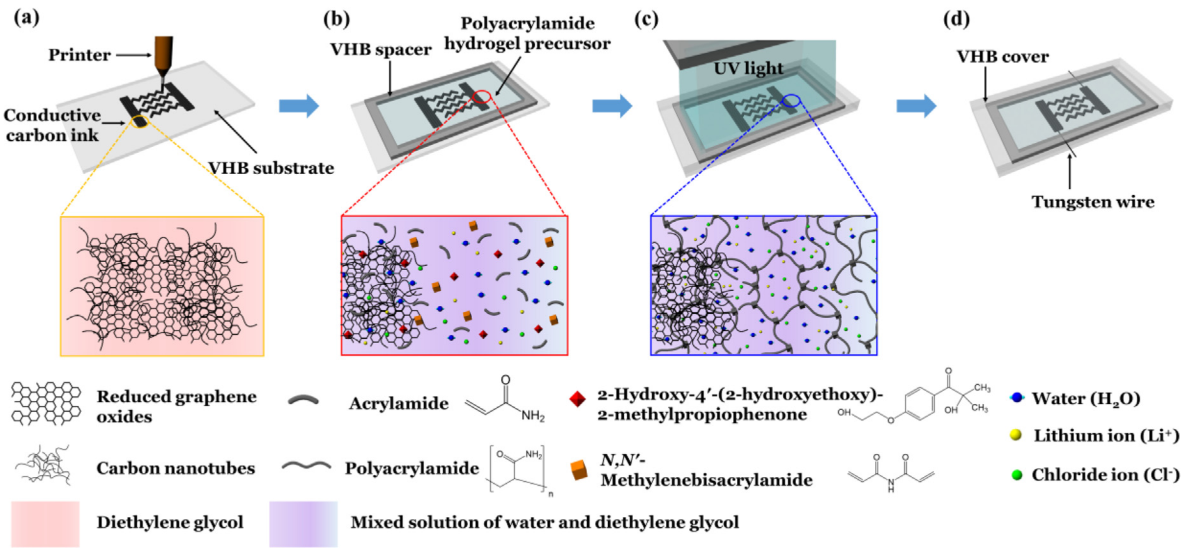

Fig. 1. Fabrication of a stretchable supercapacitor. (a) An ink of carbon nanotubes and graphene flakes is used to print two interdigitated electrodes on the surface of a dielectric elastomer (VHB). In each electrode, the nanotubes and flakes form a percolating network in diethylene glycol solution. (b) A rectangular VHB spacer and a VHB cover serve as a mold. The aqueous solution of monomer, crosslinker, photoinitiator, and salt is injected into the mold. The solution diffuses into the printed electrodes. (c) Under UV light, a polymer network forms, interpenetrating with the percolating network of each printed electrode. (d) Tungsten wires are inserted into the two electrodes as lead wires.

enclosed in an elastomer mold. We prepare an aqueous solution of monomer, crosslinker, photoinitiator, and salt, and then inject the solution into the mold (Fig. 1b). The water and diethylene glycol mix into a binary solvent, and the graphene flakes and carbon nanotubes form a percolating network. After exposure to UV light, a polymer network forms, interpenetrating with the percolation network of each electrode (Fig. 1c). The salt dissolved in the solvent forms an electrolyte. The interface between the electrolyte and carbon particles forms an electric double layer with a large area. Tungsten wires are inserted into the two printed pads as lead wires (Fig. 1d).

2. Experiments

Surface-modified graphene oxide: A 4 g 6-amino-4-hydroxy-2-naphthalenesulfonic acid (AHNs; A0371, TCI) is mixed with 4 mL deionized (DI) water and a 6 mg ammonia solution (1.05423.1000, Sigma Aldrich) to form an AHNs solution. The AHNs solution is added to a 2 mg mL^{-1} graphene oxide dispersion (N002-PS, Angstron Materials). The mixed solution is heated at 70 °C for 24 h under stirring. Then, 1 mL of hydrazine monohydrate (207942, Sigma Aldrich) is added to the solution and heated at 100 °C for 20 h. The reaction solution is washed with DI water and vacuum filtrated to remove the excess AHNs and alkali. Finally, AHNs-rGO powders are obtained by drying at 60 °C for 24 h in a vacuum oven.

Ink preparation: 40 mL ethanol (459836, Sigma Aldrich) is mixed with 0.04 g surface-modified graphene oxide, 0.01 g multi-walled carbon nanotubes (US Nano-Materials, Inc.), 2 g diethylene glycol (H26456, Sigma Aldrich), and 20 mg 10 wt% manganese chloride ethanol solution. The mixture is placed on a magnetic stirrer and treated ultrasonically for 12 h. The mixture is then kept at 80–90 °C in a double boiler for 4 h. We weigh the mixture to ensure that ethanol has been evaporated. Diethylene glycol and manganese chloride control the viscosity of the ink.

Printing of the ink: A commercial 3D printer (ENDER-3 Pro, Creality) is used to print the electrode, and the printhead is customized to install a syringe barrel, which is connected to a pneumatic tube. Nozzles with inner diameters of 100 and 600 μm are used. The initial working distances between the tip of the nozzle and the substrate are 100 and 500 μm, and the applied air pressures are 30 and 5 psi. The printing speed is maintained at 5 mm s^{-1}.

Preparation of the precursor of the polymer network: Polyacrylamide network is synthesized by a precursor containing a monomer (acrylamide, A8887, Sigma Aldrich), crosslinker (*N*, *N*′-methylenebisacrylamide (MBAA), M7279, Sigma Aldrich), photoinitiator (2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), 410896, Sigma Aldrich), and salt (lithium chloride (LiCl), 310468, Sigma Aldrich). 10 mL of 2 M acrylamide aqueous solution, 66 μL of 0.1 M MBAA aqueous solution, 15 μL of 0.1 M Irgacure 2959 ethanol solution, and 0.427 g lithium chloride are mixed together. The concentration of lithium chloride in the precursor is 1 M.

Fabrication of a supercapacitor: Two carbon electrodes are printed on a VHB substrate. The VHB elastomer is both stretchable and adhesive. Adhere a layer of rectangular VHB spacer to the VHB substrate to form a mold and a third layer of VHB on the top to seal the mold. The mold has an internal volume 30 mm × 20 mm × 1 mm. The precursor of the polymer network is injected into the mold. The polymer network is formed under UV light (15 W, 365 nm, UVP XX-15 L) for 1 h. Two tungsten wires with a diameter of 0.75 mm are inserted into both printed electrode pads.

Electrical and electrochemical measurements: The electrical resistance of the printed electrode interpenetrated with the polymer network is measured using a two-probe method. Two tungsten wires are inserted at both ends of the straight line electrode and connected to a precision multimeter (Fluke 8846 A). An electrochemical performance test is carried out using a potentiostat (Solartron Analytical 1400 cell test system). Cyclic voltammetry is performed in the two-electrode mode. The scanning rate is 50 mV s^{-1}, and the voltage ranges from 0 V to 1 V. The areal capacitance C_A (mF cm^{-2}) is calculated from the cyclic voltammetry curves using the formula $C_A = \frac{1}{va(\Delta U)} \int idU$, where v is the scan rate, U is the potential, i is the current, ΔU is the range of potential,

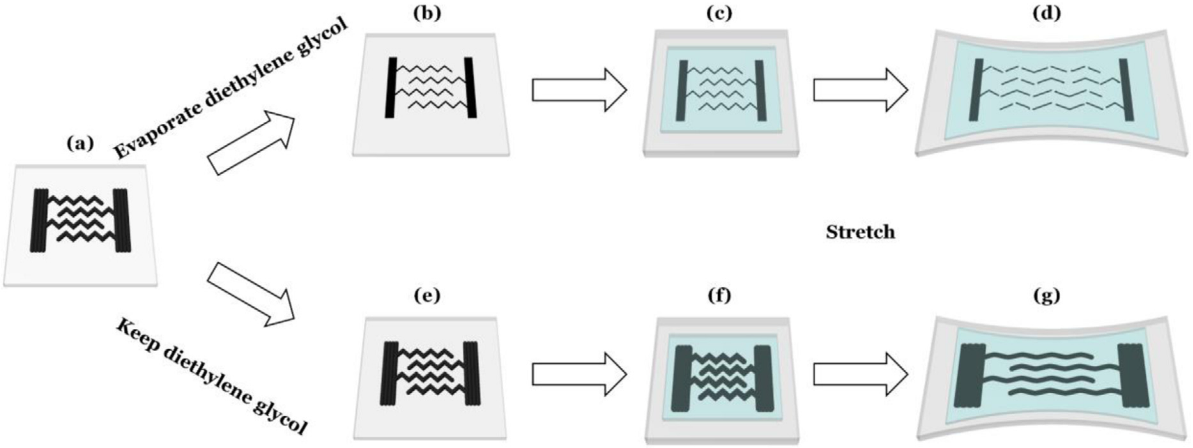

Fig. 2. The size and stretchability of the printed electrodes are affected by diethylene glycol. (a) Diethylene glycol is present in printed interdigitated electrodes. (b) The printed electrodes contract after diethylene glycol evaporates in an oven at 80 °C for 2 days. (c) When the aqueous solution is injected, the printed electrodes do not swell. (d) After polymerization, a stretch breaks the electrodes. However, if the diethylene glycol does not evaporate, (e) the printed electrodes retain the dimension for several days in the air. (f) When the aqueous solution is injected, the printed electrodes swell. (g) After polymerization, the electrodes are stretchable without breaking.

$\Delta U = 1$ V, and a is the rectangular area of the substrate occupied by the supercapacitor in the undeformed state.

Stretch: The VHB substrate of a supercapacitor is adhered to two glass slides. We fix one glass slide and pull the other through a stretch machine (Instron 5966). The supercapacitor is held at certain fixed stretches for electrical and electrochemical measurements. In cyclic tests, we stretch the supercapacitor at a strain rate ranging from 2 to 16 s^{-1} for a stretching amplitude ranging from 1.5 to 5.

3. Stretchable supercapacitor

The combination of print and cast produces a supercapacitor. In each printed electrode, the graphene flakes and carbon nanotubes form a percolating network [27]. The percolating network of each electrode interpenetrates the polymer network. Water and diethylene glycol form a binary solvent, which permeates through the interpenetrating networks. The solvent dissolves the salt into mobile ions. Each electrode is an electronic conductor, and the solution is an ionic conductor. The interfaces between the solution and the flakes and nanotubes form electric double layer capacitors (EDLC). The flakes provide large surface areas, and the nanotubes enhance electrical conductance.

The interpenetrating networks enable a highly stretchable supercapacitor. In a printed supercapacitor without a polymer network, the percolating carbon network is fragile and breaks under a small local stretch. By contrast, the percolating carbon network interpenetrated with a polymer network can sustain repeated large stretches. The flakes and nanotubes slide relative to each other to accommodate the stretch without breaking electronic conduction. Because the size of carbon particles is larger than the mesh size of the polymer network, individual carbon particles are trapped in the polymer network, and a repeated stretches neither break the percolating network nor short-circuit the two electrodes. Because the individual carbon particles are rigid, the stretch does not affect their surface areas, so that the capacitance is independent of stretch.

4. Effect of diethylene glycol

Diethylene glycol is intended to set the rheology of the ink for printing. In our experiment, we find that diethylene glycol serves another function. We remove the diethylene glycol by evaporation after the electrodes are printed, and the printed electrodes contract (Fig. 2b). When the aqueous solution of the precursor is injected, the printed electrodes do not swell (Fig. 2c). After polymerization, a stretch of substrate breaks the electrodes (Fig. 2d). These experiments demonstrate that the removal of diethylene glycol causes the carbon particles to stick strongly and resist the penetration of the aqueous solution. Consequently, the polymer network does not fully interpenetrate with the percolating carbon networks and does not prevent the electrodes from breaking upon stretch.

By contrast, if diethylene glycol is kept in the printed electrodes, the electrodes retain their dimensions (Fig. 2e). When the aqueous precursor is injected, the printed electrodes swell (Fig. 2f). After polymerization, a stretch does not break the electrodes (Fig. 2g). These experiments demonstrate that diethylene glycol enables molecules and ions in the aqueous solution to diffuse between the carbon particles and to swell the percolating carbon network. Consequently, the polymer network interpenetrates the percolating carbon networks and prevents the electrodes from breaking upon stretch.

In a preliminary experiment, we fabricate a supercapacitor by evaporating diethylene glycol right after printing the electrodes, followed by the formation of the polymer network (Fig. 2a–d). The supercapacitor consists of two interdigitated electrodes, a polymer network, and an aqueous solution of mobile ions (Fig. 3a). The electrodes break after a stretch to 1.5 times the initial dimension (Fig. 3b). We conduct cyclic voltammetry of the supercapacitor before and after the stretch. When the electrodes are broken, the current almost vanishes (Fig. 3c), and the capacitance is drastically reduced (Fig. 3d).

5. Performance of the stretchable supercapacitor

We next fabricate a supercapacitor by keeping diethylene glycol after print (Fig. 2e–g). The supercapacitor consists of two interdigitated electrodes, a polymer network, and mobile ions in the binary solvent of diethylene glycol and water (Fig. 4a). The contamination in the region off the electrodes (gray background) is caused by the diffusion of carbon particles before the polymer network forms. However, the concentration of the diffused carbon particles is low and negligibly reduces the capacitance and negligibly increases the leak current. At a uniaxial stretch of 5, the electrodes show no visible damage but high reversibility (Fig. 4b).

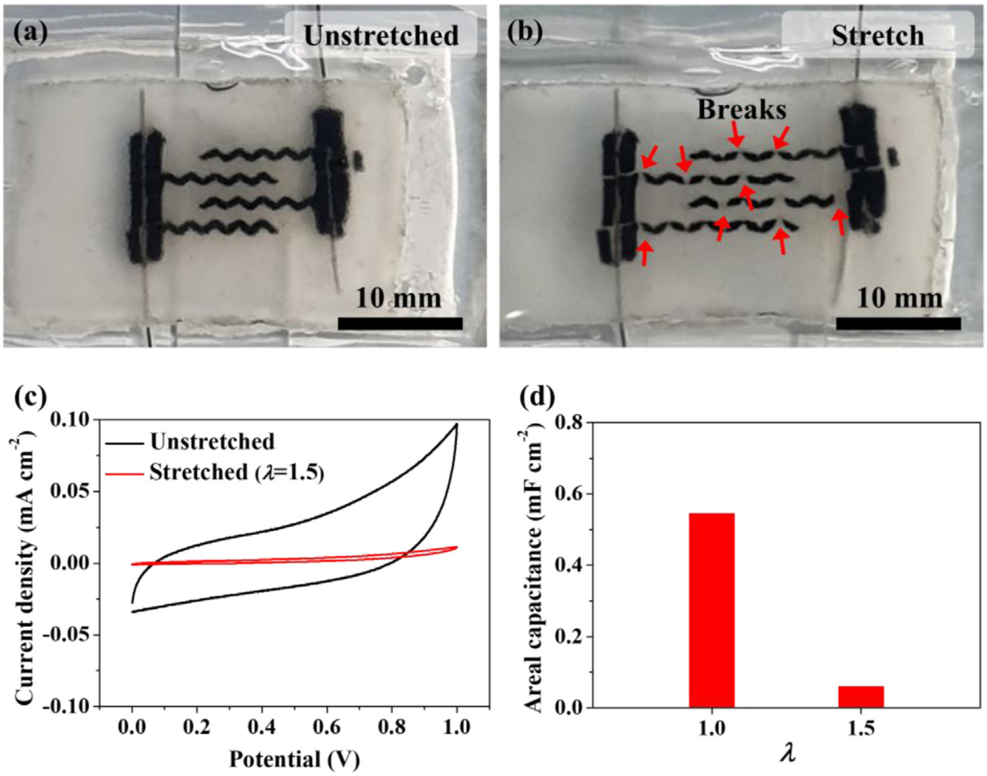

Fig. 3. A supercapacitor in which diethylene glycol is removed right after printing the electrodes. Photos of the supercapacitor in (a) unstretched state and (b) stretched state ($\lambda = 1.5$). Red arrows indicate cracks in the stretched electrodes. (c) Cyclic voltammetry of a supercapacitor in the unstretched state and in the stretched state. (d) The capacitance in the stretched state is much lower than that in the unstretched state.

When the supercapacitor is subject to various stretches, the cyclic voltammetry curves remain the same (Fig. 4c). The capacitance of the supercapacitor is independent of the stretch (Fig. 4d). We then subject the supercapacitor to a program of cyclic stretches: 200 cycles for each stretch amplitude of 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 (Fig. 4e). After every 50 cycles, we conduct cyclic voltammetry at scanning rate of 50 mV s^{-1}. The capacitance remains at 88.3% of its initial value after 1600 cycles.

We further characterize the degradation of the percolating carbon network by measuring the change in the resistance of an electrode under stretch. We print rectangular electrodes of 100 μm width and 100, 200, and 300 μm thicknesses. We polymerize the polymer network without evaporating diethylene glycol, and insert tungsten wires as leads. The resistance increases with the stretch (Fig. 4f). For an ideal stretchable resistor, the resistivity is independent of stretch. When the stretch changes the length and cross-sectional area of such an ideal resistor, the resistance is proportional to the square of the uniaxial stretch (solid line). The deviation of the experimental data points from the solid line of an ideal resistor indicates the degradation of the resistor due to stretching. The resistance of the electrode is measured in the stretched state. By comparison, the capacitance of the supercapacitor is measured in the unstretched state after cyclic stretching. This difference likely accounts for the small changes in the capacitance of the supercapacitor under cyclic stretch, but the relatively large change in the resistance of the rectangular electrodes under monotonic stretch.

6. Conclusion

We have developed a method to fabricate a highly stretchable supercapacitor. We formulate an ink to print each electrode as a percolating carbon network, and then form a polymer network using an aqueous precursor. We find that a small amount of diethylene glycol in the ink enables the aqueous precursor to swell the printed electrodes and to form a polymer network interpenetrating the percolating carbon networks. The polymer network traps the carbon particles, so that the electrodes under large stretch neither break nor short-circuit. The interpenetration of a covalent network of elastic polymer chains and a percolating network of conductive particles is generally applicable for making stretchable ionotronic devices. Suitable electronic conductors include carbon in various forms, metals, and semiconductors. Suitable polymer electrolytes include ionogels, polyelectrolytes, and ionoelastomers. It is hoped that interpenetrating networks can be further developed for broad applications in stretchable electronics and ionotronics.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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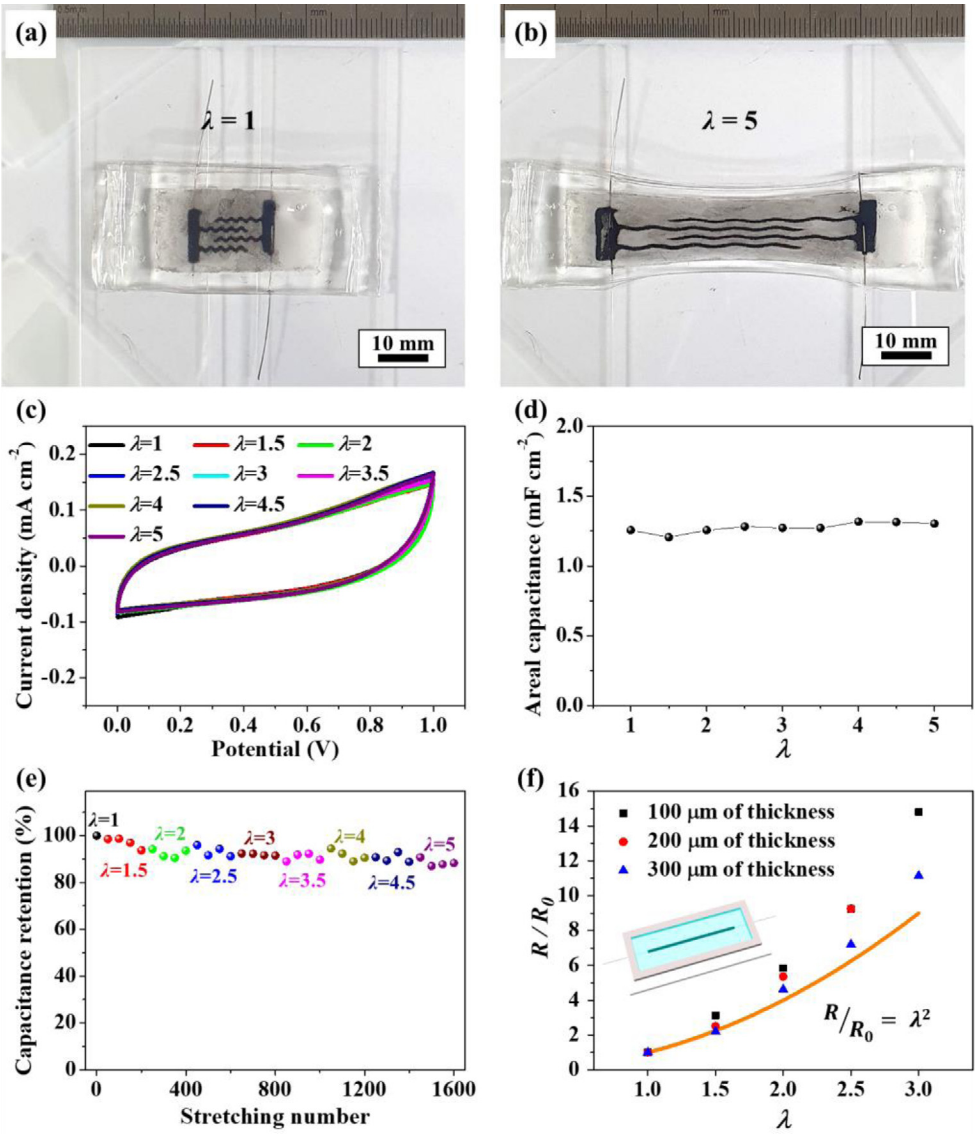

Fig. 4. A supercapacitor in which diethylene glycol is kept after print. Photos of (a) the unstretched state and (b) the stretched state ($\lambda = 5$). (c) Cyclic voltammetry of the supercapacitor is conducted under various stretches. (d) The capacitance of the supercapacitor is independent of the stretch. (e) The capacitance of the supercapacitor remains nearly unchanged after a program of cyclic stretches. (f) Change of resistance (R/R_0) of the printed electrode as a function of the uniaxial stretch. Inset: a schematic of a sample.

References

[1] L.-F. Chen, X.-D. Zhang, H.-W. Liang, M. Kong, Q.-F. Guan, P. Chen, Z.-Y. Wu, S.-H. Yu, Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors, ACS Nano 6 (8) (2012) 7092.

[2] L. Zhang, F. Zhang, X. Yang, G. Long, Y. Wu, T. Zhang, K. Leng, Y. Huang, Y. Ma, A. Yu, Y. Chen, Porous 3D graphene-based bulk materials with exceptional High Surface Area and excellent conductivity for supercapacitors, Sci. Rep. 3 (2013) 1408.

[3] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, Chem. Soc. Rev. 41 (2012) 797–828.

[4] Q. Ke, J. Wang, Graphene-based materials for supercapacitor electrodes – a review, J. Materiomics 2 (1) (2016) 37–54.

[5] W. Liu, M.-S. Song, B. Kong, Y. Cui, Flexible and stretchable energy storage: Recent advances and future perspectives, Adv. Mater. 29 (1) (2017) 1603436.

[6] D. Kim, D. Kim, H. Lee, Y.R. Jeong, S.-J. Lee, G. Yang, H. Kim, G. Lee, S. Jeon, G. Zi, J. Kim, J.S. Ha, Body-attachable and stretchable multisensors integrated with wirelessly rechargeable energy storage devices, Adv. Mater. 28 (2016) 748–756.

[7] J. Yun, C. Song, H. Lee, H. Park, Y.R. Jeong, J.W. Kim, S.W. Jin, S.Y. Oh, L. Sun, G. Zi, J.S. Ha, Stretchable array of high-performance micro-supercapacitors charged with solar cells for wireless powering of an integrated strain sensor, Nano Energy 49 (2018) 644–654.

[8] Z. Lv, Y. Luo, Y. Tang, J. Wei, Z. Zhu, X. Zhou, W. Li, Y. Zeng, W. Zhang, Y. Zhang, D. Qi, S. Pan, X.J. Loh, X. Chen, Editable supercapacitors with customizable stretchability based on mechanically strengthened ultralong MnO_2 nanowire composite, Adv. Mater. 30 (2018) 1704531.

[9] S. Jiao, A. Zhou, M. Wu, H. Hu, Kirigami patterning of mxene/bacterial cellulose composite paper for all-solid-state stretchable micro-supercapacitor arrays, Adv. Sci. 6 (2019) 1900529.

[10] S. Gong, Y. Zhao, L.W. Yap, Q. Shi, Y. Wang, J.A.P.B. Bay, D.T.H. Lai, H. Uddin, W. Cheng, Fabrication of highly transparent and flexible NanoMesh electrode via self-assembly of ultrathin gold nanowires, Adv. Electron. Mater. 2 (2016) 1600121.

[11] J.A. Fan, W.-H. Yeo, Y. Su, Y. Hattori, W. Lee, S.-Y. Jung, Y. Zhang, Z. Liu, H. Cheng, L. Falgout, M. Bajema, T. Coleman, D. Gregoire, R.J. Larsen, Y. Huang, J.A. Rogers, Fractal design concepts for stretchable electronics, Nature Commun. 5 (2014) 3266.

[12] C. Yu, C. Masarapu, J. Rong, B. Wei, H. Jiang, Stretchable supercapacitors based on buckled single-walled carbon nanotube macrofilms, Adv. Mater. 21 (2009) 4793–4797.

[13] Q. Tang, M. Chen, G. Wang, H. Bao, P. Saha, A facile prestrain-stick-release assembly of stretchable supercapacitors based on highly stretchable and sticky hydrogel electrolyte, J. Power Sources 284 (2015) 400–408.

[14] C. Choi, S.H. Kim, H.J. Sim, J.A. Lee, A.Y. Choi, Y.T. Kim, X. Lepró, G.M. Spinks, R.H. Baughman, S.J. Kim, Stretchable, weavable coiled carbon nanotube/MnO_2/polymer fiber solid-state supercapacitors, Sci. Rep. 5 (2015) 9387.

[15] Z. Cao, R. Wang, T. He, F. Xu, J. Sun, Interface-controlled conductive fibers for wearable strain sensors and stretchable conducting wires, ACS Appl. Mater. Interfaces 10 (2018) 14087–14096.

[16] J.-Y. Sun, X. Zhao, W.R.K. Illeperuma, O. Chaudhuri, K.H. Oh, D.J. Mooney, J.J. Vlassak, Z. Suo, Highly stretchable and tough hydrogels, Nature 489 (2012) 133–136.

[17] S. Lin, H. Yuk, T. Zhang, G.A. Parada, H. Koo, C. Yu, X. Zhao, Stretchable hydrogel electronics and devices, Adv. Mater. 28 (22) (2016) 4497–4505.

[18] C. Yang, Z. Suo, Hydrogel ionotronics, Nat. Rev. Mater. 3 (2018) 125–142.

[19] J.-Y. Sun, C. Keplinger, G.M. Whitesides, Z. Suo, Ionic skin, Adv. Mater. 26 (2014) 7608–7614.

[20] M. Sasaki, B.C. Karikkineth, K. Nagamine, H. Kaji, K. Torimitsu, M. Nishizawa, Highly conductive stretchable and biocompatible electrode–hydrogel hybrids for advanced tissue engineering, Adv. Healthc. Mater. 3 (2014) 1919–1927.

[21] X. Jing, H.-Y. Mi, X.-F. Peng, L.-S. Turng, Biocompatible, self-healing, highly stretchable polyacrylic acid/reduced graphene oxide nanocomposite hydrogel sensors via mussel-inspired chemistry, Carbon 136 (2018) 63–72.

[22] J. Anjali, V.K. Jose, J.-M. Lee, Carbon-based hydrogels: Synthesis and their recent energy applications, J. Mater. Chem. A 7 (2019) 15491.

[23] J. Zeng, L. Dong, W. Sha, Lu. Wei, X. Guo, Highly stretchable, compressible and arbitrarily deformable all-hydrogel soft supercapacitors, Chem. Eng. J. 383 (2020) 123098.

[24] X. Li, H. Li, X. Fan, X. Shi, J. Liang, 3D-printed stretchable micro-supercapacitor With Remarkable Areal performance, Adv. Energy Mater. 10 (14) (2020) 1903794.

[25] S. Park, K.-S. Lee, G. Bozoklu, W. Cai, S.B.T. Nguyen, R.S. Ruoff, Graphene oxide papers modified by divalent ions—Enhancing mechanical properties via chemical cross-linking, ACS Nano 3 (2008) 572–578.

[26] G. Shi, J. Liu, C. Wang, B. Song, Y. Tu, J. Hu, H. Fang, Ion enrichment on the hydrophobic carbon-based surface in aqueous salt solutions due to cation-π interactions, Sci. Rep. 3 (2013) 3436.

[27] A.V. Kyrylyuk, P. Schoot, Continuum percolation of carbon nanotubes in polymeric and colloidal media, Proc. Natl. Acad. Sci. USA 105 (24) (2008) 8221–8226.