Article type: Communication

Flexible Micro-Supercapacitor based on In-Situ Assembled Graphene on Metal Template at Room Temperature

*Zhen-Kun Wu, Ziyin Lin, Liyi Li, Bo Song, Kyoung-sik Moon, Shu-Lin Bai, * and Ching-Ping Wong**

Z. K. Wu, Prof. S. L. Bai, Department of Materials Science and Engineering, HEDPS/CAPT/LTCS, College of Engineering, Peking University Beijing 100871, (P. R. China)

E-mail: slbai@pku.edu.cn

Z. K. Wu, Dr. Z. Y. Lin, Liyi Li, Bo Song, Dr. K. S. Moon, Prof. C. P. Wong

School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

E-mail: cp.wong@mse.gatech.edu

Prof. C.-P. Wong

Department of Electronic Engineering

The Chinese University of Hong Kong, Hong Kong

Keywords: (micro-supercapacitor, graphene, flexible, self-assemble, room-temperature)

Abstract

Graphene based micro-supercapacitors (MSCs) have been extensively studied in recent years; however, few of them report room temperature fabricating methods for flexible MSC. Here we developed a convenient procedure based on simultaneous self-assembly and reduction of graphene oxide (GO) on Cu/Au interdigit at room temperature. The as-produced MSC shows a specific areal capacitance of 0.95 mF cm^{-2} and maintains 98.3% after 11,000 cycles of charge and discharge. Extremely small relaxation time constants of 1.9 ms in aqueous electrolyte and 4.8 ms in gelled electrolyte are achieved. Also the device shows great flexibility and retains 93.5% of the capacitance after 5,000 times of bending and twisting tests.

1. Introduction

The rapid development of portable and wearable electronics imposes many requirements on the energy storage units, including reduced form factor, good compatibility, fast charge/discharge response, excellent mechanical compliance [1], etc. Supercapacitors are promising candidates because of their high power density and long lifetime; however, conventional supercapacitors utilize sandwiched design and require complicated packaging, making them bulky for miniaturization.

Recently, planar micro-supercapacitors (MSCs) designed for portable and wearable applications have been reported, using onion-like carbon (OLC) [1], carbide-derived carbon(CDC) [2], activated carbon (AC) [3, 4] and graphene [5-13] as the active materials. The AC based MSCs showed large specific capacitances. However, the limited ion transport within its internal micro-porous structure resulted in a rapid capacitance decrease with increased scan rates [3, 4]. Graphene-based materials are most extensively studied for supercapacitors due to their high specific surface area and excellent electrical conductivity. Gao et al. [5] and El-Kady et al. [6, 7] used laser writers to reduce graphene oxide (rGO) and designed various rGO/GO/rGO microstructures for MSCs. Lin et al. and Zhu et al. made graphene/carbon nanotube (CNT) hybrid MSCs with chemical vapor deposition (CVD) technique [8, 9]. Majid et al. applied the electrostatic spray deposition process to fabricate rGO/CNT based MSC [10]. For some of these devices, the direct deployment in on-chip application is difficult since high temperature environment or liquid electrolytes are involved [5, 8-10]. In this regard, gelled electrolyte would largely alleviate this problem due to the all-solid-state characteristics. Niu et al. used gelled polyvinyl alcohol (PVA)/ H_3PO_4 as the electrolyte and patterned hydrazine reduced rGO stripes as the active material [11]. Wu et al. adopted gelled PVA/ H_2SO_4 electrolyte for ultrathin heteroatom-doped-graphene MSC [12] and methane-plasma-treated rGO MSC [13]. However, the loadings of the active

materials were generally too small to deliver moderate capacitance for these all-solid-state MSCs, limiting their applications.

In this work, we developed a scalable method to fabricate all-solid-state flexible MSC based on rGO hydrogel (open-porous structure formed by π - π stack force between rGO sheets) in-situ assembled on metal template at room temperature. The as-prepared MSC shows a specific areal capacitance of 0.95 mF cm⁻² and maintains 98.3% after 11,000 times of charge/discharge cycles. In addition, extremely small relaxation time constant of 4.8 ms is achieved in gelled electrolyte, which indicates high ion transfer mobility within the structure. Besides, the device also exhibits great flexibility which retains 93.5% of the capacitance after 2,500 times of bending and twisting. These properties make as-fabricated MSC a promising energy storage candidate in wearable electronics.

2. Experimental

2.1 Preparation of Cu/Au interdigit

The Kapton® polyimide substrate was used as-received. A 1.6 μ m thick layer of positive resist (Microposit S1813, Shipley, USA) was spun cast on the Kapton substrate and exposed in a mask aligner (Karl Suss MA6 Mask Aligner, Garching, Germany) with 405 nm UV light. The exposed sample was developed in Microposit MF 315 (Shipley) developer. All the samples with patterned photoresist were cleaned by oxygen plasma in a reactive ion etching (RIE) tool (Plasma Therm Inc., USA) to remove any resist residue in exposed areas. Then Cu/Au layer was deposited in an electron beam evaporator at pressure of 3×10^{-6} Torr (CVC Product Inc., USA).

A 10-finger interdigital design with finger width of 300 μ m, finger gap 200 μ m and total dimension 4.8×4.8 mm² was employed. Ti (10 nm), Au (200 nm) and Cu (200 nm) were deposited onto the substrate successively. In the end, the photoresist was lifted off with 5 minutes of sonication in acetone and dried by N₂ flow.

2.2 Preparation of all-solid-state MSC

Kapton substrate with patterned metal interdigit was immersed in GO (50 mL, 1 mg mL⁻¹) aqueous solution at room temperature for 12 hours. It was then taken out from the solution and mildly washed with deionized water. PVA/H₂SO₄ electrolyte (~10 wt% for both PVA and H₂SO₄) was drop coated onto the interdigit and the sample was dried in air for certain time (12~72 hours). All-solid-state MSC was thus obtained.

2.3 Characterization and electrochemical measurement

Morphology of rGO hydrogel was observed with SEM (Hitachi SEM SU8010) after being freeze-dried into rGO aerogel. X-ray photoelectron spectrum (XPS) characterization was performed with a Thermo K-Alpha XPS. Raman spectra were obtained with LabRAM ARAMIS, HORIBA JOBIN YVON with 532 nm laser used as the excitation source. Fourier transform infrared spectrum (FTIR) was carried out at room temperature with FTIR spectrometer (Nicolet, Magna IR 560). Sheet resistance was measured with Lucas Labs S302 four point probe system. Bulk conductivity was estimated based on the thickness measured with a micrometer. Cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) were measured with a Versastat 2-channel system (Princeton Applied Research). Specific areal capacitance was derived from discharging curve at different current densities. Gravimetric capacitance was obtained from CV data at different scan rates for comparison.

3. Results and discussion

The mechanism of the simultaneous self-assembling and reduction process is schematically illustrated in **Figure 1a**. The Cu/Au interdigit serves as current collector as well as reducing agent. Beneath that is the Ti layer used to improve the adhesion between the metal interdigit and the polyimide substrate.

The standard electrode potential was reported to be in the range of 0.4 ~ 0.6 V while is 0.337 V [14]. Thus Cu is able to reduce GO when it comes across the GO sheet due to its lower redox potential. Electrons will spontaneously transfer from Cu to GO by the following reaction:

leading to the reduction of GO and the dissolution of Cu. The reduced GO sheets will stay together by π - π stack force and form a hydrogel structure. The remaining Au layer will keep in contact with the obtained rGO hydrogel (Figure 1b) and act as current collector. Moreover, the rGO hydrogel is electrically conductive and will act as an electron pathway from Cu to GO sheets, causing continuous GO reduction and deposition until complete consumption of Cu is reached. After 12 hours of reaction, the surface of the metal interdigit turns from shiny golden to black, which also indicates successful reduction and deposition of rGO hydrogel onto the metal surface.

This method is suitable for facile fabrication of MSC due to many advantages, including 1) the rGO hydrogel coating is conformal to the metal patterns, allowing for precise control of rGO hydrogel electrodes and fine-pitch designs; 2) The reduction reaction and the assembly procedure are simultaneous, low-temperature processible and environmentally benign, eliminating the need for post-treatment that usually involves either toxic chemicals or high temperature [15]; 3) The procedure is applicable to different substrates such as ceramic, polymer film and silicon wafer as long as they are compatible with photolithography. Figure 1c presents an optical image of the original Cu/Au interdigit (left) and as-fabricated MSC (right), which indicates the conformal coating of rGO hydrogel onto the surface of metal interdigit. The rGO hydrogel maintained the same sharp and straight design after being dried out (Figure S1a). No GO residue is found between the gaps of the interdigit fingers. The conformal coating phenomenon eliminates the possibility of potential short circuit during operation and allows for convenient design. Similar rGO interdigit features are observed when Si/SiO₂ substrate was used instead (Figure S1b), which indicates that the substrate material has negligible effect on the

reducing process and thus offers various choices for substrates. In addition, Cu is electrochemically active in H_2SO_4 during operation and could introduce undesirable side reactions (Figure S3a). In our case, complete dissolution of Cu after 12 hours of reaction is confirmed by energy dispersive X-ray spectroscopy (EDX). No Cu residues were found on the substrate when the rGO hydrogel was removed (Figure S2), which implies that Cu on the substrate was fully oxidized and removed during this process. Further verification was included in the supporting information.

The rGO hydrogel is freeze-dried into aerogel and characterized with SEM. The top-view SEM image (**Figure 2a**) reveals an open porous structure similar to those obtained with hydrothermal method [16] and Zn reduction approach [17]. No obvious lateral growth is observed and the sharp edges of as-prepared rGO interdigit allow the possibility for further pitch reduction (Figure S1b). The cross-section SEM image in Figure 2b reveals an interconnected porous structure with rGO sheets lying preferentially parallel to the substrate. This open-porous quasi-parallel structure will decrease the resistance for lateral ion transport, improving the rate performance [18]. The reduction of GO is confirmed by XPS, Raman spectrum, and FTIR. Carbon-to-oxygen atom ratio increases from 2.1 of GO to 6.8 of rGO aerogel by the quantitative XPS survey, indicating that significant amount of oxygen is removed during the process [19]. In addition, the high resolution C1s XPS spectrum of rGO aerogel in Figure 2c can be deconvoluted into three characteristic peaks at 284.4 eV (C-C/C=C graphitic structure), 286.2 eV (hydroxyl and epoxy C-O groups) and 288.9 eV (carbonyl group). The peak intensity corresponding to C-O group is greatly reduced for rGO compared to that of GO. In the Raman spectra (Figure 2d), the D to G peak intensity ratio (I_D/I_G) increases from 0.9 to 1.2, probably caused by the formation of smaller sp^2 domains after reduction [20]. These small domains will increase sp^3 edge defects, which might provide extra surface area and thus enhance the specific capacitance. In the FTIR spectra (Figure 2e), the carboxyl peak at 1725 cm^{-1} disappears after the reaction, further validating the reduction of GO [21, 22]. In addition, the rGO reduced by Cu shows good electrical conductivity. The

as-prepared rGO hydrogel has sheet resistance of $192 \Omega/\square$ and bulk electrical conductivity of 0.38 S cm^{-1} , which are comparable to that prepared by vacuum filtration method (0.58 S cm^{-1}) [23]. The electrical conductive rGO hydrogel provides a fast electrical transport pathway and eliminates the need of conductive additives generally used in supercapacitor electrodes [24].

The all-solid-state MSC was fabricated utilizing PVA/H₂SO₄ gel as the solid-state electrolyte. Gelled electrolyte exhibits excellent mechanical flexibility which is suitable for wearable electronics. It also eliminates the necessity of complicated sealing components generally required in conventional supercapacitors, greatly easing the manufacturing process. During fabrication, the low-viscosity PVA/H₂SO₄ liquid electrolyte first infiltrates into the rGO hydrogel. With the evaporation of H₂O, the viscosity of the electrolyte increases so much that it turns into a gel. The as-fabricated MSC shows rectangular CV curves even at a scan rate of 6 V s^{-1} (**Figure 3a**), which indicates that the capacitance arises from electrical double layer capacitance (EDLC) and the ion transportation within the electrode is extremely fast. It is suggested that volumetric and areal capacitance are of equivalent significance as the gravimetric capacitance in real applications [26]. Here the areal performance of the as-fabricated MSC is evaluated considering the total area of device (the rGO hydrogel interdigit, the Au interdigit current collectors and the gaps between them). Figure 3b shows the CD curves at different current densities. The perfect linear charge/discharge curves further confirm that the capacitance arises from EDLC. Also, the symmetric CD curves imply high Coulombic efficiency [27], which reaches 99% for as-prepared MSC and guarantees excellent charge/discharge reversibility. Figure 3c shows the areal capacitance at different current densities. The MSC exhibits an areal capacitance of 0.95 mF cm^{-2} at a discharging current of 0.43 mA cm^{-2} , which slightly decreases to 0.82 mF cm^{-2} at 4.3 mA cm^{-2} . The areal capacitance achieved is comparable to those EDLC based MSC reported in literatures ($0.4\sim 2 \text{ mF cm}^{-2}$) [4, 28, 29]. Cycling test was carried out at a charge/discharge current of 1.3 mA cm^{-2} and the

result is shown in Figure 3d. The areal capacitance retained about 98.3% of the initial value after 11,000 cycles, suggesting an excellent cycling performance.

EIS was further used to study the performance of as-prepared MSC. The Nyquist curve (Figure 3e) is almost perpendicular to the X-axis at low frequency region, which indicates that the MSC acts like an ideal capacitor [24, 30, 31]. In addition, the semicircle typically observed at high frequency region for conventional carbon-based supercapacitors does not show up in our MSC. This semicircle is associated with nano pores within the electrode material which will impose large ionic diffusion resistance to the system [31]. The absence of this semicircle indicates fast ion transportation, which might be caused by the open-porous structure of rGO hydrogel that makes the entire surface accessible for fast ion adsorption/desorption. Figure 3f shows the plot of impedance phase angle versus frequency, also known as Bode phase plot. The phase angle stays above -80° at frequency below 3.2 Hz, indicating nearly pure capacitive behavior. The frequency at -45° is 49 Hz for the sample fully dried in air for 72 hours, corresponding to a relaxation time constant (τ_0) of 20 ms. The τ_0 can be further controlled by adjusting the evaporating time which will affect the water concentration and ion mobility within the gelled electrolyte. For example, it decreases to 4.8 ms (208 Hz) when gelled in air for 12 hours and 1.9 ms (529 Hz) when 1 M H_2SO_4 aqueous electrolyte was used (Figure S4a). These values are comparable to those of the state-of-art MSCs fabricated with onion-like nano-diamond (26 ms) [1], laser scribed graphene (19 ms) [7], and CVD grown carbon nanotube carpets (0.82~2.62 ms) [8].

The excellent rate performance probably arises from the quasi-parallel structure of the rGO hydrogel and the in-plane design of the electrodes, which greatly reduce the in-plane ion transport barrier. For comparison, the performance of our work and those of state-of-the-art MSCs are listed in **Table 1**. Our sample exhibits a specific areal capacitance comparable to those reported in literature [1, 8, 10]. What's more, the relaxation time constant of our all-solid-state MSC is even competitive compared with those of liquid electrolyte based MSCs. Traditional supercapacitors (TSC) were also fabricated using rGO

hydrogel reduced on Cu foil for comparison. Figure S4b shows the Bode phase plot of as-fabricated supercapacitor in 1 M H₂SO₄ aqueous electrolyte. The frequency corresponding to -45° (10 Hz) is much smaller than that of MSC with 1 M H₂SO₄ aqueous electrolyte (529 Hz, Figure S4a). In addition, a semicircle at high frequency region is clearly shown in the impedance spectrum (Figure S5b), indicating large ionic diffusion resistance at high frequency in the device. Besides, the knee frequency of TSC (100 Hz), above which the supercapacitor will act more resistive, is an order of magnitude smaller than that obtained for MSC with an aqueous electrolyte (~2.0 kHz Figure S4a). As a result, the CV curves at high scan rates (Figure S6a) are much more deformed (Figure 3a). For convenience, gravimetric capacitance is compared between TSC and MSC (Figure S6b). It can be seen that MSC shows a higher specific capacitance of 147 F g⁻¹ compared to 110 F g⁻¹ of TSC at a scan rate of 50 mV s⁻¹ and retains 66.0% of that value at 6 V s⁻¹ compared to 48.9% for TSC.

In addition, our MSC shows great mechanical compliance. **Figure 4a** shows an image of the all-solid-state MSC bent around a fingertip. Electrochemical characterizations of the MSCs bent at different curvatures were carried out to test the flexibility. CV curves for samples bent around columns with different diameters exhibit nearly identical profiles to those of the unbent sample (Figure 4b). The sample was further bent around an 11 mm diameter column for 2,500 times and then twisted around the same column for another 2,500 times (the diagonal of the sample parallel to the column axis). Charge/discharge tests were carried out every 100 bending/twisting operations to test the mechanical reliability (Figure 4c). It retained 95.9% of the initial capacitance after 2,500 times of bending and 93.5% after another 2,500 times of twisting. The excellent flexibility and stability make the as-fabricated MSC suitable for flexible and wearable applications.

4. Conclusion

In summary, an all-solid-state flexible MSC is fabricated by in situ reduction and assembly of GO on a Cu interdigit template. The interdigital design and quasi-parallel alignment of rGO hydrogel provide a

rapid charge and electron transport pathway. Excellent rate performance and extremely small relaxation time constant are achieved even in solid state. In addition, the superior mechanical compliance and stability of MSC make it suitable for wearable electronic applications. The fabrication process is room temperature operated, environmentally-friendly, and easily scalable by using Cu interdigit prepared by industrialized methods such as inkjet printing. This approach might play an important role as on-chip energy storage in the future.

Acknowledgments

This research work was partially supported by Advanced Research Project Agency- Energy (ARPA-E) program # DE-AR0000303 and the National Natural Science Foundation of China (Nos. 11272008 and 11361161001). Chinese Scholarship Council financially supported Zhenkun Wu in participating GT-PKU Joint Ph.D. Program during his study in the United States. Zhenkun Wu and Ziyin Lin contributed equally to this work. The authors gratefully acknowledge Dr. Yunnan Fang, Mr. Wentian Gu and Ms. Taoran Le for their helpful discussion.

- [1] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, *Nature nanotechnology* 5 (2010) 651-654.
- [2] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Science* 328 (2010) 480-483.
- [3] H. Xing, X. Wang, C. Shen, S. Li, *Micro & Nano Letters, IET* 7 (2012) 1166-1169.
- [4] D. Pech, M. Brunet, P.-L. Taberna, P. Simon, N. Fabre, F. Mesnilgrete, V. Conédéra, H. Durou, *Journal of Power Sources* 195 (2010) 1266-1269.
- [5] W. Gao, N. Singh, L. Song, Z. Liu, A.L.M. Reddy, L. Ci, R. Vajtai, Q. Zhang, B. Wei, P.M. Ajayan, *Nature nanotechnology* 6 (2011) 496-500.
- [6] M.F. El-Kady, V. Strong, S. Dubin, R.B. Kaner, *Science* 335 (2012) 1326-1330.
- [7] M.F. El-Kady, R.B. Kaner, *Nature communications* 4 (2013) 1475.
- [8] J. Lin, C. Zhang, Z. Yan, Y. Zhu, Z. Peng, R.H. Hauge, D. Natelson, J.M. Tour, *Nano letters* 13 (2012) 72-78.
- [9] Y. Zhu, L. Li, C. Zhang, G. Casillas, Z. Sun, Z. Yan, G. Ruan, Z. Peng, A.-R.O. Raji, C. Kittrell, *Nature communications* 3 (2012) 1225.
- [10] M. Beidaghi, C. Wang, *Advanced Functional Materials* 22 (2012) 4501-4510.
- [11] Z. Niu, L. Zhang, L. Liu, B. Zhu, H. Dong, X. Chen, *Advanced Materials* 25 (2013) 4035-4042.
- [12] Z.S. Wu, K. Parvez, A. Winter, H. Vieker, X. Liu, S. Han, A. Turchanin, X. Feng, K. Müllen, *Advanced Materials* (2014).
- [13] Z.S. Wu, K. Parvez, X. Feng, K. Müllen, *Nature communications* 4 (2013).
- [14] X. Cao, D. Qi, S. Yin, J. Bu, F. Li, C.F. Goh, S. Zhang, X. Chen, *Advanced Materials* 25 (2013) 2957-2962.
- [15] M.S. Kim, B. Hsia, C. Carraro, R. Maboudian, *Carbon* 74 (2014) 163-169.
- [16] Y. Xu, K. Sheng, C. Li, G. Shi, *ACS nano* 4 (2010) 4324-4330.
- [17] U.N. Maiti, J. Lim, K.E. Lee, W.J. Lee, S.O. Kim, *Advanced Materials* 26 (2014) 615-619.
- [18] Y. Yoon, K. Lee, S. Kwon, S. Seo, H. Yoo, S. Kim, Y. Shin, Y. Park, D. Kim, J.-Y. Choi, *ACS nano* (2014).
- [19] O.C. Compton, B. Jain, D.A. Dikin, A. Abouimrane, K. Amine, S.T. Nguyen, *ACS nano* 5 (2011) 4380-4391.
- [20] H. Wang, J.T. Robinson, X. Li, H. Dai, *Journal of the American Chemical Society* 131 (2009) 9910-9911.
- [21] Z. Lin, Y. Liu, Y. Yao, O.J. Hildreth, Z. Li, K. Moon, C.-p. Wong, *The Journal of Physical Chemistry C* 115 (2011) 7120-7125.
- [22] T. Szabó, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanakis, D. Petridis, I. Dékány, *Chemistry of materials* 18 (2006) 2740-2749.
- [23] X. Yang, L. Qiu, C. Cheng, Y. Wu, Z.F. Ma, D. Li, *Angewandte Chemie International Edition* 50 (2011) 7325-7328.
- [24] Y. Zhu, S. Murali, M.D. Stoller, K. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychoz, M. Thommes, *Science* 332 (2011) 1537-1541.
- [25] J.J. Yoo, K. Balakrishnan, J. Huang, V. Meunier, B.G. Sumpter, A. Srivastava, M. Conway, A.L. Mohana Reddy, J. Yu, R. Vajtai, *Nano letters* 11 (2011) 1423-1427.
- [26] Y. Gogotsi, P. Simon, *Science Magazine* 334 (2011) 917-918.
- [27] Z. Niu, W. Zhou, J. Chen, G. Feng, H. Li, W. Ma, J. Li, H. Dong, Y. Ren, D. Zhao, *Energy & Environmental Science* 4 (2011) 1440-1446.
- [28] H.J. In, S. Kumar, Y. Shao-Horn, G. Barbastathis, *Applied Physics Letters* 88 (2006) 083104.
- [29] M. Kaempgen, C.K. Chan, J. Ma, Y. Cui, G. Gruner, *Nano letters* 9 (2009) 1872-1876.
- [30] K. Sheng, Y. Sun, C. Li, W. Yuan, G. Shi, *Scientific reports* 2 (2012).

[31] J. Gamby, P. Taberna, P. Simon, J. Fauvarque, M. Chesneau, Journal of Power Sources 101 (2001) 109-116.

Figure 1. Schematic procedure for preparing MSC using in situ reduced rGO hydrogel as electrode material. a) MSC fabrication process: I) Fabricate Cu/Au interdigit. II) Immerse the substrate into GO solution for 12 hours to reduce GO in situ. III) Wash the device with deionized water. IV) Drop coat PVA/H₂SO₄ electrolyte onto the rGO hydrogel interdigit and dry it in air. b) Schematic illustration of the reducing mechanism. c) Optical images of as-fabricated devices. On the left is the substrate before immersed into GO solution. In the middle is an all-solid-state MSC and on the right is a one-dime coin of U.S. as a reference.

Figure 2. (a) Top and (b) cross-section SEM images of freeze-dried rGO aerogel on Kapton substrate. (c) XPS spectra, (d) Raman spectra, and (e) FTIR spectra of GO film and rGO aerogel.

Figure 3. Electrochemical characterization of as-fabricated MSC in PVA/ H₂SO₄ gelled electrolyte dried in air for 72 hours. (a) CV curves at scan rates of 1 V s⁻¹, 2 V s⁻¹, and 6 V s⁻¹, respectively. (b) CD curves at current densities of 0.43, 1.3, and 4.3 mA cm⁻², respectively. (c) Specific areal capacitance calculated from discharge curves at different current densities. (d) Capacitance retention during 11,000 times of charging and discharging at current density of 1.3 mA cm⁻². (e) Electrochemical impedance spectrum measured from 10 mHz to 100 kHz. Inset shows magnified view of high frequency region. (f) Bode phase plot against frequency. $f_0=49$ Hz corresponds to phase angle of -45°.

Figure 4. Performance of MSC at deformed situation. (a) Photo image of the device at bent state. (b) CV curves of device bent around columns with different diameters as well as that of unbent state as a reference (Scan rate 1 V s^{-1}). (c) Capacitance retention during bending and twisting test for 5,000 times.

Table 1. Comparison of as prepared MSC with state-of-art MSCs

electrode materials	electrolyte	specific areal capacitance [mF cm ⁻²]	relaxation time constant [ms]	substrate requirement	Ref.
rGO	solid	0.87	4.8~20	any substrate	this work
rGO	solid	0.14 ^{a)}	N/A	Si/SiO2	[12]
rGO	solid	0.16 ^{a)}	N/A	any substrate	[11]
laser reduced GO	solid	1.6 ^{a)}	19	any substrate	[7]
CVD grown and water etched Graphene/CN T	liquid	0.97 ^{a)}	2.6	Si/SiO2	[8]
rGO/CNT	liquid	4.5	4.8	Si/SiO2	[10]
Onion like carbon	liquid	1.1 ^{a)}	26	any substrate	[1]

^{a)}These values were adjusted to specific areal capacitance at a scan rate of 1 V s⁻¹ based on information from the papers.

FIG1

FIG2

FIG3

FIG4

FIG1 GRAY

FIG2 GRAY

FIG3 GRAY

FIG4 GRAY