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Layer-by-layer printing of laminated graphene-based interdigitated microelectrodes for flexible planar micro-supercapacitors

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Abstract

Graphene-based planar micro-supercapacitors are layer-by-layer printed on flexible substrates using micro-extrusion technique. The laminated graphene films and polyvinyl alcohol-H₂SO₄ gel serve as the interdigitated micro-electrodes and electrolyte, respectively. The resultant solid-state micro-supercapacitors exhibit high capacitive performance, excellent flexibility and cycling stability. Such device promises potential applications in flexible electronics and lab-on-a-chip systems.

Keywords: graphene; micro-supercapacitor; flexible; planar; layer-by-layer printing

1. Introduction

Planar micro-supercapacitors (PMSCs) have attracted considerable efforts in recent years because of their amenability to be integrated with microelectronics and

lab-on-a-chip devices.[1]In addition, their in-plane structure renders high power density because electrolyte ions are transported laterally between closely placed electrodes, without the necessity of any binder or separator.[2-3] PMSCs have been fabricated using photolithographic micro-fabrication and laser patterning.[4-5]These methods, however, are tedious, not cost-effective, and not compatible with flexible substrates. A Screen-printed PMSC on flexible substrate has been demonstrated.[6]But screen-printing requires pre-fabricated masks or stamps and substrate-specific in formulation. Current PMSCs usually require a layer of metallic current collector on the substrate.[4]This not only complicates the fabrication but also compromises the device flexibility. Furthermore, the practical applications of current PMSCs are often limited by the low specific capacitance.[2]

Owing to its high specific surface area, excellent electrical conductivity, and exceptional mechanical properties, graphene is an ideal electrode material for PMSCs.[7-8] Thin-film graphene electrodes can be fabricated by vacuum-assisted infiltration, chemical vapor deposition, electrophoretic deposition, ink-jet printing, layer-by-layer deposition and spray deposition.[9-10] These methods, however, are not amenable for PMSC fabrication or require complicated procedures. The amphiphilic properties of graphene oxide (GO) sheets (thus high solubility in various solvents) make them suitable inks for printing processes.[11-12] In this work, we demonstrate a reduced-GO (rGO) based PMSC layer-by-layer printed on flexible substrate using the micro-extrusion printing technique. Micro-extrusion process involves extruding viscous ink through a deposition nozzle, with controlled speed and

nozzle size as well as pre-programmed printing trajectory. In contrast to traditional micro-fabrication process and other printing techniques, micro-extrusion method enables programmable and convenient patterning (for both 2D and 3D architectures), high throughput printing on arbitrary substrates, and broad choices of printing materials (*e.g.*, aqueous dispersions, metal or ceramic pastes, polymer melts, even live cells).[13-14] The herein demonstrated graphene-based solid-state PMSC (free of metallic collector, binder, and separator) exhibits high specific volumetric capacitance (41.8 F/cm^3), cycling stability, and flexibility.

2. Experimental

The GO sheets were synthesized from graphite flake powders using a modified Hummers method.[15] The obtained GO aqueous solution was concentrated (to 20 mg/mL) by centrifugation. A self-built 3D micro-extrusion system was used to print graphene-based interdigitated electrodes. The printing system consists of a desktop XYZ motor (Technodigm, Model: DR3331T-EX), a temperature-controlled substrate holder (100 °C used here), and a high-precision displacement pump (Technodigm, Model: PDP 1000). The printing head mounted on the precision XYZ motor (20 μm resolution) prints along the pre-programmed tracks with an adjustable speed (50 mm/s used). The printing head includes a piston, a syringe and a changeable micro-needle (inner diameter of 210 μm used). The displacement pump drives the piston with a controllable speed (0.001 mm/s) to extrude GO suspension from the syringe onto the substrate. To obtain the all-carbon solid-state PMSC, printed GO patterns were chemically reduced into rGO using hydroiodic acid (HI) followed by coating a layer

of polyvinyl alcohol (PVA)-H₂SO₄ gel electrolyte on top. PVA-H₂SO₄ gel electrolyte was prepared by mixing H₂SO₄ solution (1M, 10 mL) with PVA powder (1g), and subsequent heating at 90 °C with vigorous stirring. The printed electrodes were examined by a field-emission scanning electron microscope (JEOL, JSM-6700F). The electrochemical measurements were performed using CHI 660D Electrochemical Work Station (CH Instruments).

3. Results and discussion

Fig. 1A illustrates the fabrication process. Viscous GO suspension (20 mg/mL) was filled in an injection syringe mounted on a programmable positioning motor. Extrusion of GO ink through the micro-needle leads to assembly of GO sheets into a highly-laminated thin film on the substrate due to the liquid crystalline behavior of highly concentrated GO suspension and the shear stress between the viscous solution and the inner wall of the needle.[16] The width and thickness of the printed patterns can be readily tuned by the needle diameter, extrusion speed, and scan rate. Identical interdigitated GO electrode (width of 650 μm, inter-spacing of 500 μm) were printed on both hard (glass) and flexible (polyethylene terephthalate-PET) substrates. After chemically reducing GO into rGO using HI and coating a layer of PVA-H₂SO₄ gel electrolyte, an all-carbon solid-state PMSC was ready for electrochemical characterizations.

The thickness of rGO electrodes can be readily scaled via repetitive layer-by-layer printing.[17] As shown in **Fig. 1B**, each run of printing produces a rGO layer of ~1.04 μm thickness, and the final electrode thickness is linearly proportional

to the number of printing cycles (layers). Scanning electron microscopy (SEM) reveals the laminated structure of rGO electrode (**Fig. 1B** inset). Such structure ensures high mechanical robustness, electrical conductivity, and importantly, lateral permeability to electrolytes.[3] The conductivities of rGO electrodes with 1, 2 or 4 printed layers are 58.3 ± 13.0 ($n = 4$), 59.1 ± 4.9 S/cm ($n = 3$), 114.0 ± 17.7 S/cm ($n = 5$), respectively.

The nearly symmetric charge-discharge curves of the PMSCs printed on transparent glass substrate suggest that electrical double layer capacitance (EDLC) dominates the performance (**Fig. 2A**). The specific areal (C_A) and volumetric (C_V) capacitance can be calculated from discharge curve. C_A and C_V are normalized to the area and volume of the electrodes excluding inter-spacing. As shown in **Fig. 2B**, C_A is linearly proportional to the number of rGO layers (19.8 mF/cm^2 with 4 printed layers). Evidently, the specific surface area of the electrode is not compromised by layer-to-layer stacking. In other words, the electrolyte ions can easily infiltrate between rGO sheets. On the other hand, C_V reaches plateau beyond 2-layers (41.8 F/cm^3 with a 2 printed layers), indicating that both specific surface area and volume are linearly dependent on the layer numbers because of the electrolyte-permeable laminated structure. Electrochemical impedance spectroscopy (EIS) shows that larger printed layer number leads to smaller equivalent series resistance (**Fig. 2C**). On the other hand, the EIS slope at low frequency range is similar between single and multiple layered electrodes, indicating that ion infiltration is not compromised by the layered structures. In the following experiments, we choose double-layered PMSCs as

the case study.

Fig. 2D depicts the charge-discharge curves of double-layered micro-supercapacitors, at different current densities. The calculated C_V decreases from 56.5 (at 0.06 A/cm³) to 18.2 F/cm³ (at 3 A/cm³), indicating that ion transport in the solid-state electrolyte is the limiting factor at high current density (**Fig. 2E**). These values are higher than that from the previously reported PMSCs made by laser patterning.[5] The performance of our all-carbon PMSC is compared with other graphene-based solid-state supercapacitors reported in the literatures in Ragone plot as shown in **Fig. 2F**. [4-5, 18-19] However, it should be aware that more careful comparison can only be made in view of the difference in experimental conditions and device architectures in different studies. Our layer-by-layer printed PMSC shows volumetric energy density (E_V) of 7 mWh/cm³, and volumetric power density (P_V) of 30 mW/cm³ (corresponding to an areal energy and power density of 7.6 mWh/cm² and 29.2 mW/cm², respectively) at the current density of 0.06 A/cm³. It outperforms the micro-supercapacitors fabricated by photolithographic micro-fabrication and laser patterning process.[4-5]

As shown in **Fig. 3A-B**, two PMSCs in series double the working voltage while two PMSCs in parallel double the capacity as evidenced by doubled discharging time. These experiments indicate the small device-to-device variation and the feasibility to scale up the output by combining several PMSCs. Moreover, the voltage drop at the onset of discharging phase is small, suggesting a small internal resistance. While connecting supercapacitors in series for an extended period, large leakage current is of

an important concern, e.g., large leakage current leads to fast self-discharging.[5] As shown in **Fig. 3C** and **D**, two PMSCs in series exhibit a small leakage current and sustained self-discharging.

To demonstrate the possibility for the applications in flexible electronics, PMSCs were also printed on PET thin films. Because of its high mechanical strength and flexibility, graphene is desirable for flexible and stretchable electronics. The printed rGO films stably adhere onto PET film due to large surface area of flat graphene sheets and their self-alignment resulting from the extrusion process (inset of **Fig. 4A**). As demonstrated in **Fig. 4A**, CV of the PMSC with double-layered rGO electrodes doesn't alter while the device is highly curved. As shown in **Fig. 4B**, the volumetric capacitance (C_V) moderately drops from 38.4 F/cm³ in the initial 300 cycles and remains stable at ~20.3 F/cm³ afterwards (till 10000 cycles). And the cycling stability of C_V remains after the device understating 1000 times of bending-unbending. These experiments demonstrate the excellent flexibility and mechanical robustness of the device.

The excellent performance of our devices can be attributed to 1) the good conductivity and large surface area of graphene sheets;[5] 2) laminated rGO structure resulted from extrusion of liquid crystalline GO suspension, which allows readily penetration of electrolytes.[3] In addition, the method demonstrated here permits convenient patterning on arbitrary substrates and does not require the use of organic binder, conductive additive, metallic current collector or polymer separator that are commonly needed in commercial supercapacitors.

4. Conclusions

In this study, we demonstrate a new layer-by-layer printing method to fabricate planar micro-supercapacitors on flexible substrates. The resultant solid-state PMSCs, using patterned laminated rGO films as interdigitated electrodes and PVA-H₂SO₄ gel as electrolyte, exhibit high volumetric energy and power density as well as good cycling stability. Such devices promise applications in microelectronics, lab-on-a-chip systems, and flexible electronics. As the amphiphilic GO sheets can be well dispersed in various solvents, electrochemically active inks could be devised by decorating GO sheets with other functional nanomaterials in order to further improve the performance of printed supercapacitors.

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References

- [1] G. Xiong, C. Meng, R.G. Reifengerger, P. Irazoqui, T. Fisher, A Review of Graphene-Based Electrochemical Microsupercapacitors, *Electroanalysis* 26 (2014) 30-51.
- [2] J. Chmiola, C. Largeot, P.L. Taberna, P. Simon, Y. Gogotsi, Monolithic Carbide-Derived Carbon Films for Micro-Supercapacitors, *Science* 328 (2010) 480-483.
- [3] J.J. Yoo, K. Balakrishnan, J.S. Huang, V. Meunier, B.G. Sumpter, A. Srivastava, M. Conway, A.L.M. Reddy, J. Yu, R. Vajtai, P.M. Ajayan, Ultrathin Planar Graphene Supercapacitors, *Nano Lett.* 11 (2011) 1423-1427.
- [4] Z.S. Wu, K. Parvez, X.L. Feng, K. Mullen, Graphene-based in-plane micro-supercapacitors with high power and energy densities, *Nat. Commun.* 4 (2013) 2487.
- [5] M.F. El-Kady, R.B. Kaner, Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage, *Nat. Commun.* 4 (2013) 1475.
- [6] Y. Wang, Y.M. Shi, C.X. Zhao, J.I. Wong, X.W. Sun, H.Y. Yang, Printed all-solid flexible microsupercapacitors: towards the general route for high energy storage devices, *Nanotechnology* 25 (2014) 094010.

- [7] G.Z. Sun, L.X. Zheng, Z.Y. Zhan, J.Y. Zhou, X.B. Liu, L. Li, Actuation triggered exfoliation of graphene oxide at low temperature for electrochemical capacitor applications, *Carbon* 68 (2014) 748-754.
- [8] X.W. Wang, G.Z. Sun, P. Routh, D.H. Kim, W. Huang, P. Chen, Heteroatom doped graphene materials: syntheses, properties and applications, *Chem. Soc. Rev.* 43 (2014) 7067-7098.
- [9] D. Janas, K.K. Koziol, A review of production methods of carbon nanotube and graphene thin films for electrothermal applications, *Nanoscale* 6 (2014) 3037-3045.
- [10] L.T. Le, M.H. Ervin, H.W. Qiu, B.E. Fuchs, W.Y. Lee, Graphene supercapacitor electrodes fabricated by inkjet printing and thermal reduction of graphene oxide, *Electrochem. Commun.* 13 (2011) 355-358.
- [11] J. Cao, Y.Y. Zhang, C.L. Men, Y.Y. Sun, Z.N. Wang, X.T. Zhang, Q.W. Li, Programmable Writing of Graphene Oxide/Reduced Graphene Oxide Fibers for Sensible Networks with in Situ Welded Junctions, *ACS Nano* 8 (2014) 4325-4333.
- [12] G.Z. Sun, Y.Z. Pan, Z.Y. Zhan, L.X. Zheng, J.Y. Lu, J.H.L. Pang, L. Li, W.M. Huang, Reliable and Large Curvature Actuation from Gradient-Structured Graphene Oxide, *J. Phys. Chem. C* 115 (2011) 23741-23744.
- [13] J. An, C.K. Chua, T. Yu, H.Q. Li, L.P. Tan, Advanced nanobiomaterial strategies for the development of organized tissue engineering constructs, *Nanomedicine* 8 (2013) 591-602.
- [14] C.K. Chua, K.F. Leong, N. Sudarmadji, M.J.J. Liu, S.M. Chou, Selective laser sintering of functionally graded tissue scaffolds, *MRS Bull.* 36 (2011) 1006-1014.
- [15] S.L. Ting, C.X. Guo, K.C. Leong, D.H. Kim, C.M. Li, P. Chen, Gold nanoparticles decorated reduced graphene oxide for detecting the presence and cellular release of nitric oxide, *Electrochim. Acta* 111 (2013) 441-446.
- [16] G.Z. Sun, J.Q. Liu, X. Zhang, X.W. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, Fabrication of Ultralong Hybrid Microfibers from Nanosheets of Reduced Graphene Oxide and Transition-Metal Dichalcogenides and their Application as Supercapacitors, *Angew. Chem. Int. Ed.* in press (2014).
- [17] K. Sun, T.S. Wei, B.Y. Ahn, J.Y. Seo, S.J. Dillon, J.A. Lewis, 3D Printing of Interdigitated Li-Ion Microbattery Architectures, *Adv. Mater.* 25 (2013) 4539-4543.
- [18] J. Lin, C.G. Zhang, Z. Yan, Y. Zhu, Z.W. Peng, R.H. Hauge, D. Natelson, J.M. Tour, 3-Dimensional Graphene Carbon Nanotube Carpet-Based Microsupercapacitors with High Electrochemical Performance, *Nano Lett.* 13 (2013) 72-78.
- [19] B. Yao, L.Y. Yuan, X. Xiao, J. Zhang, Y.Y. Qi, J. Zhou, J. Zhou, B. Hu, W. Chen, Paper-based solid-state supercapacitors with pencil-drawing graphite/polyaniline networks hybrid electrodes, *Nano Energy* 2 (2013) 1071-1078.

Figures

Fig. 1. (A) Schematic illustration of device fabrication. (B) The thickness of laminated rGO film is linearly proportional to the number of printing cycles. Error bars indicate the standard deviation (n=4 samples).

Fig. 2. (A) Charge-discharge curves (at current of 100 μ A) of PMSCs with 1 layer, 2 layers and 4 layers of printed rGO electrodes. (B) Specific areal (C_A) and volumetric (C_V) capacitance vs. the number of printed-layers. Error bars represent the standard deviations ($n=3$ samples). (C) Electrochemical impedance spectra (EIS) of PMSCs based on rGO electrodes with 1, 2, and 4 printed layers. Sinusoidal voltage (5 mV) ranging from 100 K to 0.01 Hz was used. (D and E) Charge-discharge curves of PMSCs with 2-layer printed rGO electrode at different current densities (0.06, 0.03, 0.6, 3 A/cm²) and the corresponding specific volumetric capacitance (C_V). (F) Energy

and Power densities of PMSCs compared with other graphene-based solid-state supercapacitors reported in the literatures.

Fig. 3. (A and B) Charge-discharge curves of single, and two devices connected in series or in parallel. (C) Leakage current of two PMSCs in series. (D) Self-discharge curve of two PMSCs in series obtained immediately after precharging to $V_{\max}$ (2 V) till 50% drop.

Fig. 4. (A) CVs of PMSC at flat or bent states. Inset shows the photograph of a bent PMSC device on a PET film. Each rGO finger is 1.5 cm long and 650 μm wide. (B) Dependence of volumetric capacitance on charge-discharge cycling numbers. The solid cycles represent the measurements after the device undertaking 1000 times of bending-unbending.