Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Flexible Patterned Micro-Electrochemical Capacitors based on PEDOT

Lishuang Fan, [c] **Naiqing Zhang***[a,b] **and Kening Sun***[ab]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We reported fabrication of patterned flexible MECs with inkjet printing. The strategy can effectively simplify the fabrication process, thus reduce the cost. The obtained flexible MECs exhibited very high specific capacitance of 6.4 mF cm^{-2}, and revealed long-term cycling stability.

Nowadays, there is a strong interest in flexible energy storage devices to meet the requirements from wearable electronics, electronic newspapers, paper-like mobile phones, and other easily collapsible gadgets.[1] Meanwhile, the current development trend of miniaturized electronic equipment has raised the demand for flexible micro-scale storage power system.[2] Compared with batteries, electrochemical capacitors (ECs), also called supercapacitors, can offer a higher power density, high cycle life and superior safety.[3] Furthermore, micro-scale ECs (MECs) can achieve high ratio of energy delivery at high charge-discharge rates due to a shortened diffusion length.[4] There have been notable advances in the MECs field, which were mostly focused on increasing MECs energy density by using different active materials and device designs.[5] To our knowledge, very few work has been reported on the integration of flexible and patterned MECs.[6] Unfortunately, in the previous reports, the preparation of flexible MECs often contained several steps. For example, the flexible MECs needs extra conducting current collectors (Au or Ag) fabricated by the screen printing or magnetron sputtering techniques, meanwhile the active material needs a further treatment. This complicated manufacturing process is time consuming, and high-cost assisting by expensive equipments, which is not easy to scale up. So it is an urgent need for developing a facile, simple, scale up, and patterned method to fabricate flexible MECs. Inkjet printing technique provides a new route to deposit versatile thin films, which are low-cost, high efficiency, easy pattern design and scalability to large scale manufacturing. Therefore, inkjet printing has being widely used in various fields, such as bio-sensors, light-emitting devices, and thin-film transistors. [7]

In this work, we reported fabrication of patterned flexible MECs with inkjet printing. The PEDOT was chosen as the raw material for conductive ink due to its unique electrical conductivity and high capacity.[8] Herein, PEDOT:PSS was used as current collectors and active materials simultaneously. The strategy can effectively simplify the fabrication process, thus reduce the cost. The obtained flexible MECs exhibited very high specific capacitance of 6.4 mF cm^{-2}, and revealed long-term cycling stability. The flexible MECs did not show any apparent performance degradation in the bending test. These remarkable results demonstrate the exciting commercial potential for flexible and miniaturized electronic equipments such as wearable energy storage devices, portable consumer electronics and computer memory backup systems.

For inkjet printing technology, the ink plays a very important role in the whole system. The applicability of this technology is limited by the viscosity, solubility of the ink, and substrate surface wettability. Commercial available PEDOT:PSS cannot be directly used as conductive ink due to the low viscosity, solubility and poor wettability, which would cause the clogging of the print head and inconsistence of ink droplet. The different status of ink would also affect the morphology of obtained film. In our experiments, the viscosity and surface tension of solution was adjusted by APU (water soluble Polyurethane) and Tween additives (details see the experimental section). Figure S2 compares SEM images of PEDOT:PSS film obtained with and without additives in ink. Figure S1a is a typical surface profile of PEDOT:PSS featuring with discrete islands of 40 nm size, which would cause the poor conduction and clogging of the print head.

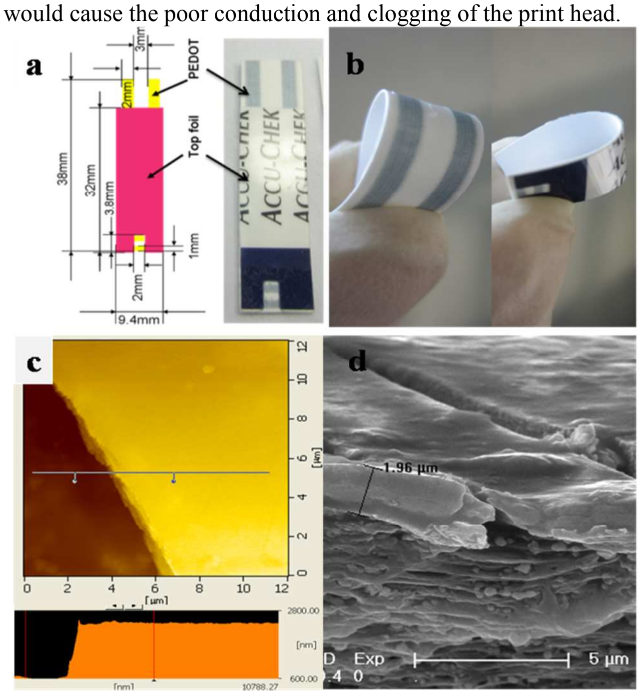

Figure 1. Architecture of the flexible MECs and morphology of the electrode. a) The size and pattern of the fabrication of MECs integrated using computer. b) The optical picture of flexible MECs unit on flexible substrates based on inkjet printing technology. c, d) AFM and SEM images of PEDOT:PSS obtained from inkjet printing.

However, the surface morphology of PEDOT:PSS with additives shows uniform and continuous structure and avoid coffee-stain effect (Fig. S2b and Fig. 1c) after optimizing the composition of the ink due to a conformational change from compact to spread with good wettability, which will contribute to the improvement of electrical conductivity of the PEDOT:PSS film.

The detailed pattern of PEDOT:PSS film fabricated with inkjet printer was illustrated in Figure 1a. It is worth mentioning that the pattern can be easily designed according to power needed and the space of the chip. Figure 1b presents optical images of flexible substrates with PEDOT:PSS printed according to the designed pattern (Figure 1a). The electrodes showed excellent flexible properties and good mechanical rigidity (Figure 1b). AFM and SEM measurements showed that the printed PEDOT:PSS film had a slick and uniformity of thickness about 2 µm attributed to TEG (Triethylene glycol) (Figure 1c,d). The PEDOT:PSS films showed higher conductivity (900 S cm^{-1}) than those of activated carbons and graphene (in the range of 10-100 S cm^{-1}),[9] which are the state-of-the-art materials used in commercial devices. Therefore, the high conductivity implied PEDOT:PSS could act as current collector and active material simultaneously in the ECs.

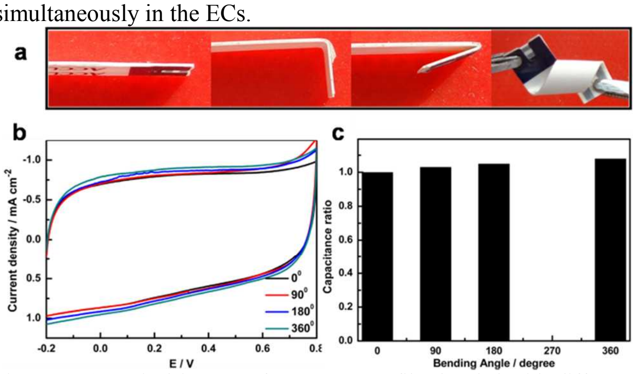

Figure 2. a) Optical images of PEDOT:PSS film bended with different angles. b) Cycle voltammetry of MECs at different bending angles. Scan rate: 0.08 V s^{-1}. c) Capacitance ratio of MECs with different angles.

For practical application consideration, flexible electronics may work at different degree of deformation, and thus, the electrochemical properties under different bending states are critical. The effect of curvature on the performance of the MECs was examined in Figure 2. We checked CV curves (Figure 2b) of the MECs under four different bending angles (0°, 90°, 180°, 360°, Figure 2a) and found their electrochemical performance was hardly affected (Figure 2c). This result clearly demonstrates that the MEC possesses excellent bend tolerance properties. The packaged MECs either in series or parallel can meet the energy and power requirements from cells.

CVs were recorded at different scan rates (0.01-1 V s^{-1}) to test the power capability of the MECs (Figure S3a). The near-rectangular CV curves in 1 M KCl electrolyte can be attributed to small mass-transfer resistance, good charge propagation behaviour of ions and low contact resistance in the capacitors.[10] A nearly rectangular CV shape at a scan rate of 1000mV s^{-1}, indicated an ideal capacitive behaviour even though no metal current collector were used in this work. The discharge current showed a linear dependence on scan rates ranging from 0.01 to 1 V s^{-1}, indicating the high power output capability, a reproducible and stable capacitive behaviour. These results reveal the fast charge transport and higher conductivity of PEDOT:PSS, which

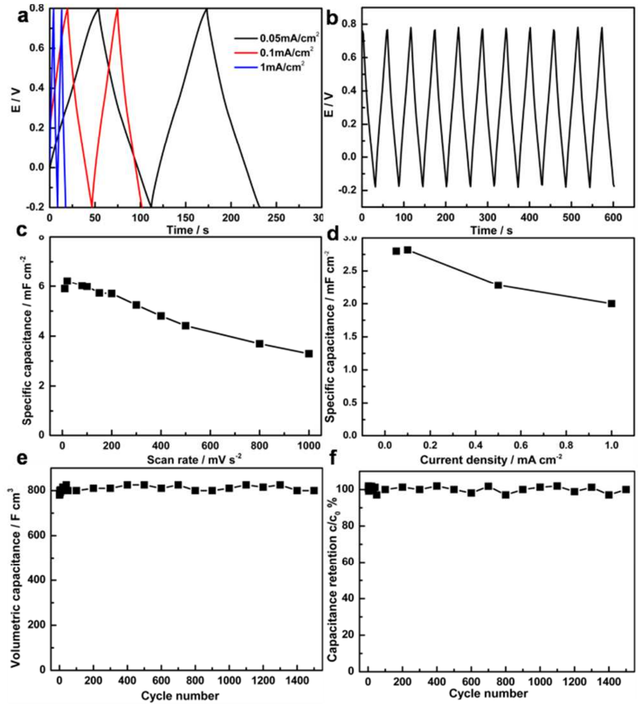

Figure 3. a) Galvanostatic charge/discharge curves for flexible MECs at different densities. b) Galvanostatic charge/discharge curves for the flexible MECs at the high current density 0.1 mA cm^{-2}. c, d) Gravimetric capacitance and surface-area normalized capacitance at various scan rates and current density. e,f) Capacitance value versus the number of cycles during long-term cycling and evolution of the relative capacitance retentions versus the number of electrochemical cycles at 0.1 mA cm^{-2} of a PEDOT:PSS based MECs made of 2 µm thick electrodes in a 1 M KCl.

is significantly superior for supercapacitors.[11] When the scan rates exceed 1 V s^{-1}, the current values deviated from the linear region, probably owing to the limited ionic doping and diffusion in the solid film (Figure S3b).[4a]

The galvanostatic charge/discharge curves of the flexible MECs at various current densities ranging from 0.05 to 1 mA cm^{-2} are shown in Figure 3a. It was observed that all charge-discharge curves were linear and symmetrical at various current densities. This is a typical characteristic for an ideal capacitor.[12] Galvanostatic cycling of MECs electrodes was performed at a constant current density 0.1 mA cm^{-2}. As shown in Figure 3b, the discharge curves were linear in the total range of potential with constant slopes, showing nearly perfect capacitive behavior. The specific capacitance of electrode was 6.4 mF cm^{-2} at 20 mV s^{-1} (Figure 3c), which is comparable to values reported in literatures for electrochemical double layer micro-capacitors (0.4-2 mF cm^{-2}) at scan rates in the range of 1-100 mV s^{-1}[6a, 13], and the electrode maintained high capacitance (3.2 mF cm^{-2}) at a high scan rate at 1 V s^{-1}. The specific capacitance was evaluated from the slope of the charge-discharge curves, according to $C=Q/A\Delta V=I\Delta t/(A\Delta V)$, where A is the surface area of the flexible film electrode. The maximum specific capacitance of the obtained device was evaluated to be 2.0 mF cm^{-2} at current density of 5 mA cm^{-2}. The result in Figure 3d demonstrates a good rate capability (Figure 3d). The long-term cycling stability of the supercapacitor was tested through a cyclic charge/discharge process at a fixed current density of 0.1 mA cm^{-2}, (see Figures 3b and 3e). The nearly symmetric charge discharge curve with no obvious IR drops revealed a good capacitive behaviour and a highly reversible charge double layer at the interface and mass doping in PEDOT:PSS film.[14] The cycling performance of the PEDOT:PSS film showed negligible capacitance change after 1500 cycles, indicating a stable electrode material (Figures 3e and 3f).

To test electrochemical responses and suitability for capacitance applications, the PEDOT:PSS film was screened by an electrochemical impedance spectroscopy test in a frequency range from 100 kHz to 10 mHz with a potential amplitude of 5 mV. As shown in the Nyquist plots (Figure S4), a negligible high frequency resistor capacitor loop or semicircle was related to the electronic resistance inner of film. The inconspicuous arc in the high frequency region indicated low resistance. This result is attribution to an excellent electrode contact and good ion response of PEDOT:PSS film.[15] A slope of the 45° portion of the curve was observed due to the Warburg resistance. It is a result of the frequency dependence of ion diffusion in the electrolyte to the electrode interface [16] and the large slopes of these plots are, the closer the material resembles an ideal capacitor [17]. From the EIS curve, the PEDOT:PSS film exhibits a short diffusion path length of the ions, determined by the short Warburg region which could be ascribed to the unique electrochemical properties of PEDOT:PSS, where much more ions have access to active surfaces and doped into the composite.[18]

Conclusions

In summary, a flexible MEC was designed and fabricated using inkjet printing technique. The PEDOT:PSS was introduced as current collectors and active materials simutaneously in the flexible MECs. The strategy can effectively reduce the fabrication steps and the cost. The supercapacitor exhibited high specific capacitance with the values of 6.4 mF cm^{-2}, and revealed excellent long-term cycling stability. The results demonstrated that PEDOT:PSS can be considered as a promising material to fabricate flexible MECs. It is worth pointing that our approach and design can be easily applied to other supercapacitor materials and will extent to other flexible/wearable energy storage devices, such as portable consumer electronics and computer memory backup systems et al.

Notes and references

[a] State Key Laboratory of Urban Water Resource and Environment,
[b]Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, China. Fax: +86 451-86412153; Tel: XX +86 451-86412153; E-mail: znqmww@163.com
[c]Department of Chemistry, Harbin Institute of Technology.

† Electronic Supplementary Information (ESI) available: [details of experemental, CV and EIS]. See DOI: 10.1039/b000000x/

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