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Highly Compressible Solid-State Supercapacitor with Folded Paper-Based Electrode

Yu Song, Xiao-Liang Cheng, Hao-Tian Chen, Meng-Di Han, Xue-Xian Chen, and Hai-Xia Zhang*
National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Institute of Microelectronics, Peking University, Beijing 100871, CHINA
Corresponding author: Hai-Xia Zhang, Email: zhang-alice@pku.edu.cn

***Abstract*—In this paper, we present a novel compressible solid-state supercapacitor with PVA/H_3PO_4 solid-state electrolyte and folded carbon-nanotube (CNT)/paper electrode. In this structure, both of the compression tolerance of folding structure and the strain capability of CNT film contribute to achieve high compression-tolerant abilities of the electrode, which can be widely used in various environments. This solid-state supercapacitor has achieved the specific capacitance to 11.07 mF/cm^2, and capacitance retention retains more than 90% after 100 cycling tests. In addition, the performance of this supercapacitor is very stable even when it is compressed under 50% strain, which enlightens a broad field of compressible energy storage devices to be compatible with high compression-tolerant electronics and flexible self-powered systems.**

Keywords—supercapacitor; carbon nanotube; compressible; folded structure

I. INTRODUCTION

With the rapid development of the consumer electronics as well as advance in wearable electronics[1], harvesting mechanical energy from the environment is widely considered an attractive approach. In recent research, novel energy harvesting devices such as triboelectric nanogenerators have been well-developed[2,3]. Besides various nanogenerators, high-performance energy storage device, as another critical components in self-powered system, are in great demands.

Supercapacitor, as a promising state-of-the-art energy storage device, fills the blank between the batteries with high specific energy density and the conventional electrostatic capacitors with high specific power density[4,5]. Solid-state supercapacitors integrating electrodes, solid-state electrolyte and separator, are superior to the liquid-based supercapacitor[6] due to easy fabrication, light-weight, high safety and compatible with environment. Meanwhile, electronic devices with highly deformation-tolerant have attracted tremendous attention[7,8]. They can easily maintain the desired levels of performance and reliability due to their flexibility of integration into various forms systems[9,10]. As a crucial component of electronics system, power source devices should definitely have the ability to accommodate large strains and own long-term stability in various environments.

However, there has been limited progress in developing supercapacitors which could withstand pressure and shape changing. Recent demonstrations have shown that graphene [11], CNTs[12] and their composite sponge[13] can serve as compressible electrodes, which can be assembled into the supercapacitor with a complicated figuration. However, sponge electrode is fragile, suffering from the low stability in mechanical manufacture. On the other hand, sponge is not suitable for many electronic device, which could extremely restrict its application.

By now, paper is the cheapest and most popular substrate, which can be integrated in microfluidics system[14], energy storage device[15] and radio frequency device[16]. Carbon materials such as CNTs and graphene could be efficiently absorbed into paper, improving its conductivity and electrochemical activity[17]. Additionally, paper is available to form a designed structure with strong mechanical strength, like folded shapes. Undoubtedly, this folded structure could broaden its compressible and flexible abilities without damaging its intrinsic performance.

Therefore, considering that gel electrolytes are favored over liquid counterparts and folded structure owns the highly compression-tolerant ability, this compressible supercapacitor is innovatively designed based on folded paper-based electrode and solid-state electrolyte, which can solve mentioned problems and make great progress in flexible electronics and wearable devices.

II. EXPERIMENTAL PROCEDURES

2.1 Fabrication process

The schematic diagram of proposed compressible solid-state supercapacitor is shown in Figure 1a, which is composed by the flexible folded CNT/paper electrode, solid-state Polyvinyl alcohol (PVA)/phosphoric acid (H_3PO_4) electrolyte and the separator membrane. Additionally, optical image of proposed compressible solid-state supercapacitor is also shown in Figure 1b, which owns the uniformly folded structure and excellently mechanical strength. The total side length and thickness of the device is 4 cm and 0.7 mm, respectively.

The detailed fabrication process is illustrated in Figure 2. Firstly, two pieces of filter paper and a cellulose membrane (TF44, NKK, Japan) as a separator film with an area of 16 cm^2 were both folded as wavy shape. Secondly, CNT ink solution was prepared by dispersing 60 mg of CNTs with 60 mg of sodium dodecylbenzenesulfonate (SDBS) surfactant in 60 ml of deionized water. After the CNT ink solution was bath-sonicated for 4 h to disperse

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evenly, approximately 30 ml CNT ink was drop-dried on each folded paper for several times and dried at 80°C for 1 h in an oven.

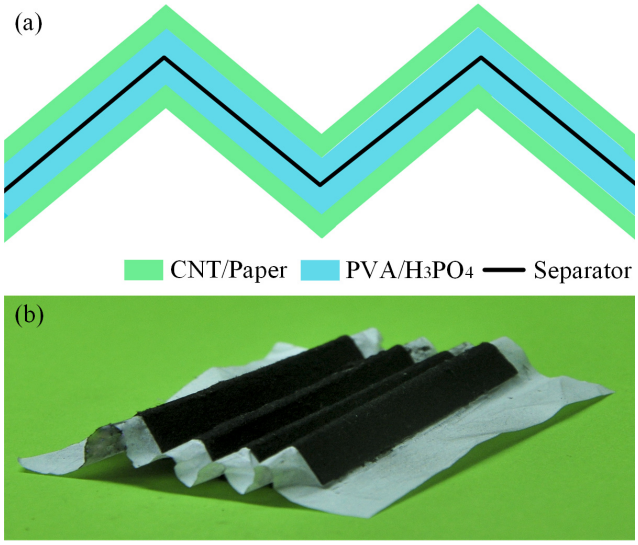

Figure 1: (a) Schematic diagram and (b) optical image of compressible solid-state supercapacitor based on folded structure.

Then PVA/H_3PO_4 electrolyte was prepared by adding PVA powder (6 g) into H_3PO_4 aqueous solution (6 g H_3PO_4 into 60 ml deionized water). The whole mixture was heated to 85°C under vigorous stirring until the solution became clear. After cooling down, two folded CNT/paper electrodes were immersed into the solid-state PVA/ H_3PO_4 electrolyte for 5 min and then all of them were assembled into a symmetrical supercapacitor by sandwiching the separator between them. Finally, the device was dried in a regular oven at 45°C for about 12 h to fully vaporize the excess water.

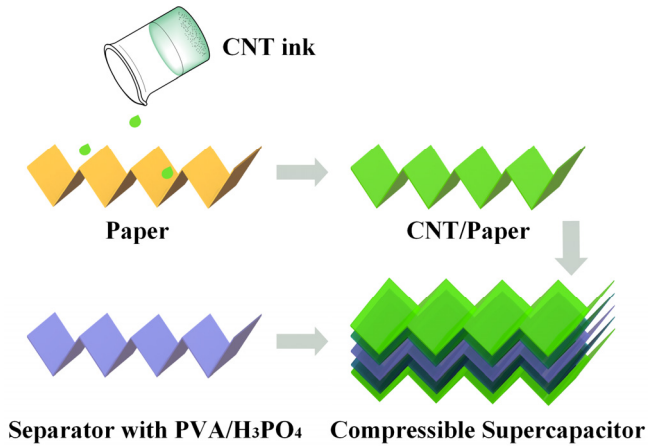

Figure 2: Fabrication flow process of compressible supercapacitor, consisting of folded CNT/paper electrode, PVA/H_3PO_4 electrolyte and NKK TF44 separator membrane.

2.2 *Measurement and Analysis*

The morphologies, structure of the compressible CNT/paper electrode and the assembled supercapacitor were all analyzed using a scanning electron microscope (SEM) (Quanta 600F, FEI Co.). All of the electrochemical tests of the compressible solid-state supercapacitor were carried out by a two-electrode system using CHI660C (CH instrument) electrochemical workstation at room temperature.

III. RESULTS AND DISCUSSIONS

3.1 *Optical and SEM analysis*

Figure 3a presents the cross-sectional SEM image of the sandwiched structure of the compressible supercapacitor. The enlarged view was shown in Figure 3b where one of the folded structure of the proposed device was displayed in detail. As mentioned before, flexible and conductive paper electrodes were prepared by simply drop-drying CNT solution onto filter papers. And Figure 3c illustrates that the proposed paper was relatively uniformly coated with CNTs, thus exerting a significant role as CNT/paper electrode.

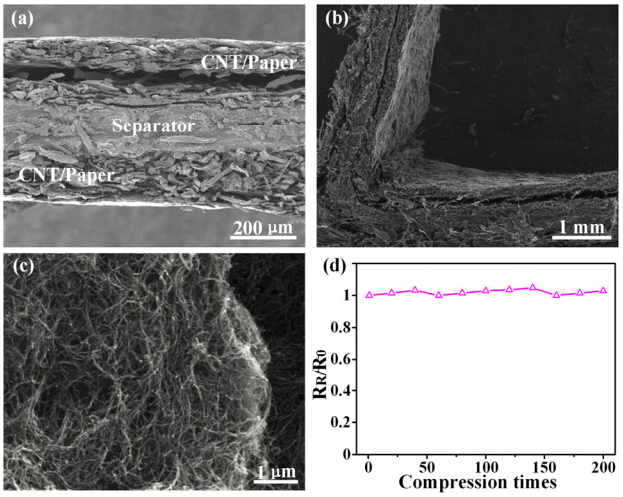

Figure 3: (a) SEM image of the cross section of the compressible supercapacitor. (b) Enlarged view of the folded structure. (c) SEM image and (d) the variation of electrical resistance of CNT/paper electrode in the first 200 compressing–releasing cycles.

Furthermore, the resistance of CNT/paper electrode is almost steady in spite of repeated compressing-releasing process in the first 200 cycles, showing the excellently tolerant ability (Figure 3d). Therefore, this electrode would be promising candidate of highly compressible solid-state supercapacitor electrode, without either an insulating binder or a low capacitance conducting additive.

3.2 *Compressible test*

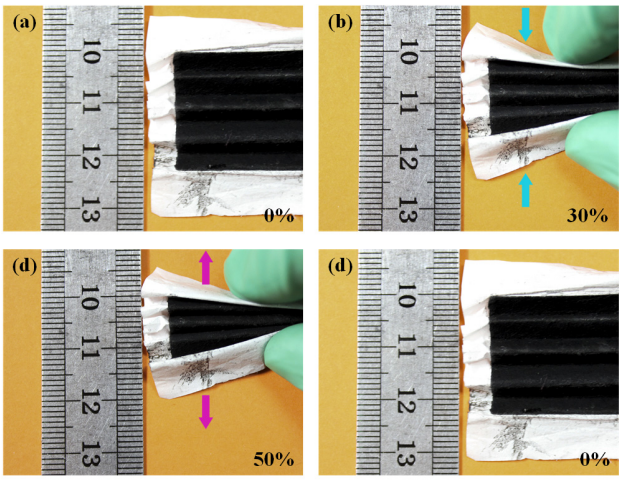

Figure 4: Real-time optical images of a supercapacitor showing the compressing and recovering process without any structural damage.

With the folded electrodes and solid-state electrolyte assembled to the integral device, experiments were performed where the device was operated under different compression ratio (Figure 4a-4d), demonstrating the device highly compressible. The device can sustain large-strain deformations (ε=50%) under manual compression and recover to the initial state without any observable structural crack. Additionally, the compressible supercapacitor can restore most of length after several repeated compressing-releasing cycles.

3.3 Electrochemical analysis

To further explore the electrochemical performance of the compressible folded structure, we fabricated an all solid-state supercapacitor, the area of which is 16 cm^2. The electrochemical performance of the solid-state symmetrical supercapacitor was carefully evaluated through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and cycle life measurements via electrochemical workstation. Firstly, electrochemical performance was analyzed by CV curves at scan rates from 10 mV/s to 200 mV/s. The CV curves retained roughly rectangular shape approximately symmetrical about the zero-current line, indicating an ideal electrochemical behavior.

Then GCD was also analyzed to further evaluate the electrochemical performance of solid-state supercapacitor. Typical GCD curves were shown in Figure 5b, the charging-discharging currents of which are from 0.8 mA to 6 mA. Discharge profile of the fabricated supercapacitor was found to depend on the applied current and similar curve shapes have been obtained for different current densities. It reveals that all of the charging curves are symmetrical with their corresponding discharge counterparts, as well as their excellent linear voltage-time profiles, indicating good electrochemical behavior of the device.

Besides, the areal capacitance (C_A) was calculated using the CV curves of the supercapacitor achieved by the following equations:

$$C = \frac{Q}{\Delta V} = \frac{1}{\mathrm{k}\cdot\Delta V}\int_{V_1}^{V_2} I(V)dV \qquad (1)$$

$$C_A = \frac{C}{A} = \frac{1}{\mathrm{k}\cdot A\cdot\Delta V}\int_{V_1}^{V_2} I(V)dV \qquad (2)$$

, where C is the total capacitance, $I(V)$ is the discharge current function, k is the scan rate, ΔV is the potential window during the discharge process and A is the area of the supercapacitor. The maximum areal capacitance is 11.07 mF/cm^2 at 10 mV/s and areal capacitance decreases with the scan rate increasing (Figure 5c), demonstrating a good electrochemical capability. Furthermore, the specific capacitance cycling performance of the device is also discussed in Figure 5d. The fabricated solid-state supercapacitor shows long-term stability after 100 charge–discharge cycling times, and Columbic efficiency retains more than 90%.

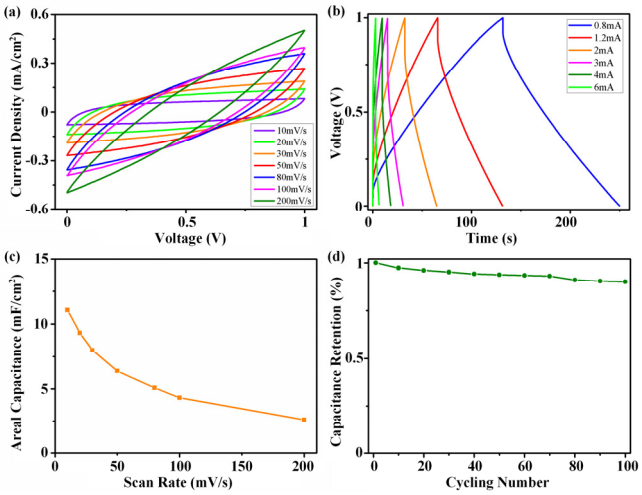

Figure 5: Electrochemical characterization of the supercapacitor. (a) CV curves, (b) GCD curves, (c) calculated areal capacitance and (d) cycling tests at 100 mV/s of the device.

When such compressible supercapacitor is applied different strains from initial state to 50% strain, no significant change is observed in the CV curves at voltage scan rate of 100 mV/s and GCD curves at charging-discharging current of 1.2 mA, respectively, thus indicating the electrochemical stability performance of the device (Figure 6a and 6b). Figure 6c illustrates that the normalized capacitance of the compressible supercapacitor with different strains. The areal capacitance is also calculated through eq. 2. It can be found that specific capacitance of the compressible supercapacitor is nearly not altered under the strain, which maintains more than 90% at 50% strain state.

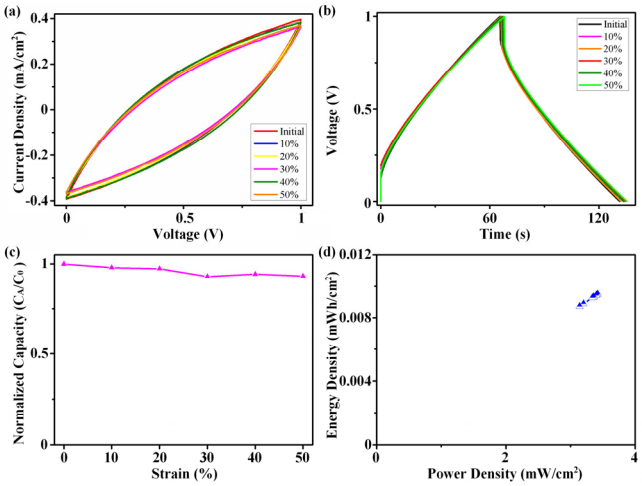

Figure 6: (a) CV curves, (b) GCD curves, (c) normalized specific capacity and (d) Ragone plot of compressible supercapacitor at different strains. Scan rate: 100 mV/s, charge/discharge current: 1.2 mA.

A Ragone plot showing the energy density with respect to the power density of fabricated solid-state supercapacitor at initial state is presented in Figure 6d at different voltage scan rates. The energy density and power density of the device could be calculated by the following equations:

$$E = \frac{1}{2}C_A(\Delta V)^2 \qquad (3)$$

$$P = \frac{3600E}{\Delta t} \quad (4)$$

, where C_A is the areal capacitance of the supercapacitor which can be achieved through eq. 2, ΔV is also the potential window during discharging process, and Δt is the discharging time. The highest energy density of the supercapacitor is 0.0095 mWh/cm^2 at the scan rate of 10 mV/s, at the same time, the highest power density is 3.42 mW/cm^2 at the scan rate of 200 mV/s, respectively. Definitely, both of them vary slightly with the increase of the applied strain.

IV. CONCLUSIONS

In summary, we fabricated compressible CNT/paper electrodes by simply "drop-drying" process with folded structure. The resistance of CNT/paper electrode is almost steady during spite of repeated compressing-releasing process in the first 200 cycles. It remains excellent tolerant stability under different compressible strains, which performs a promising candidate in compression-tolerant devices. Based on PVA/H_3PO_4 gel electrolyte, highly compressible solid-state supercapacitor could be fabricated with proposed folded CNT/paper electrodes. With this unique configuration, the whole device could be compressed as an integrated unit, which accounts for the fact that it can fully recover to the initial state without any structural damage under several compressing-releasing cycles. The specific capacitance of this compressible supercapacitor reaches 11.07 mF/cm^2 at the scan rate of 10 mV/s, and capacitance retention retains more than 90% after 100 charge-discharge cycling times, thus showing long-term stability. In addition, when the compressible supercapacitor is applied different strains from initial state to 50% strain, the performance is relatively stable, which maintains more than 90% at 50% strain state. Therefore, the highly compressible solid-state supercapacitor provides a marvelous power storage choice for the advanced applications of compression-tolerant electronics.

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REFERENCES

[1] B. Meng, X. Cheng, X. Zhang, M. Han, W. Liu and H. Zhang, "Single-friction-surface triboelectric generator with human body conduit", Appl. Phys. Lett., 2014, 104, 103904.

[2] X. Zhang, M. Han, B. Meng, H. Zhang, "High performance triboelectric nanogenerators based on large-scale mass-fabrication technologies", Nano Energy, 2015, 11, pp. 304-322.

[3] Z. Wang, "Triboelectric nanogenerators as new energy technology for self-powered systems and as active mechanical and chemical sensors", ACS Nano, 2013, 7. pp. 9533-9557.

[4] P. Simon, Y. Gogotsi, "Materials for electrochemical capacitors", Nat. Mater., 2008, 7, pp. 845-854.

[5] J. Miller, P. Simon, "Electrochemical capacitors for energy management", Science, 2008, 321, pp. 651-652.

[6] S. Sathyamoorthi, V. Suryanarayanan, D. Velayutham, "Organo-redox shuttle promoted protic ionic liquid electrolyte for supercapacitor". J. Power Sources, 2015, 274, pp. 1135-1139.

[7] H Hu, Z. Zhao, W. Wan, Y. Gogotsi and J. Qiu, "Ultralight and highly compressible graphene aerogels", Adv. Mater., 2013, 25, pp. 2219-2223.

[8] Y. Li, J. Chen, L. Huang, C. Li, J. Hong and G. Shi, "Highly compressible macroporous graphene monoliths via an improved hydrothermal process", Adv. Mater., 2014, 26, pp. 4789-4793.

[9] X. Zhang, M. Han, R. Wang, F. Zhu, Z. Li, W. Wang and H. Zhang, "Frequency-multiplication high-output triboelectric nanogenerator for sustainably powering biomedical microsystems", Nano Lett., 2013, 13, pp. 1168-1172.

[10] X. Cheng, B. Meng, X. Zhang, M. Han, Z. Su and H. Zhang, "Wearable electrode-free triboelectric generator for harvesting biomechanical energy", Nano Energy, 2015, 12, pp. 19-25.

[11] Y. Zhao, J. Liu, Y. Hu, H. Cheng, C. Hu, C. Jiang, L. Jiang, A. Cao and L. Qu, "Highly Compression-Tolerant Supercapacitor Based on Polypyrrole-mediated Graphene Foam Electrodes", Adv. Mater., 2013, 25, pp. 591-595.

[12] Z. Niu, W. Zhou, X. Chen, J. Chen, J. Xie, "Highly Compressible and All-Solid-State Supercapacitors Based on Nanostructured Composite Sponge", Adv. Mater., 2015, 27, pp. 6002-6008.

[13] Y. Zhang, Z. Zhen, Z. Zhang, J. Lao, J. Wei and H. Zhu, "In-situ synthesis of carbon nanotube/graphene composite sponge and its application as compressible supercapacitor electrode", Electrochim. Acta, 2015, 157, pp. 134-141.

[14] R. Niedl, C. Beta, "Hydrogel-driven paper-based microfluidics", Lab Chip, 2015, 15, pp. 2452-2459.

[15] V. Pushparaj, M. Shaijumon, A. Kumar, S. Murugesan, L. Ci, R. Vajtai, R. Linhardt, O. Nalamasu and P. Ajayan, "Flexible energy storage devices based on nanocomposite paper", P. Natl. Acad. Sci. USA, 2007, 104, pp. 13574-13577.

[16] V. Subramanian, J. Fréchet, P. Chang, D. Huang, J. Lee, S. Molesa and S. Volkman, "Progress toward development of all-printed RFID tags: materials, processes, and devices", P. IEEE, 2005, 93, pp. 1330-1338.

[17] G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J. McDonough and Z. Bao, "Solution-processed graphene/MnO2 nanostructured textiles for high-performance electrochemical capacitors", Nano Lett., 2011, 11, pp. 2905-2911.