Journal of
Materials Chemistry A

COMMUNICATION

View Article Online
View Journal | View Issue

Sticky-note supercapacitors†

Jingyu Cao,‡ Yang Zhao,‡ Yifan Xu, Ye Zhang, Bo Zhang* and Huisheng Peng*

Cite this: *J. Mater. Chem. A*, 2018, **6**, 3355

Received 7th December 2017
Accepted 23rd January 2018

DOI: 10.1039/c7ta10756k

rsc.li/materials-a

With the rapid development in portable and wearable electronics, it will be of great convenience if flexible supercapacitors can be easily mounted/disassembled from different substrates at our will, which will largely expand their application scenarios. Herein, inspired by a sticky note, a new family of flexible sticky-note supercapacitors with repeated adhesive performance has been developed by employing a novel kind of sticky aligned carbon nanotube array electrode. The sticky-note supercapacitor demonstrated high capacitance and can be easily and repeatedly attached onto various substrates including cloth, glass, paper, plastic and metal. For up to 200 attaching/removing cycles on different substrates, the capacitance of the supercapacitor note can be well maintained at above 99%.

Introduction

As a promising alternative or complement to batteries, supercapacitors have fast charge and discharge rates, high power densities and long lifespans for over tens of thousands of cycles.[1–5] With the fast-growing requirements of portable and wearable electronic equipment, great efforts have also been made to develop flexible,[6–12] stretchable,[13–17] and multifunctional supercapacitors.[18–24] Generally, these portable supercapacitors cannot be conveniently mounted onto substrates, especially irregular and flexible ones. Furthermore, they always need a certain and pretreated substrate and a complicated installation procedure to ensure a stable electronic connection and electrochemical performance. However, the electrode structure of these portable supercapacitors might be destroyed during complex deformations or washing processes of the wearable electronic textiles, which will cause huge electrochemical performance decay and might cause serious safety problems in case of a short circuit. Therefore, to better fulfill the requirements of portable and wearable electronics, an ideal supercapacitor should not only possess high capacitance and flexibility, but also exhibit good compatibility and reusability, and should be able to be easily and repeatedly mounted/disassembled from a variety of substrates such as cloth, glass, paper and plastic to meet different practical requirements.

Sticky notes are a meaningful invention which has brought tremendous convenience to people's daily life in the past few decades. The preferable adhesive performance and durability endow sticky notes with high compatibility for various substrates for several attaching/removing cycles. Motivated by this method, we propose that if a flexible supercapacitor can be easily and repeatedly attached, removed and re-attached onto any substrate without leaving a residue or electrochemical performance decay, it would be of great significance for wearable electronic devices. To this end, the electrodes for supercapacitors are required to be functionalized with stable and repeated stickiness. Generally, sticky electrodes can be achieved by means of glue or tape, whereas the assembly process and connection will be much complicated and unstable due to the non-conductivity of the glue or tape. Furthermore, the strong bonding between the glue and electrodes will dramatically destroy the original structure of the electrodes so that the electrochemical performance of the supercapacitor will be shattered. Therefore, as an electrode for a good sticky-note supercapacitor, it needs to be highly conductive, easily transferable and inherently sticky without using any extra glue, tape or conductors. With the above unique properties, these flexible supercapacitors can be directly connected with conductive substrates or be easily stacked for in-series electrical connection to realize integration without using extra conducting wires. Also, these sticky-note supercapacitors can be easily taken off during charging or ironing/washing the wearable electronic fabrics when compared with their conventional counterparts. Unfortunately, to date, there is still no way to achieve inherently sticky and easily transferable supercapacitors with conductive stickiness and repeated adhesive performance.

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200438, China. E-mail: bozhang@fudan.edu.cn; penghs@fudan.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ta10756k

‡ The first two authors contributed equally to this work.

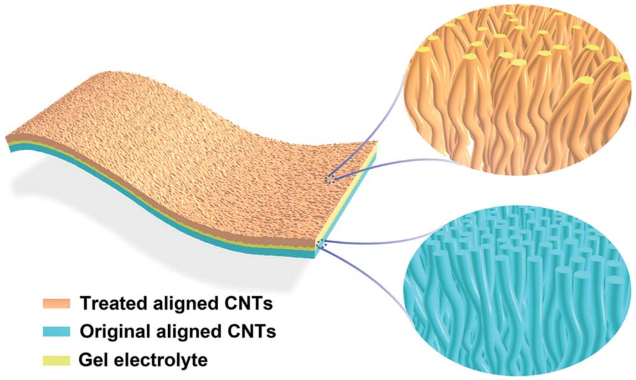

Fig. 1 Schematic illustration of the structure of the flexible sticky-note supercapacitor.

Herein, a new family of flexible and transferable sticky-note supercapacitors (Fig. 1) with repeatedly conductive stickiness has been developed by designing a novel kind of sticky aligned carbon nanotube (CNT) array electrode. Owing to the vertically aligned CNT structure and ordered nanoscale CNT junctions formed in the top region, the sticky CNT array electrode demonstrates decent conductivity, high porosity and more importantly superior repeated adhesive properties for up to 2000 attaching/removing cycles with the well-retained CNT junction structure. The as-fabricated sticky-note supercapacitors are highly flexible and can be easily attached onto a variety of common substrates to power specific portable devices without a soldering procedure. Moreover, they demonstrate a decent capacitance of 73 mF cm^{-2}, which can be well maintained for 200 attaching/removing cycles or during changing between different common substrates including cloth, paper, metal, planks, glass and plastic. After using, they can be easily removed and re-attached elsewhere to power other devices without structural damage or electrochemical performance decay. Their surface CNT layers were electrically conducting, so they can be brought into direct contact for electrical connection in series to realize integration without the use of extra conducting wires. These sticky note supercapacitors will tremendously expand the application scenarios of flexible supercapacitors, especially in future wearable electronics and flexible circuits.

Experimental section

Preparation of sticky CNT array electrodes

CNT arrays were first synthesized by chemical vapor deposition on a silicon wafer in a tube furnace. The catalysts of Al_2O_3 (5 nm) and Fe (1.2 nm) were successively deposited on a silicon wafer through electron beam evaporation deposition at rates of 2 and 0.5 Å s^{-1}, respectively. The CNT arrays were then obtained on the silicon wafer in a tube furnace through a chemical vapor deposition process. Ar (400 sccm) was first supplied for 8 min to fully remove the air in the tube furnace. During the growth process, ethylene (30 sccm) served as the carbon precursor and a mixture of Ar (400 sccm) and H_2 (90 sccm) served as the carrier gases. At a heating rate of 73 °C min^{-1}, the tube furnace was kept at 750 °C for 80 min to obtain the CNT array. The CNT arrays were further treated by using a microwave plasma of oxygen (300 sccm) at 600 W in the time range from 10 to 30 min, followed by pressing them into thin films and scrapping off as the sticky CNT array electrode.

Fabrication of the sticky-note supercapacitor

The poly(vinyl alcohol) (PVA)/H_3PO_4 gel electrolyte was prepared by dissolving 1 g of PVA in 9 g of deionized water at 95 °C for 5 h, followed by addition of 1.5 g H_3PO_4 at room temperature. The sticky and original CNT array electrodes were coated with the PVA/H_3PO_4 gel electrolyte on the side close to the silicon wafer using a toothpick, and the obtained two electrodes were then gently pressed together to make the sticky-note supercapacitor. A two tandem sticky-note supercapacitor was fabricated by pressing the sticky side of one note to the original side of the other note together. The short circuit can be easily avoided because of the barrier of the polymer electrolyte. A four tandem sticky-note supercapacitor was fabricated by subsequently stacking four notes one by one. The CNT electrodes of the sticky-note supercapacitor were pressed onto tiny copper foils for the convenience of the attaching/removing electrical measurements.

Results and discussion

The CNT arrays were first synthesized by chemical vapor deposition[25–28] typically with heights of ~1.2 mm (Fig. S1†). The CNTs were generally aligned while had been randomly entangled with each other at the top surface of the array (Fig. S2†). To make the CNT array adhesive, we further performed oxygen plasma treatment[29,30] to produce more junction points among the CNTs at the top surface layer. After the above treatment, the vertically aligned structure of the CNTs at the bottom offered the electrode with high electrical conductivity, while the crossed structure of the CNT at the top layer was designed to endow the electrode with repeating stickiness.

With increasing the plasma treatment time from 0 to 10 min, the randomly entangled CNTs at the top surface of the array were partly destroyed (Fig. S2 and S3a†). The randomly entangled CNTs at the top layer disappeared and ordered CNT junction points were formed with the treatment time increased from 10 to 20 min (Fig. S3a and b†). The ordered CNT junction points and the aligned structure were further destroyed with the treatment time increased to 30 min (Fig. S3c†). The CNT arrays with different treatment times after pressing down (Fig. S4†) into film electrodes were compared for the adhesive properties. Under the same other conditions, the highest adhesive force with the best stability occurred at 20 min (Fig. S5†), and it was 20 times that of the original CNT array electrode. As shown in Fig. S6,† the CNT array with the plasma treatment time of 20 min also displayed the lowest electrical resistance. From 10 to 20 min, the entangled CNTs disappeared and ordered and aligned CNT junction points formed (Fig. S3†). Therefore, the CNT array electrode with the treatment time of 20 min had better electron transport paths and showed much lower electrical resistance. With the treatment time further increased to 30 min, the aligned CNT junction points were destroyed and the CNTs were entangled, which led to a largely increased resistance. Therefore, the 20 min-treated CNT array electrodes were used in further experiments unless otherwise specified. After being stored for two weeks, the structure (Fig. S7a†) and adhesive performance (Fig. S7b†) of the sticky CNT array electrode were well maintained.

The modified CNT array electrode (Fig. S8† and 2a) showed good stickiness on a variety of available substrates including plastic, cloth, metal and glass (Fig. 2b). For instance, upon attaching onto the glass substrate, the sticky CNT array electrode was able to hang an object with a weight as high as 150 g, which was almost 10^5 times of its own weight. For the attaching process, the CNT junctions were first embedded into the cavities of different substrates (Fig. S9†) with increasing contacting surface areas and then the CNT–substrate bonds were formed (Fig. S10†), which offered an effective and stable adhesive force. Owing to the fact that numerous CNT junctions at the nanoscale were stably bonded/locked with tiny cavities at the surface of different substrates by van der Waals forces, the whole CNT array electrode was therefore solidly adhered on the substrates. For the removing process, the CNT junctions were gradually separated from the substrate under a larger external tractive force and the CNT–substrate bonds were totally destroyed and disappeared finally.

Different from other dry adhesives, the sticky CNT array electrode demonstrated well-repeated stickiness on various substrates (Fig. 2c). Furthermore, the adhesive force was maintained at 91% after 2000 attaching/removing cycles on glass (Fig. 2d), and the junction structure of the sticky CNT array electrode had been well maintained after 2000 cycles (Fig. 2e and S11†). The repeated stickiness of the CNT array electrode on various substrates was derived from the high reversibility of the attaching/removing process, which was due to the high mechanical stability of the CNT junction structures and the substrates. The sticky CNT array electrode demonstrated low electrical resistances (*e.g.*, 1.7 Ω for 1 × 1 cm^2) that remained almost unchanged during repeated attaching/removing cycles (Fig. S12†), which was important for maintaining the high electrochemical properties of the resulting supercapacitor

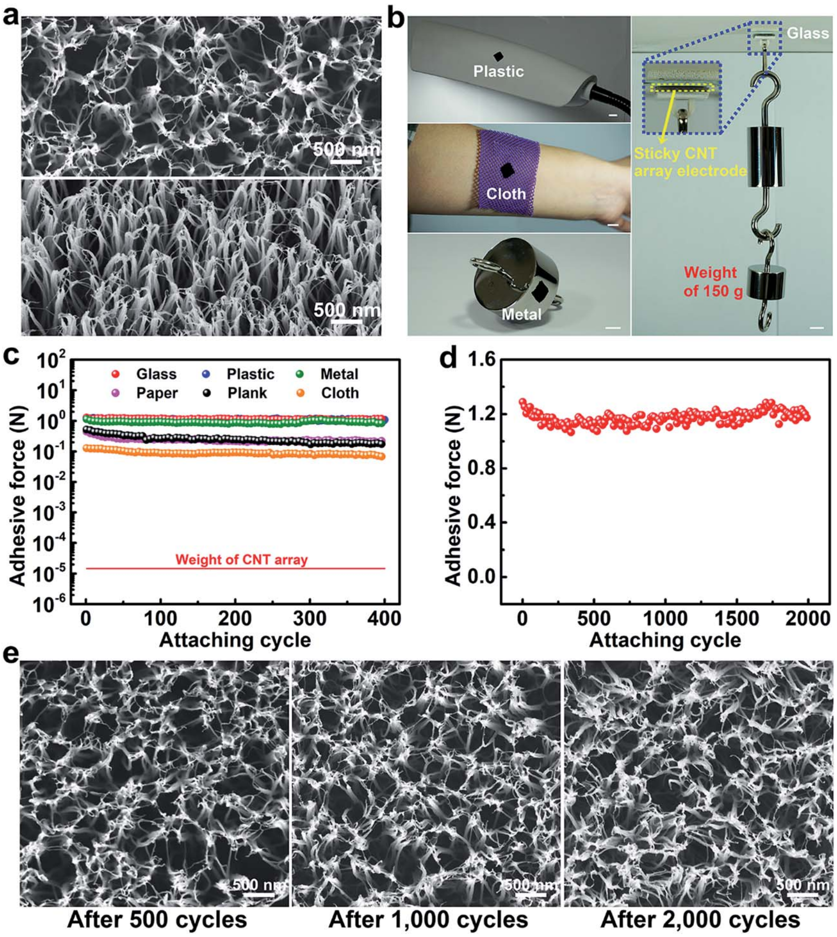

Fig. 2 Structural characterization and adhesive performance of the sticky aligned CNT array electrode. (a) SEM images from top and oblique views. (b) A sticky CNT array electrode being attached on the plastic, cloth, metal substrate and glass (an object with a weight of 150 g being hung). Scale bar: 1 cm. (c) The adhesive force retention curves for 400 attaching/removing cycles on different substrates. (d) The adhesive force retention curve for 2000 attaching/removing cycles on glass. (e) SEM images of the sticky CNT array electrode after 500, 1000 and 2000 attaching/removing cycles from the top view.

during use. The sticky CNT array electrode was also free-standing, flexible and highly porous (Fig. S13–S15†).

The sticky-note supercapacitor was finally fabricated by assembling the sticky and original CNT array electrodes with the PVA/H_3PO_4 gel electrolyte between them (Fig. S16 and S17†). Fig. 3a shows galvanostatic charge–discharge curves at different current densities, and a high areal specific capacitance of 73 mF cm^{-2} was achieved at a current density of 1 mA cm^{-2} with superior rate capability. The sticky-note supercapacitor demonstrated an energy density of 1.7 W h kg^{-1} and a high power density of 835 W kg^{-1}. The cyclic voltammograms of the supercapacitor note demonstrated typical electric double-layer behavior with maintained symmetrical rectangles at increasing scan rates (Fig. 3b). The sticky-note supercapacitor also showed good cycling performance for 10 000 charge–discharge cycles (Fig. S18†). To investigate the influence of the adhesion time on the electrochemical performance, the specific capacitances were traced with increasing attaching/removing cycles (Fig. 3c). They could be maintained at >99% after 200 cycles on various substrates. The almost overlapped electrochemical impedance spectra also verified the high mechanical and electrochemical stability of the supercapacitor (Fig. S19†).

To further investigate the stability and compatibility of the sticky-note supercapacitor, its specific capacitances had been traced by transferring it onto different substrates, and no obvious variation was observed (Fig. 3d). In addition, the adhesive force had been maintained at >96% after 200 attaching/removing cycles on three substrates (Fig. 3e), exhibiting both high repeatability and compatibility of these sticky-note supercapacitors. Furthermore, a high percentage of 97% of the original adhesive force remained after 1800 adhesion cycles on glass (Fig. 3f). The stable attaching and removing performance was also verified by the well maintained CNT junction structures before and after 1800 operation cycles (Fig. S20†). As expected, the sticky-note supercapacitor was also highly flexible, and the high electrochemical properties had been well maintained under bending (Fig. S21 and S22†).

Due to the high electrical conductivity and sticky structure of CNT array electrodes, the sticky-note supercapacitors can be

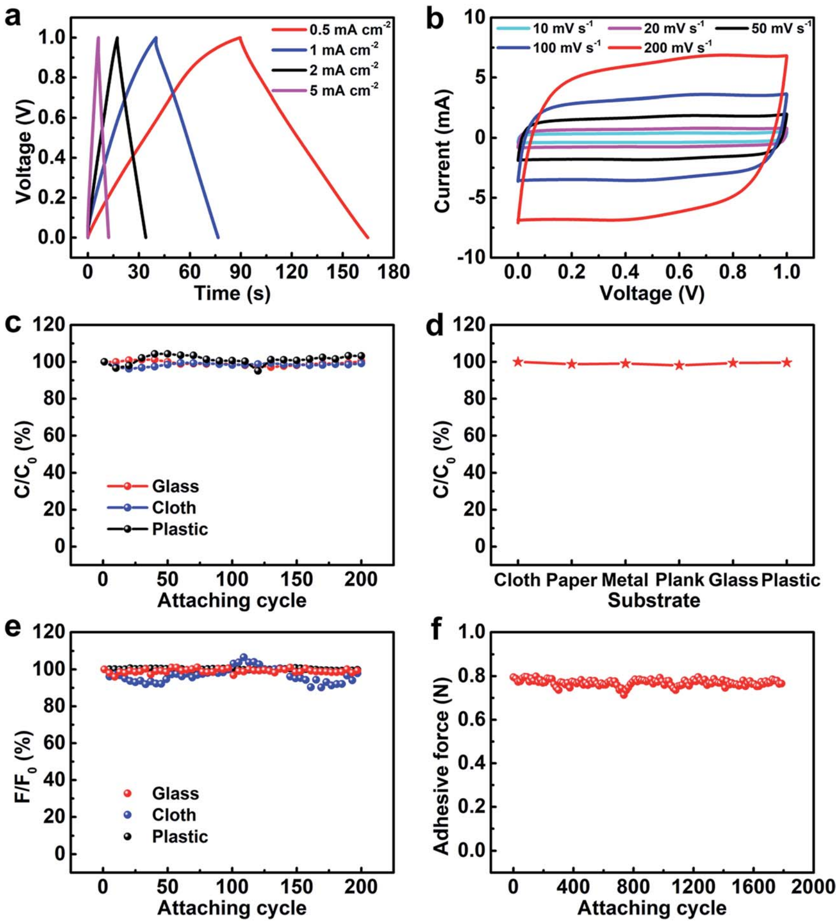

Fig. 3 The electrochemical and adhesive performance of the sticky-note supercapacitor. (a) Galvanostatic charge–discharge curves at different current densities. (b) Cyclic voltammograms at different scan rates. (c) Capacitance retention curves of the sticky-note supercapacitor for 200 attaching/removing cycles on different substrates at a current density of 1 mA cm^{-2}. The C_0 values on the glass, cloth and plastic were 74.2, 72.6 and 73.2 mF cm^{-2}, respectively. (d) Capacitance retention curve of the sticky-note supercapacitor under transferring among different substrates at a current density of 1 mA cm^{-2}. C_0 was 73.2 mF cm^{-2}. (e) Adhesive force retention curves of the supercapacitor note on various substrates for 200 attaching/removing cycles. The F_0 values on the glass, cloth and plastic were 0.80, 0.09 and 0.75 N, respectively. (f) Adhesive force retention curve of the supercapacitor note on glass for 1800 attaching/removing cycles.

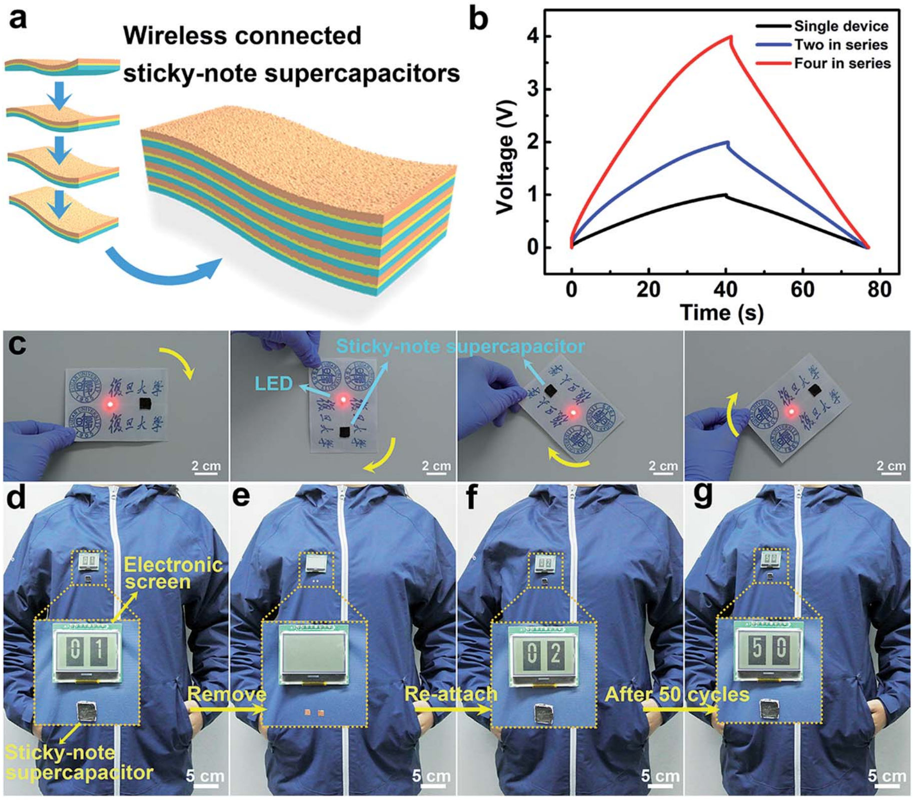

Fig. 4 The tandem structure and application demonstration of the sticky-note supercapacitor. (a) Schematic illustration of the wireless connected sticky-note supercapacitors in series. (b) Galvanostatic charge–discharge curves of the sticky-note supercapacitors with a single device and two and four both in series at a current density of 1 mA cm^{-2}. (c) Assembled two supercapacitors in series being attached on the plastic card to power a red LED during rotating. (d) Four tandem supercapacitors being attached on a coat to power an electronic screen with a cut-off numbering function. (e and f) The assembled four tandem supercapacitors being removed and re-attached onto the coat to power the electronic screen again, respectively. (g) After 50 attaching/removing cycles (the supercapacitor note can be well attached onto the coat to power the electronic screen).

effectively connected in series by directly stacking them (Fig. 4a) to increase the output voltage, without the use of extra conducting wires (Fig. S23†). For instance, the output voltages of the two tandem and four tandem sticky-note supercapacitors were increased to two and four times of a single one, respectively, with the discharge time almost unchanged at the same current density (Fig. 4b). As application demonstrations to reveal the above advantages, the assembled two supercapacitors in series were used to power a red light-emitting diode (LED) lamp fixed onto a glass door (Fig. S24†). They were then transferred and stably attached onto a plastic card to power a red LED, and the effective connection can be maintained during rotating and swinging rapidly (Fig. 4c and Movie S1†). Two tandem supercapacitors can power a red LED for about 50 seconds (Fig. S25†). Furthermore, the four tandem supercapacitors were attached onto a blue coat to power an electronic screen with a cut-off numbering function (Fig. 4d). For the four tandem supercapacitors, they were removed and re-attached onto the coat and were able to drive the electronic screen again to display a number of two (Fig. 4e and f). They could still stably work even after 50 attaching/removing cycles (Fig. 4g and S26†), suggesting the high potential of these sticky-note supercapacitors as lightweight, flexible, durable and portable power sources.

Conclusions

In summary, a flexible sticky-note supercapacitor with repeated adhesive performance has been developed by employing a novel kind of sticky aligned CNT array electrode. The sticky CNT electrode demonstrates a specific ordered nanoscale CNT junction structure and super-stable repeated stickiness with 91% of the adhesive force retained after 2000 continuous attaching/removing cycles. The sticky-note supercapacitor demonstrates a decent capacitance of 73 mF cm^{-2} and can be attached onto various substrates for 200 attaching/removing cycles with the capacitance well maintained at above 99%. These flexible sticky-note supercapacitors will tremendously expand the applications of flexible supercapacitors, especially in future wearable and integratable electronics, electronic skin and flexible circuits.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by MOST (2016YFA0203302), NSFC (21634003, 51573027, 51403038, 51673043, 21604012, and

21503079), STCSM (16JC1400702, 17QA1400400, 15XD1500400, and 15JC1490200) and SHMEC (2017-01-07-00-07-E00062).

Notes and references

1 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845–854.
2 G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Lett.*, 2011, **11**, 4438–4442.
3 M. R. Lukatskaya, S. Kota, Z. Lin, M. Q. Zhao, N. Shpigel, M. D. Levi, J. Halim, P. L. Taberna, M. W. Barsoum, P. Simon and Y. Gogotsi, *Nat. Energy*, 2017, **2**, 17105.
4 L. Liu, Z. Niu and J. Chen, *Chem. Soc. Rev.*, 2016, **45**, 4340–4363.
5 L. F. Chen, Y. Lu, L. Yu and X. W. Lou, *Energy Environ. Sci.*, 2017, **10**, 1777–1783.
6 J. Ren, L. Li, C. Chen, X. Chen, Z. Cai, L. Qiu, Y. Wang, X. Zhu and H. Peng, *Adv. Mater.*, 2013, **25**, 1155–1159.
7 B. C. Kim, J. Y. Hong, G. G. Wallace and H. S. Park, *Adv. Energy Mater.*, 2015, **4**, 1300759.
8 H. Cheng, Z. Dong, C. Hu, Y. Zhao, Y. Hu, L. Qu, N. Chen and L. Dai, *Nanoscale*, 2013, **5**, 3428–3434.
9 J. Yan, C. E. Ren, K. Maleski, C. B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva and Y. Gogotsi, *Adv. Funct. Mater.*, 2017, **27**, 1701264.
10 B. Wang, Q. Wu, H. Sun, J. Zhang, J. Ren, Y. Luo, M. Wang and H. Peng, *J. Mater. Chem. A*, 2017, **5**, 925–930.
11 L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun and C. Gao, *Nat. Commun.*, 2014, **5**, 3754.
12 Y. Luo, Y. Zhang, Y. Zhao, X. Fang, J. Ren, W. Weng, Y. Jiang, H. Sun, B. Wang, X. Chen and H. Peng, *J. Mater. Chem. A*, 2015, **3**, 17553–17557.
13 Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen and S. Xie, *Adv. Mater.*, 2013, **25**, 1058–1064.
14 T. Chen, R. Hao, H. Peng and L. Dai, *Angew. Chem., Int. Ed.*, 2014, **54**, 618–622.
15 Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie and C. Zhi, *Nat. Commun.*, 2015, **6**, 10310.
16 D. Qi, Z. Liu, Y. Liu, W. R. Leow, B. Zhu, H. Yang, J. Yu, W. Wang, H. Wang, S. Yin and X. Chen, *Adv. Mater.*, 2015, **27**, 5559–5566.
17 C. Choi, J. H. Kim, H. J. Sim, J. Di, R. H. Baughman and S. J. Kim, *Adv. Energy Mater.*, 2017, **7**, 1602021.
18 P. Huang, C. Lethien, S. Pinaud, K. Brousse, R. Laloo, V. Turq, M. Respaud, A. Demortière, B. Daffos, P. L. Taberna, B. Chaudret, Y. Gogotsi and P. Simon, *Science*, 2016, **351**, 691–695.
19 Z. Zhang, S. Liu, J. Xiao and S. Wang, *J. Mater. Chem. A*, 2016, **4**, 9691–9699.
20 N. A. Kyeremateng, T. Brousse and D. Pech, *Nat. Nanotechnol.*, 2017, **12**, 7–15.
21 A. S. Westover, B. Baer, B. H. Bello, H. Sun, L. Oakes, L. M. Bellanab and C. L. Pint, *J. Mater. Chem. A*, 2015, **3**, 20097–20102.
22 M. Zhu, Y. Huang, Y. Huang, H. Li, Z. Wang, Z. Pei, Q. Xue, H. Geng and C. Zhi, *Adv. Mater.*, 2017, **29**, 1605137.
23 D. Qi, Y. Liu, Z. Liu, L. Zhang and X. Chen, *Adv. Mater.*, 2016, **29**, 1602802.
24 Y. Wang, W. Lai, N. Wang, Z. Jiang, X. Wang, P. Zou, Z. Lin, H. J. Fan, F. Kang, C. P. Wong and C. Yang, *Energy Environ. Sci.*, 2017, **10**, 941–949.
25 M. Zhang, K. R. Atkinson and R. H. Baughman, *Science*, 2004, **306**, 1358–1361.
26 Y. Zhao, Y. Zhang, H. Sun, X. Dong, J. Cao, L. Wang, Y. Xu, J. Ren, Y. Hwang, I. H. Son, X. Huang, Y. Wang and H. Peng, *Angew. Chem., Int. Ed.*, 2016, **55**, 14384–14388.
27 L. Qu, L. Dai, M. Stone, Z. Xia and Z. L. Wang, *Science*, 2008, **322**, 238–242.
28 M. Xu, F. Du, S. Ganguli, A. Roy and L. Dai, *Nat. Commun.*, 2016, **7**, 13450–13457.
29 W. Wang, L. Xu, F. Liu, X. Li and L. Xing, *J. Mater. Chem. A*, 2013, **1**, 776–782.
30 S. He, P. Chen, L. Qiu, B. Wang, X. Sun, Y. Xu and H. Peng, *Angew. Chem., Int. Ed.*, 2015, **54**, 14880–14884.