A High-performance Flexible Pseudo-supercapacitor Constructed on Conductive Cloth

Yang Xu, Teng Wang, Cheng Yang, Ronghe Wang*
Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University, Xili University Town, Lishui Road, Nanshan District, Shenzhen City, Guangdong Province, China, 518055
Email: yang.cheng@sz.tsinghua.edu.cn

Abstract—**Cloth-like electronic devices are of great interest for the rapid development of wearable electronics. Herein we report a flexible and high-performance supercapacitor constructed on conductive cloth. In order to improve the electrochemical capacity, nickel nanocone arrays were electrodeposited onto a piece of conductive cloth (nickel plated polyester plain cloth) for the nickel current collector (NCC). The NCC@MnO_2 and NCC@polypyrrole were prepared as binder-free electrodes via a facile electro-deposition process for both cathode and anode. The NCC contributes to enhance electron transport/collection and makes it easy to release stress generated in the charge-discharge cycles of the active materials. Due to the design of highly ordered array electrode architecture, our NCC electrodes display excellent capacitive performance with high gravimetric and areal capacitances, excellent rate capability and outstanding cycling stability. Furthermore, the as-obtained pseudo-supercapacitor shows unique mechanical property of flexibility due to the presence of conductive cloth. The present study provides an alternative strategy for the development of cost effective, flexible, and high-performance energy storage devices.**

Keywords—flexible supercapacitor; MnO_2; polypyrrole; nickel nanocone arrays

I. INTRODUCTION

With the development of wearable electronics, flexibility of the electrical components becomes a prerequisite, and thus flexible energy storage devices have been widely investigated over many years[1-3]. Batteries and supercapacitors are the two most investigated energy storage devices. Unlike batteries[4], supercapacitors show much higher power density[5-8]. Moreover, supercapacitors have advantages over the device design, which allows it break the limit of the traditional packaging technology and makes it possible to achieve flexibility of the devices[9, 10].

One of the key factors to attain flexible supercapacitors is the flexible conductive substrate, which can be consisted of active carbon cloth[11-14], graphene[15-17] and metal conductive cloth[18-20]. In our previous work[2], we prepared an ultrathin, flexible and laser-processed graphene coated polyethylene terephthalate film, which was assembled into micro-planar supercapacitor and showed outstanding flexibility and high capacity performance. Yeong Hwan Ko and Jae Su Yu et al. have created conductive textile fibers entrapped by hierarchical Ni–Co layered double hydroxide nanosheets to obtain a kind of novel cloth-like conductive metal substrate[18], which provided good adhesion between active materials and substrates. These works broadened the horizons of the research of flexible electrodes. However, challenges still remain in a facile process to prepare highly conductive substrates with good adhesion to electrode materials as powerful current collectors.

Herein we report a flexible and high-performance supercapacitor constructed on conductive cloth via a facile preparation process. The conductive cloth, which has been widely used in industry, was electrodeposited by nickel nanocone arrays (NCA) in a fabrication technology that we developed in previous works[21], marked as nickel conductive cloth (NCC), aiming to boost the adhesion of the active materials and the substrates. The NCC was then loaded with MnO_2 and polypyrrole (PPy) by electro-deposition (marked as NCC@MnO_2 and NCC@PPy respectively), which presented excellent performances, for instance, the specific capacitance was 201F/g for NCC@MnO_2 at a scan rate of 1 mV/s and 413.3F/g for NCC@PPy at a scan rate of 5mV/s. Moreover, the NCC electrodes exhibited excellent cycling stability with retentions of 99.84% after 4000 cycling test for NCC@MnO_2 and 87.1% after 5000 cycling test for NCC@PPy. The flexible supercapacitor was constructed by NCC@MnO_2 and NCC@PPy, and the cycle stability measurement of the device undergone with 4500 cycles was excellent with capacity retention of 166%. Combining the technologies of electrodeposition and packaging process, our technology of flexible device fabrications shows great prospects on scalable production.

II. EXPERIMENTAL SECTION

A. The preparation of NCCs

The NCCs were fabricated through an electro-deposition method. The synthetic method of NCA was reported in our previous work[22]. A piece of commercial nickel foam was employed as the anodic electrode and NCAs were deposited on purchased conductive cloth cathode. The conductive cloth and nickel foam were carefully cleaned in a mixed solution of acetone and ethanol by ultra-sonication for half an hour. The electro-deposition solution contained 200 g/L $NiCl_2 \cdot 6H_2O$, 100 g/L H_3BO_3 and 40 g/L NH_4Cl. The solution was stirred magnetically at a temperature of 60 °C. $NH_3 \cdot 6H_2O$ (10 wt%) was used to adjust the pH value of the electrolyte solution to be 4.0. The electro-deposition process was carried out at a current density of 10 mA/cm^2 for 10 min. After the deposition process, the samples were rinsed with deionized water and dried in 60°C oven. Then the NCCs were obtained.

B. The synthesis of NCC@MnO_2 and NCC@PPy

All chemicals were used as received without further purification. Electro-deposition of MnO2 was performed in a

978-1-5090-1396-8/16/$31.00

two-electrode configuration with NCC as the working electrode and a platinum sheet as the counter electrode. The preparation process was carried out at a constant current density of 10 mA/cm2 in an aqueous electrolyte solution containing 0.1 M manganese acetate. Deposition time varied from 30 s to 90 s, after which every sample was carefully washed by deionized water the dried for 3 h in 60℃ vacuum oven. The mass loading of MnO2 on the NCC was measured by a microbalance before and after the deposition of active materials.

The preparation of NCC@PPy was carried out by electro-polymerization in a two-electrode system with a constant potential of 1 V for 3 min, and the 100 mL aqueous electrolyte contained 1.8 g oxalic acid, 0.69 mL pyrrole monomer. The three-electrode cell was placed in an ice-bath tank. The mass loading of PPy on the NCC was measured by a microbalance before and after the deposition.

C. Characterizations

The morphologies of the as-prepared samples were analyzed by field emission scanning electron microscopy (FE-SEM, HITACH S4800, Japan). The electrochemical properties of the as-prepared samples were investigated by cyclic voltammetry (CV), galvanic charge/discharge (GCD) measurements on an electrochemical station (VMP3, BioLogic, France), and electrochemical impedance spectroscopy (EIS) with a CHI 760D electrochemical workstation (Chenhua, Shanghai). The electrochemical measurements were performed in a three-electrode system (active materials as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode as the reference electrode) with 0.5 M aqueous Na2SO4 as the electrolyte. The cycle life tests were performed by the GCD measurements. EIS was performed over a frequency range from 100 kHz to 0.01 Hz at amplitude of 5 mV.

D. Calculations

The specific (mass or areal) capacitance can be calculated from the CV and GCD curves according to the equations:

$$C = \frac{\int i(V)dV}{m \cdot v \cdot \Delta V} \quad (1)$$

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta U} \quad (2)$$

where C is the specific capacitance of the material, m is the mass loading of active materials on NCC electrode, v is the scan rate, ΔV is the potential window in the CV curves, i(V) is the voltammetry current, I is the applied current, ΔU is the potential window in the discharging process and Δt is the discharging time. The energy and power density (E and P) were calculated by the following equations:

$$E = \frac{\int IU(t)dt}{m} \quad (3)$$

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

Where I is the charging current, U is the voltage, dt is the time differential, t is the discharging time and m refers to the total mass of active materials of both positive and negative electrode.

III. RESULTS AND DISCUSSIONS

The morphologies of the samples are shown in Fig. 1. As we can see from Fig. 1a, the original conductive cloth, which uses nickel as the conductive layer, has many defects and disordered texture. After the electro-deposition of NCA, the NCAs were grown on the surface of the conductive cloth with regular morphology (Fig. 1b), which can modify the surface condition of the conductive cloth and improve the interfacial adhesion. Moreover, the NCC showed excellent flexibility, implying that the combination of NCA and conductive cloth is a feasible method to fabricate the flexible current collectors.

The morphologies of NCC@MnO_2 and NCC@PPy were shown in Fig. 1c-f. MnO_2 was covered on the NCC homogeneously after 1 min of electro-deposition. Porous structure could be found in Fig. 1d, which could increase the contact of the electrolyte and the materials. The NCC@PPy could also be seen in Fig. 1e and 1f, which demonstrated the uniformly growth of both PPy on NCC.

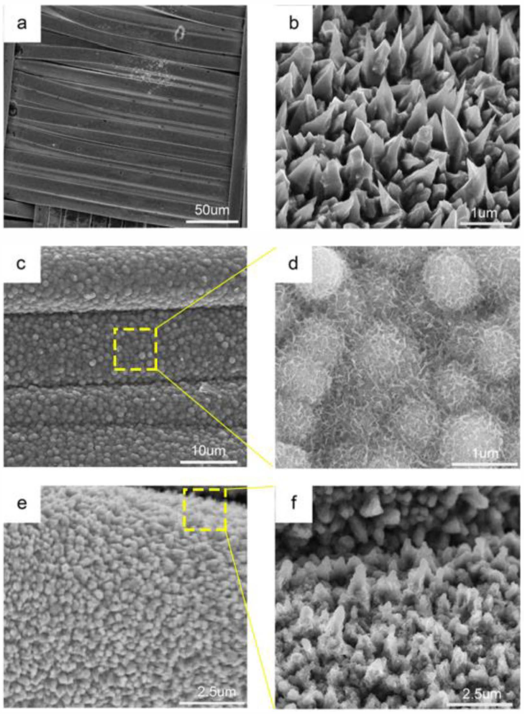

Fig. 1. (a) SEM image of the purchased conductive cloth; (b) SEM image of the NCC; (c and d) SEM images of the NCC@MnO_2 with a electro-deposition time of 1min; (e and d) SEM images of the NCC@PPy with a deposition time of 3min.

In the sample preparation experiments, the thickness of the MnO_2 layer was totally controlled by the time of electro-deposition. After electro-depositing MnO_2 for 75 s, the 6 cm^2 electrode was loaded with 1.77 mg (0.295 mg/cm^2), which was marked as Sample A. When controlling the time of electro-deposition to be 30 s, the mass loading was reduced to 0.8 mg (1.33 mg/cm^2), marked as Sample B. Several electrochemical measurements were carried out to investigate the NCC@MnO_2, and the results are shown in Fig. 2. The samples of NCC@MnO_2 were used as working electrodes in a three-electrode system with a potential window ranging from 0 V to 0.8 V. The CV curves of these two electrodes are shown in Fig. 2a. Sample A presented a perfect capacitance curve as compared with Sample B, which implies that the NCC can hold active materials reaching up to 1.77 mg and maintain the standard capacitance property. The capacity of Sample A was calculated to be 201 F/g at a scan rate of 1 mV/s, according to the equation 1. The CV curves of NCC@MnO_2 with the mass loading of 1.77 mg at different scan rates are shown in Fig. 2b, from which no evident polarization was found, and a quasi-rectangular shape was well retained from 1 mV/s to 100 mV/s, indicating excellent electrochemical capacitive characteristics. This was confirmed by the charge-discharge curves as shown in Fig. 2c, which exhibits nearly symmetrical feature, in which the IR drop of the NCC@MnO_2 was calculated as little as 0.018 V at a current density of 1 A/g, also demonstrating reversible Faradaic reaction between Na^+ and MnO_2. As shown in Fig. 2d, when the scan rate increased by 10 times (from 5 mV/s to 50 mV/s), the capacity was still remained as high as 60% (from 68 F/g to 41 F/g), indicating the good rate performance.

In addition, the cycling test and electrochemical impedance spectroscopy (EIS) measurement were carried out to make a further study of this system. The NNC@MnO_2 electrode exhibited excellent cycle stability as shown in Fig. 2e. The capacity retention was 99.84% after a 4000 cycling test, showing negligible change. According to the EIS analysis of NCC@MnO_2 electrode in Fig. 2f, which was fitted into an equivalent electrical circuit using the nonlinear least-squares method, the electrolyte resistance (R_e) and charge transfer resistance (R_{ct}) of NCC@MnO_2 were 2.472 and 122.4 Ω, respectively.

The excellent cycle stability results can be ascribed to the following reasons: First, the nickel nanocone array structure grown on the conductive cloth provides abundant contact sites for active materials and current collectors to enable the fast ion transport. Second, the flexible conductive cloth plays an important role in releasing the stress generated during the charge-discharge cycling test, which otherwise would be devastating to the structure of active material and lead to capacity loss.

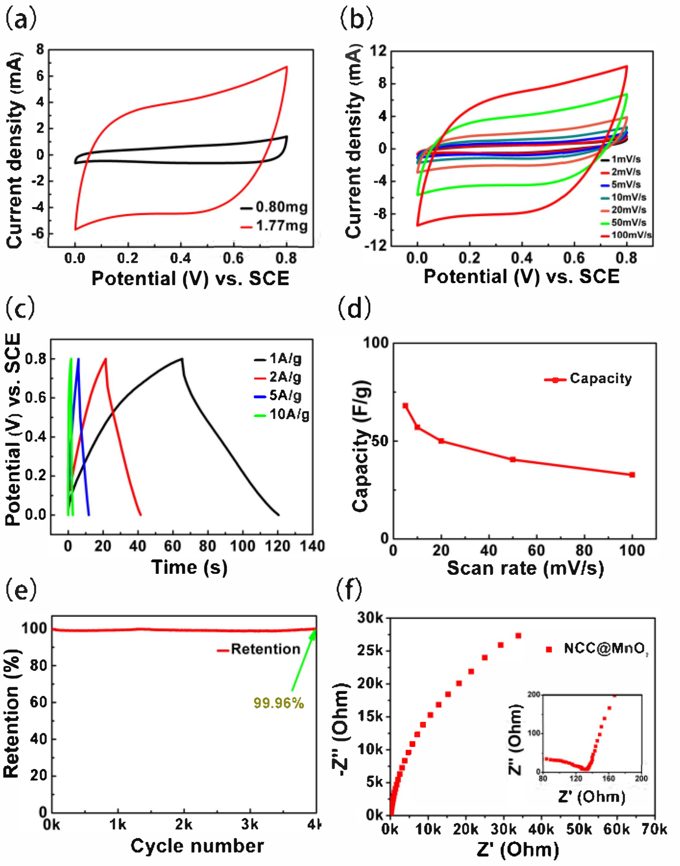

Fig. 2. (a) CV curves of NCC@MnO_2 with the mass loading of 0.80 mg and 1.77 mg at 50 mV/s; (b) CV curves of NCC@MnO_2 with the mass loading of 1.77 mg at different scan rates; (c) GCD curves of NCC@MnO_2 at different current densities; (d) the rate performance of NCC@MnO_2 with the mass loading of 1.77 mg at 5, 10, 20, 50, and 100 mV/s. (e) cyclic performance of NCC@MnO_2 at 5 A/g; (f) EIS plots of NCC@MnO_2 (inset: magnified plots in the high-frequency region)

To verify the excellent cycling performance of the NCC based electrode, a commonly used active material PPy was adopted[23]. CV and Galvanic charge–discharge tests were carried out and the results are shown in Fig. 3. The testing condition was same to that of NCC@MnO_2, and the potential window was ranged from 0 V to -0.8 V. The active material was weighted as 0.25 mg, with a deposition time of 2 min. The CV curves of NCC@PPy showed a little polarization in Fig. 3a, which was resulted from polymer shrinking and cracking at high scan rates. Meanwhile, the NCC@PPy exhibited an outstanding capacity performance of 413.3 F/g at 5 mV/s. A very little IR drop of 0.05 V can be found in Fig. 3b, implying the resistance of the system was small. The cycling test result of the NCC@PPy is shown in Fig. 3c, which exhibits capacity retention of 87.1% after 5000 cycles at 5A/g. Fast ion transport in this system can be seen in Fig. 3d according to the slope of the EIS curve, demonstrating the excellent stability of the NCC@PPy electrode.

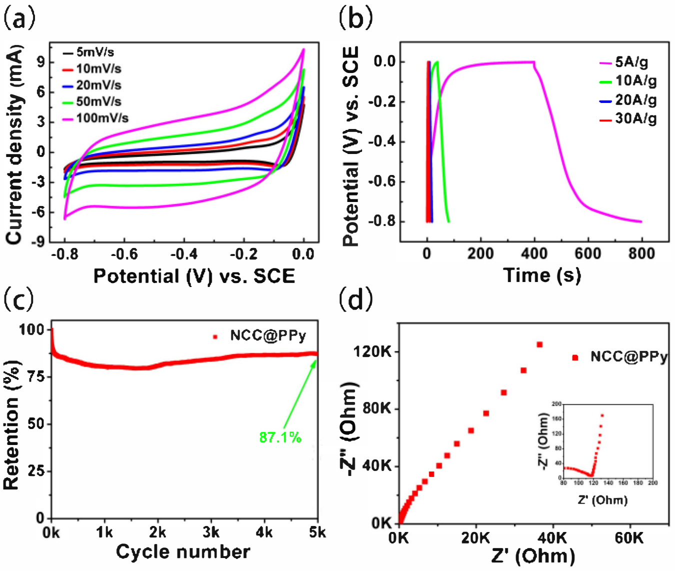

Fig. 3. (a) CV curves of the NCC@PPy electrode with the mass loading of 0.25 mg at different scan rates; (b) GCD curves of the NCC@PPy electrode at different current densities; (c) cyclic performance of NCC@PPy electrode at 5 A/g; (d) EIS plots of the NCC@PPy electrode (inset: magnified plots in the high-frequency region).

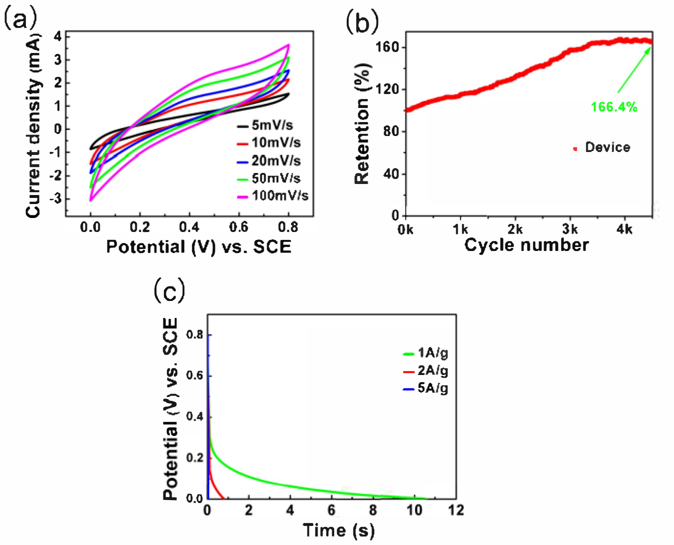

Fig. 4. (a) CV curves of the device with the total active materials mass loading of 0.8mg at different scan rates; (b) cyclic performance of the device at 5 A/g; (c) GCD curves of the device at different current densities.

To further demonstrate the application of the NCC electrodes, we assembled a flexible supercapacitor in an aqueous electrolyte (0.5 M Na_2SO_4), with NCC@MnO_2 as the positive electrode and NCC@PPy as the negative electrode. The as-obtained supercapacitor could excellently work in the potential range 0 V to 1.6 V with almost no polarization. Fig. 4a and 4c show the typical CV and GCD curves of the device, respectively. The cyclic curves keeps going up in Fig. 4b, which was resulted from the fact that the contact of active materials and electrolyte was improved during the charge and discharge process. Moreover, the overall capacitance retention was about 166% after 4500 cycles of charging and discharging at a current density of 5 A/g, indicating excellent cycling performance. To avoid polarization during the test, the device was set under an operating voltage of 0.8 V. Our supercapacitor achieved a maximum energy density of 28.8 Wh/kg at a power density of 8W/g, respectively (according to equation 3 and 4).

IV. CONCLUSIONS

In summary, we have developed a convenient fabrication technology of flexible and high-performance supercapacitor device which is constructed on conductive cloth. Taking advantages of both the flexible conductive cloth and nickel nanocone arrays, the NCC presented as a kind of powerful current collector which can well enhance the cyclic performance of the active materials grown on it. This electrode delivered excellent capacity (413 F/g for NCC@PPy at 5 A/g) and superior longevity (0.16% capacity loss after 4000 cycles for NCC@MnO_2 and 2.9% capacity loss after 5000 cycles for NCC@PPy). The supercapacitor based on the NCC demonstrated high energy density (28.8 Wh/kg at 8 W/g) and excellent cycling performance (166% capacitance retention after 4500 cycles). We believe that such a facile process would contribute to the further research of high-performance flexible supercapacitors and be instructive for the issue tackling in the application of the wearable electronics.

ACKNOWLEDGMENT

The authors thank National Key Basic Research Program of China (Project No. 2014CB932400), National Nature Science Foundation of China (Project No. 51578310), Guangdong Province Science and Technology Department (Project No. 2014B090915002 & 2014A010105002 & 2015A030306010), Shenzhen Government (Project No. JCYJ20150518162144944), and Nanshan District "Rising Stars" (Project No. KC2014JSQN0010A) for financial supports.

REFERENCES

[1] Y. Huang, H. Li , Z. Wang , M. Zhua, Z. Pei , C. Zhi and et al., "Nanostructured Polypyrrole as a flexible electrode material of supercapacitor," Nano Energy, vol. 22,pp. 422–438, April 2016.

[2] B. Xie, Y. Wang, W. Lai, W. Lin, Z. Lin, C. Yang and et al., "Laser-processed graphene based micro-supercapacitors for ultrathin, rollable, compact and designable energy storage components," Nano Energy, vol. 26, pp. 276–285, August 2016.

[3] S. Chou, J. Wang, S.n Chew, H. Liu, Shi-Xue Dou, "Electrodeposition of MnO2 nanowires on carbon nanotube paper as free-standing, flexible electrode for supercapacitors," Electrochemistry Communications, vol. 10, pp. 1724–1727, november 2008.

[4] Q. Xiao, Q. Zhang, Y. Fan, X. Wang and R. A. Susantyoko, “Soft silicon anodes for lithium ion batteries,” Energy Environ. Sci., vol. 7, p. 2261, May 2014.

[5] C. Xu, Z. Li, C. Yang, P. Zou, B. Xie, Z. Lin, and et al., “An Ultralong, Highly Oriented Nickel-Nanowire-Array Electrode Scaffold for High-Performance Compressible Pseudocapacitors,” Adv. Mater., vol. 28, pp.4105-10, June 2016.

[6] A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. Van Schalkwijk, "Nanostructured materials for advanced energy conversion and storage devices," Nature materials, vol. 4, pp. 366-377, May 2005.

[7] Y. Li , K. Sheng , W. Yuan and G. Shi, “A high-performance flexible fibre-shaped electrochemical capacitor based on electrochemically reduced graphene oxide,” Chemical Communications, vol. 49, pp. 291-293, November 2013.

[8] Y. Tao, X. Xie, W. Lv, D. M. Tang, D. Kong, Z. Huang, et al., “Towards ultrahigh volumetric capacitance: graphene derived highly dense but porous carbons for supercapacitors,” Scientific reports, vol. 3, p.2975, October 2013.

[9] Z. Yu , L. Tetard , L. Zhai and J. Thomas, “Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions,” Energy Environ. Sci, vol. 8, p. 702, December 2015.

[10] S. Shi, C. Xu, C. Yang, Y. Chen, J. Liu and F. Kang, “Flexible asymmetric supercapacitors based on ultrathin two-dimensional nanosheets with outstanding electrochemical performance and aesthetic property,” Scientific Reports, vol. 3, p. 2598, September 2013.

[11] D. Ye, Y. Yu, J. Tang, L. Liu and Y.Wu, “Electrochemical activation of carbon cloth in aqueous inorganic salt solution for superior capacitive performance,” Nanoscale, vol. 8, pp.10406-10414, April 2016.

[12] T. Zhang, C. H. J. Kim, Y. Cheng, Y. Ma, H. Zhang and J. Liu, “Making a commercial carbon fiber cloth having comparable capacitances to carbon nanotubes and graphene in supercapacitors through a”top-down” approach,” nanoscale, vol. 7, p. 3285, January 2015.

[13] Y. Horng, Y. Lu, Y. Hsu, C. Chen, L. Chen and K. Chen, “Flexible supercapacitor based on polyaniline nanowires/carbon cloth with both high gravimetric and area-normalized capacitance,” Journal of Power Sources, vol. 195, pp. 4418–4422, July 2010.

[14] J. Torop, V. Palmre, M. Arulepp, T. Sugino, K. Asaka and A. Aabloo, “Flexible supercapacitor-like actuator with carbide-derivedcarbon electrodes,” carbon, vol. 49, pp.3113–3119, August 2011.

[15] Y. Huang, H. Hu, Y. Huang, M. Zhu, W. Meng, C. Liu and et al., “From Industrially Weavable and Knittable Highly Conductive Yarns to Large Wearable Energy Storage Textiles,” ACS nano, vol. 9, pp. 4766–4775, May 2015.

[16] H. Tang, C. Yang, Z. Lin, Q. Yang, F. Kang and C. P. Wong, “Electrospray-deposition of graphene electrodes: a simple technique to build high-performance supercapacitors,” Nanoscale, vol. 7, p. 9133, April 2015.

[17] M. Xiao, T. Kong, W. Wang, Q. Song, D. Zhang, Q. Ma and et al., “Interconnected Graphene Networks with Uniform Geometry for Flexible Conductors,” Adv. Funct. Mater. , vol. 25, pp. 6165–6172, September 2015.

[18] G. Nagaraju, G. S. R. Raju, Y. H. Ko and J. S. Yu, “Hierarchical Ni–Co layered double hydroxide nanosheets entrapped on conductive textile fibers: a cost-effective and flexible electrode for high-performance pseudocapacitors,” Nanoscale, vol. 8, p. 812, October 2016.

[19] Z. Su, C. Yang, C. Xu, H. Wu, Z. Zhang, T. Liu and et al, “Co-electro-deposition of the MnO2–PEDOT:PSS nanostructured composite for high areal mass, flexible asymmetric supercapacitor devices,” J. Mater. Chem. A, vol. 1, August 2013.

[20] X. Y. Liu, Y. Q. Gao and G.W. Yang, “A flexible, transparent and super-long-life supercapacitor based on ultrafine Co3O4 nanocrystal electrodes,” Nanoscale, vol. 8, p. 4227, January 2016.

[21] Z. Su, C. Yang, B. Xie, Z. Lin, Z. Zhang, J. Liu and et al., “Scalable Fabrication of MnO2 Nanostructure Deposited on Free-standing Ni Nanocone Arrays for Ultrathin, Flexible, High-performance Micro-supercapacitor,” Energy Environ. Sci., vol. 7, pp. 2652-2659, May 2014.

[22] Y. Huang, H. Li, Z. Wang, M. Zhu, Z. Pei, Q. Xue and et al., “Nanostructured Polypyrrole as a flexible electrode material of supercapacitor,” Nano Energy, vol. 22, pp. 422－438, April 2016.