[Article]

doi: 10.3866/PKU.WHXB201602222

www.whxb.pku.edu.cn

柔性复合织物电极 Graphene/Cotton 和 MnO₂/Graphene/Cotton 的合成及在电化学电容器中的应用

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摘要: 通过热还原法成功地制备出了柔性复合织物电极石墨烯/棉布(graphene/cotton)。热还原条件对电极的导电性能具有较大的影响。导电柔性织物电极 graphene/cotton 特有的多级结构使其既有利于进一步负载赝电容材料, 又有利于电子和电解质离子的传输与扩散。通过电化学沉积方法, 利用导电柔性织物电极 graphene/cotton 进一步制备出了电极 MnO₂/graphene/cotton。利用扫描电子显微镜(SEM), 傅里叶变换红外(FTIR)光谱, 四探针测试法等表征技术对电极的结构进行了较为详细的表征。结果表明电极 MnO₂/graphene/cotton 的比电容可以达到 536 F·g⁻¹。良好的电化学性能和柔性使得此类电极在柔性储能材料应用中具有极大的应用前景。

关键词: 石墨烯; 棉布; 电化学电容器; 柔性电极; 织物

中图分类号: O646

Fabrication of Graphene/Cotton and MnO₂/Graphene/Cotton Composite Fabrics as Flexible Electrodes for Electrochemical Capacitors

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Abstract: Graphene/cotton composite fabrics for use as flexible electrodes were prepared using a thermal reduction method. The reducing condition significantly influenced the conductivity of the graphene/cotton fabrics. The conductive graphene/cotton fabrics with hierarchical structures used as flexible electrode substrates facilitate the loading of pseudocapacitor materials, enhancing electron transport and electrolyte ion diffusion. The electrode structure was characterized in detail using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and the standard four-point probe method. After further electrochemical deposition of MnO₂ sheets on the composite fabrics, the resulting MnO₂/graphene/cotton composite fabrics for use as electrode materials had excellent electrochemical performance and great flexibility. The specific capacitance reached 536 F·g⁻¹ at a scan rate of 5 mV·s⁻¹. The electrochemical test results indicate that it can be further used for flexible energy storage materials.

Key Words: Graphene; Cotton; Electrochemical capacitor; Flexible electrode; Textile

1 Introduction

Multifunctional and environmentally-friendly energy-storage

materials and devices have attracted tremendous attention due to the increasing demand for sustainable energy¹⁻³. Among various

Received: November 16, 2015; Revised: February 15, 2016; Published on Web: February 22, 2016.

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The project was supported by the National Natural Science Foundation of China (51402048), Fundamental Research Funds for the Central Universities, China, DHU Distinguished Young Professor Program, and Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of China.

国家自然科学基金(51402048), 中央高校基本科研业务费和东华大学励志计划及教育部留学回国人员科研启动资金资助项目

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energy storage systems, electrochemical capacitors have drawn considerable attention during recent years due to their special properties, including high power density, safe operation, fast charge-discharge characteristics, grate cycle stability and long cycling lifetime^{4–10}. Electrochemical capacitors have already showed high potentials in memory backup systems, portable consumer electronic products, hybrid electric vehicles, and industrial scale power and energy management^{11–14}.

Recently, flexible and wearable electronic devices have aroused general concern^{10,15,16}. Achieving a rapid development of flexible and wearable electronics requires the electrochemical capacitors and electrode materials to possess the merits including high cycle stability, low cost, light weight, good flexibility, fast ion adsorption, and surface redox reactions^{6,7,10,17}. Textile-based electrode materials are one of the most promising flexible electrode materials for energy storage due to their hierarchical structure, low cost, easy cutting, and excellent flexibility. However, the practical application of textile-based electrode materials is always hindered due to the insulated nature of textiles and poor electrochemical performance.

Coating textiles with various carbon materials is one of the most efficient strategies for enhancing the conductivity and electrochemical performance^{1,10,18–20}. Jost *et al.*¹⁸ reported a flexible and light-weight fabric as electrode materials using a traditional printmaking technique by impregnating porous carbon materials into woven cotton and polyester fabrics. Hu *et al.*¹⁹ reported a "SWNT ink" method to prepare CNT-enabled conductive textiles, which were further used as a electrode substrates for the loading metal oxides. Bian *et al.*¹⁰ prepared conductive graphene/cotton composite fabrics as flexible electrode materials using a "dipping and drying" process followed by the NaBH_4 reduction method. Shateri-Khalilabad and Yazdanshenas²¹ used a dip-pad-dry method followed by reduction with ascorbic acid to prepare a conductive graphene-coated cotton fabric with a sheet resistance of $91.8 \text{ k}\Omega \cdot \square^{-1}$. As mentioned above, most current methods for carbon coating involve the use of organic surfactant, binder, toxic reagent, and complex process, which inevitably influence the practical production of flexible textile-based electrode materials. Moreover the low specific capacitance of carbon/cotton composite fabrics generated by the electrochemical double-layer mechanism is incapable of meeting the requirements for the future development of flexible and wearable electronic devices.

Metal oxides with high theoretical capacitance are one kind of pseudocapacitor materials. However, the poor conductivity of metal oxides is the main obstacle preventing their further application^{22,23}. Further incorporating pseudocapacitor materials in conductive textile-based electrode materials is a promising strategy for enhancing electrochemical performance²⁴. The conductive composite fabrics coated with carbon materials as electrode substrates facilitate the electron transport, electrolyte ion diffuse and enhancing the conductivity of metal oxides. These structure features will endow the textile-based electrode materials with excellent electrochemical performance.

In this work, flexible and conductive graphene/cotton com-

posite fabrics were synthesized using a thermal reduction method. The organic surfactant, binder and toxic reagent are uninvolved in this synthesis method. After further electrochemical deposition of MnO_2 pseudocapacitor material on the graphene/cotton composite fabrics, the obtained MnO_2 /graphene/cotton electrode material showed a high specific capacitance of $536 \text{ F} \cdot \text{g}^{-1}$ at a scan rate of $5 \text{ mV} \cdot \text{s}^{-1}$, which is higher than bare graphene/cotton composite fabrics. It shows that the composite fabrics are highly desirable for preparing flexible electrochemical capacitors.

2 Experimental

2.1 Materials

Graphite was purchased from Alfa Aear China Co., Ltd. $\text{K}_2\text{S}_2\text{O}_8$, P_2O_5 , H_2O_2 , $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and NaOH were provided by Sinopharm Chemical Reagent Co., Ltd. KMnO_4 was purchased from Lingfeng Chemical Reagent Co., Ltd. HCl and H_2SO_4 were obtained from Pinghu Chemical Reagent Co., Ltd. All chemical reagents were analytical grade (AR) and directly used without further purification.

2.2 Preparation of graphene oxide sheets

Graphene oxide (GO) sheets were prepared and purified according to the modified Hummer's method^{3,10}. In a typical preparation, 1.5 g of graphite powder was added into an aqueous solution containing 10 mL of 98% H_2SO_4 , 1.25 g of $\text{K}_2\text{S}_2\text{O}_8$, and 1.25 g of P_2O_5 . Then the solution was maintained at 80°C for 4.5 h. The resulting preoxidized product was cleaned using double-distilled water and dried in a vacuum oven at 50°C . After it was mixed with 60 mL of 98% H_2SO_4 and 7.5 g of KMnO_4 at a temperature below 20°C , then 125 mL of double-distilled water was slowly added. After 2 h, 200 mL of double-distilled water and 10 mL of 30% H_2O_2 were slowly added into the solution to completely react with the excess KMnO_4 . The appearance of a bright yellow solution was observed after 10 min. The resulting mixture was washed with diluted HCl aqueous (1/10 (V/V)) solution and double-distilled water. GO sheets were obtained after drying in a vacuum oven at 40°C .

2.3 Preparation of GO/cotton composite fabrics

GO suspension with a concentration of $2 \text{ mg} \cdot \text{mL}^{-1}$ was prepared by dispersing GO sheets in double-distilled water under sonication for 30 min.¹⁰

The commercial cotton fabrics were cleaned by immersing in a boiled $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution for 1 h, washed thoroughly with double-distilled water, and dried at 120°C in an oven. Then the cotton fabrics were dipped in GO suspension, soaked for 30 min at room temperature and dried in a vacuum oven at 50°C for 2 h. Because of the strong adsorption, the cotton fabrics were quickly coated by GO sheets. The coating process was repeated twenty times for increasing the GO loading.

2.4 Preparation of graphene/cotton composite fabrics

The GO/cotton composite fabrics were reduced in a tube furnace at 300°C with a heating rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ for different time intervals under N_2 flow. GO sheets coated on the cotton fabrics

were successfully converted to graphene sheets.

2.5 Preparation of MnO₂/graphene/cotton composite fabrics

MnO₂/graphene/cotton composite fabrics were prepared in an aqueous solution consisting of 1.0 mol·L⁻¹ Na₂SO₄ and 0.1 mol·L⁻¹ Mn(CH₃COO)₂·4H₂O. The electrochemical deposition of MnO₂ sheets was carried out by a three electrode configuration at a constant current density of 0.5 mA·cm⁻² for 40 min. The corresponding potential was ca 0.7 V during the electrochemical deposition process. After deposition, the MnO₂/graphene/cotton composite fabrics was washed with double-distilled water and ethanol, and then dried at 60 °C in vacuum oven for 2 h.

2.6 Materials characterization

The microscopic features of the samples were characterized by SEM (Hitachi S-4800 and JEOL JSM-5600LV, Japan). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Fisher Nicolet 6700 spectrometer. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer with Al K_α (1486.6 eV) as the X-ray source. The MnO₂ loading was determined by prodigy inductively coupled plasma (ICP)-OES. The sheet resistance of the composite fabrics was measured by using a standard four-point probe method (RTS-9, 4 Probes Tech, China).

2.7 Electrochemical test

Electrochemical test experiments were carried out using a three-electrode system, in which platinum wire and saturated calomel electrode were used as the counter and reference electrodes in an electrolyte solution of 1.0 mol·L⁻¹ Na₂SO₄, respectively. The electrochemical properties of the composite fabrics were evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) using a CHI 600E electrochemical analyzer and a CHI 660E electrochemical workstation at room temperature, respectively. The specific capacitance was calculated from the CV and GCD curves based on the following equations (1) and (2), respectively¹⁰:

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

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

where, I is the constant discharging current (A·g⁻¹); m is the mass of active materials (g); v is the scan rate (mV·s⁻¹); ΔV is the potential window during the discharge process after IR drop (V); Δt is the discharge time.

3 Results and discussion

The schematic representation of the preparation of conductive graphene/cotton composite and fabrics MnO₂/graphene/cotton composite fabrics was shown in Scheme 1. The cotton fabrics were immersed in GO suspension. GO sheets were absorbed on the cotton fabrics through electrostatic interaction, van der Waals force, and hydrogen bond between oxygen-containing functional groups on cotton fabrics and GO sheets¹⁰. Then the GO sheets on the cotton fabrics were converted to graphene sheets *via* a thermal

Scheme 1 Schematic representation of the preparation of conductive graphene/cotton and MnO₂/graphene/cotton composite fabrics

reduction process N₂ atmosphere, resulting in the formation of conductive graphene/cotton composite fabrics. Finally, the MnO₂/graphene/cotton composite fabrics were obtained after the electrochemical deposition of MnO₂ nanosheets on graphene/cotton composite fabrics.

Fig.1a shows a typical optical image of white cotton fabrics. When immersing the white cotton fabrics in GO suspension and drying in a vacuum oven, the colour of cotton fabrics changed from white to brown (see Fig.1b), indicating that GO sheets can be firmly absorbed on the cotton fabrics. The loading of GO was determined to be around 9.3% (w, mass fraction) after 20 dipping and drying cycles. After thermal reduction at 300 °C in N₂, the colour of GO/cotton composite fabrics further changed from brown to black (see Fig.1(b, c)), indicating that GO sheets on cotton fabrics were successfully converted to graphene sheets. As shown in Fig.1d, the graphene/cotton composite fabrics can be bended to arbitrary angle, showing good flexibility.

Compared to the insulated GO/cotton composite fabrics, converting GO sheets on cotton fabrics to graphene sheets using a thermal reduction method makes the composite fabrics conductive¹⁰. Fig.2a shows the effect of heating temperature on the sheet resistance of graphene/cotton composite fabrics prepared in N₂. When heating at 200 °C for 1 h, the sheet resistances was mea-

Fig.1 Typical optical images of (a) cotton fabrics, (b) GO/cotton composite fabrics, and (c, d) graphene/cotton composite fabrics

Fig.2 Effects of (a) heating temperature and (b) heating time on the sheet resistances of graphene/cotton composite fabrics

sured to be around $30 \text{ k}\Omega \cdot \square^{-1}$. The sheet resistances of the composite fabrics significantly decreased with increasing the heating temperature to 250°C . When further increasing the heating temperature above 300°C , the sheet resistances slightly decreased and tended to be stable. The lowest sheet resistance was measured to be around $3 \text{ k}\Omega \cdot \square^{-1}$ at 350°C , which is similar to some reported results²⁰. It indicates increasing the heating temperature can effectively remove the oxygen-containing functional groups of GO sheets on the cotton fabrics. In a control experiment, bare cotton fabrics heated at 300°C in N_2 were still insulated, indicating the enhanced conductivity due to graphene coating layers²⁵. Fig.2b shows the effect of heating time on the sheet resistance of graphene/cotton composite fabrics at 300°C . The sheet resistances significantly decreased with increasing the heating time from 10 to 30 min. However, further increasing heating time resulted in increasing the sheet resistance. It may due to the material structure change of three dimensional conductive network constructed by graphene sheets on cotton fabrics (see Fig.3).

SEM was used to explore the material structure change of graphene/cotton composite fabrics during the thermal reduction in N_2 . As shown in Fig.3(a–c), graphene/cotton composite fabrics show a hierarchical network structure. GO sheets on the cotton fabrics were converted to graphene sheets, which wrapped around the cotton fibers tightly. After increasing the heating time to 30 min (Fig.3(d–f)), the material structure and morphology of graphene/cotton composite fabrics were almost unchanged. Long heating time facilitates completely removing the oxygen-containing functional groups of GO sheets, resulting in lower sheet resistance (see Fig.2). However, the material structure and morphology of graphene/cotton composite fabrics were changed when further increasing the heating time above 30 min. As shown in Fig.3(g–i), the broken graphene/cotton composite fibers were clearly observed when the heating time was above 30 min. It indicates that heating time applied for too long resulted in significantly breaking the three-dimensional conductive network constructed by the graphene sheets and cotton fabrics, and resulting in high sheet resistance.

FTIR analysis was carried out for further investigating the chemical structure changes of GO/cotton composite fabrics during the thermal reduction reaction in N_2 . As shown in Fig.4, GO/cotton

composite fabrics show some peaks at around 3340, 2900, 1650, 1427, and 1050 cm^{-1} , which are attributed to the OH stretching, CH stretching, OH of water absorbed from cellulose, CH_2 symmetric bending, and C–O stretching, respectively. The presence of N_2 resulted in appearing two new peaks at around 1700 and 1580 cm^{-1} , which are attributed to C–C and C=C skeletal vibrations of graphene sheets²⁶. The intensity of these two peaks increased when increasing the heating time, indicating long heating time facilitates completely removing oxygen-containing functional groups on GO sheets. Meanwhile, the cotton fabrics were partially carbonized with increasing heating time, resulting in further increasing the intensity of these two peaks at around 1710 and 1580 cm^{-1} . The peaks at around 3340, 2900, 1427, and 1050 cm^{-1} almost completely disappeared, indicating the removal of oxygen-containing groups on GO sheets²⁶.

XPS was used to characterize the oxygen-containing functional groups on GO and graphene sheets coated on the cotton fabrics²⁷. Fig.5(a, b) shows the survey spectra of GO/cotton composite fabrics and graphene/cotton composites, revealing the presence of C and O. Fig.5c shows the C 1s peak, which consists of two main components arising from C–O (hydroxyl and epoxy, $\sim 286.5 \text{ eV}$) and C=O (carbonyl, $\sim 288.3 \text{ eV}$) groups and two minor components from C=C/C–C (carboxyl, $\sim 290.3 \text{ eV}$) groups^{27–29}. A considerable degree of oxidation was predominant in the XPS spectrum of GO sheets on the cotton fabrics, largely attributed from the C–O bonding. After heating in N_2 , the hydroxyl and epoxy groups, which are the majority of oxygen-containing groups in GO/cotton composite fabrics, were nearly removed and the C=C bonds became dominant, as shown by the strong single peak with a small tail in higher binding energy region in Fig.5d. The C/O ratio of graphene/cotton composites was determined to be 6.4, which is higher than that of GO/cotton composite fabrics (2.2), further indicating that GO sheets on the cotton fabrics could be successfully converted to graphene sheets.

As mentioned above, graphene sheets on cotton fabrics acted as active materials for storing energy based on the electrochemical double-layer mechanism always show poor electrochemical performance, which is unable to meet the requirement of practical applications. For enhancing the electrochemical performance, graphene/cotton composite fabrics prepared at 300°C for 30 min

Fig.3 SEM images of graphene/cotton composite fabrics prepared in different gas atmosphere with different heating time
(a, b, c) 10 min, (d, e, f) 30 min, (g, h, i) 300 min

as an electrode substrate was further used to load pseudocapacitor materials. The conductive substrate with hierarchical structure can improve the conductivity and increase the active surface area of MnO₂, ensuring a high electrochemical performance. Fig.6a shows

Fig.4 FTIR spectra of GO/cotton composite fabrics heated in N₂ at 300 °C with different heating time

the hierarchical structure of MnO₂/graphene/cotton composite fabrics, which is similar to cotton fabrics and graphene/cotton composite fabrics. As shown in Fig.6(b, c), the high magnification SEM images clearly exhibit that a layer of MnO₂ nanosheets was evenly deposited on the outer surface of fibres in MnO₂/graphene/cotton composite fabrics. The MnO₂ sheets with a thickness in nanometer scale interested with each other resulting in an open and 3D porous structure. The MnO₂ loading was determined to be 0.172 mg · cm⁻². The porous structure constructed by MnO₂ nanosheets facilitates the diffusion and transportation of the electrolyte ion, resulting in high electrochemical performance.

Fig.7a shows the CV curves of graphene/cotton composite fabrics and MnO₂/graphene/cotton composite fabrics with different electrochemical deposition times at a scan rate of 5 mV · s⁻¹. The CV curves of MnO₂/graphene/cotton composite fabrics exhibits a nearly rectangular shape^{9,30}. The CV area of MnO₂/graphene/cotton composite fabrics is much larger than graphene/cotton composite fabrics, indicating that the deposition of MnO₂ greatly enhanced the specific capacitance. For MnO₂/graphene/cotton composite

Fig.5 XPS survey spectra and C 1s spectra of (a, c) GO/cotton composite fabrics and (b, d) graphene/cotton composite fabrics

Fig.6 SEM images of MnO₂/graphene/cotton composite fabrics prepared with an electrochemical deposition time of 30 min

fabrics, the CV curves increased with increasing the electrochemical deposition time from 0 to 30 min, and then slightly decreased. The electrochemical deposition time of 30 min resulted in the largest CV curve. The CV area of MnO₂/graphene/cotton composite fabrics is much larger than graphene/cotton composite fabrics, indicating that the incorporating MnO₂ greatly enhanced the specific capacitance. Fig.7b shows the CV curves of MnO₂/graphene/cotton composite fabrics at various scan rates. As shown in Fig.7c, the specific capacitance of MnO₂/graphene/cotton composite fabrics was calculated at various scan rates. The specific capacitance decreased with increasing the scan rate. The maximum specific capacitance was measured to be 536 F·g⁻¹. As shown in Fig.7d, the GCD curves of MnO₂/graphene/cotton composite fabrics are approximately triangular at various current densities, indicating an ideal capacitive performance. In order to

evaluate the effect of mechanical bending on the electrode, MnO₂/graphene/cotton composite fabrics were bent from 0° to 180°, and back to the initial state. Fig.7(e, f) show that the CV curves and capacitance retention of MnO₂/graphene/cotton composite fabrics were almost unchanged during 100 times of bending at a scan rate of 5 mV·s⁻¹. It suggests that the connection between MnO₂ sheets and graphene/cotton composite fabrics is stable, indicating that the obtained MnO₂/graphene/cotton composite fabrics have good flexibility. The cycling stability of MnO₂/graphene/cotton composite fabrics was evaluated at a current density of 1 mA·cm⁻². Less than 10% loss of the specific capacitance after 1000 cycles of galvanostatic charge-discharge was observed (see Fig.7g). Fig.7h shows the typical GCD curves for MnO₂/graphene/cotton composite fabrics after 500 cycles, revealing no significant electrochemical change during the long-term charging and discharging process

Fig.7 (a) CV curves of MnO₂/graphene/cotton composite fabrics as electrode materials with different electrochemical deposition of times; (b) CV curves, (c) specific capacitance, and (d) GCD curves of MnO₂/graphene/cotton composite fabrics; (e) CV curves and (f) capacitance retention of MnO₂/graphene/cotton composite fabrics with various bending times; (g) capacitance retention and (h) typical GCD curves of MnO₂/graphene/cotton composite fabrics during the cycling test

after cycling 1000 times, indicating excellent cycling stability.

4 Conclusions

In summary, graphene/cotton composite fabrics were successfully prepared using a thermal reduction method. The graphene sheets firmly absorbed on the cotton fabrics significantly greatly improve the conductivity of the composite fabrics. After electrochemical deposition of MnO₂ on the composite fabrics, the obtained MnO₂/graphene/cotton composite fabrics with hierarchical structure, large surface area, and high conductivity showed an enhanced electrochemical performance and greatly flexibility. The specific capacitance reached 536 F·g⁻¹. It suggests that MnO₂/graphene/cotton composite fabrics are a promising electrode material for flexible energy storage materials.

References

- (1) Xue, J. L.; Zhao, Y.; Cheng, H. H.; Hu, C. G.; Hu, Y.; Meng, Y. N.; Shao, H. B.; Zhang, Z. P.; Qu, L. T. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8042. doi: 10.1039/c3cp51571k
- (2) Bian, S. W.; Zhu, L. *RSC Adv.* **2013**, *3*, 4212. doi: 10.1039/c3ra40333e
- (3) Xu, L. L.; Bian, S. W.; Song, K. L. *J. Mater. Sci.* **2014**, *49*, 6217. doi: 10.1007/s10853-014-8346-5
- (4) Jiang, H.; Lee, P. S.; Li, C. Z. *Energy Environ. Sci.* **2013**, *6*, 41. doi: 10.1039/c2ee23284g
- (5) Chen, J.; Sheng, K. X.; Luo, P. H.; Li, C.; Shi, G. Q. *Adv. Mater.* **2012**, *24*, 4569. doi: 10.1002/adma.201201978
- (6) Meng, C. Z.; Liu, C. H.; Chen, L. Z.; Hu, C. H.; Fan, S. S. *Nano Lett.* **2010**, *10*, 4025. doi: 10.1021/nl1019672
- (7) Pech, D.; Brunet, M.; Durou, H.; Huang, P. H.; Mochalin, V.; Gogotsi, Y.; Taberna, P. L.; Simon, P. *Nature Nanotech.* **2010**, *5*, 651. doi: 10.1038/nnano.2010.162
- (8) Lin, J.; Zhang, C. G.; Yan, Z.; Zhu, Y.; Peng, Z. W.; Hauge, R. H.; Natelson, D.; Tour, J. M. *Nano Lett.* **2013**, *13*, 72. doi: 10.1021/nl300000a001

- 10.1021/nl3034976
- (9) Bian, S. W.; Zhao, Y. P.; Xian, C. Y. *Mater. Lett.* **2013**, *111*, 75. doi: 10.1016/j.matlet.2013.08.028
- (10) Xu, L. L.; Guo, M. X.; Liu, S.; Bian, S. W. *RSC Adv.* **2015**, *5*, 25244. doi: 10.1039/c4ra16063k
- (11) Simon, P.; Gogotsi, Y.; Dunn, B. *Science* **2014**, *343*, 1210. doi: 10.1126/science.1249625
- (12) Simon, P.; Gogotsi, Y. *Nature Mater.* **2008**, *7*, 845. doi: 10.1038/nmat2297
- (13) Wang, Y. F.; Zuo, S. L. *Acta Phys. -Chim. Sin.* **2016**, *32*, 481. [王永芳, 左宋林. 物理化学学报, **2016**, *32*, 481.] doi: 10.3866/PKU.WHXB201511041
- (14) Su, P.; Guo, H. L.; Peng, S.; Ning, S. K. *Acta Phys. -Chim. Sin.* **2012**, *28*, 2745. [苏鹏, 郭慧林, 彭三, 宁生科. 物理化学学报, **2012**, *28*, 2745.] doi: 10.3866/PKU.WHXB201208221
- (15) Liang, G.; Zhu, L.; Xu, J.; Fang, D.; Bai, Z.; Xu, W. *Electrochim. Acta* **2013**, *103*, 9. doi: 10.1016/j.electacta.2013.04.065
- (16) Xin, C.; Ming, P.; Xiao, Y.; Yongping, F.; Dechun, Z. *J. Mater. Chem. C* **2013**, *2*, 1184. doi: 10.1039/c3tc31706d
- (17) Zhao, Y.; Hu, C. G.; Hu, Y.; Cheng, H. H.; Shi, G. Q.; Qu, L. T. *Angew. Chem. Int. Edit.* **2012**, *51*, 11371. doi: 10.1002/anie.201206554
- (18) Jost, K.; Perez, C. R.; McDonough, J. K.; Presser, V.; Heon, M.; Dion, G.; Gogotsi, Y. *Energy Environ. Sci.* **2011**, *4*, 5060. doi: 10.1039/c1ee02421c
- (19) Hu, L. B.; Chen, W.; Xie, X.; Liu, N. A.; Yang, Y.; Wu, H.; Yao, Y.; Pasta, M.; Alshareef, H. N.; Cui, Y. *ACS Nano* **2011**, *5*, 8904. doi: 10.1021/nn203085j
- (20) Lu, Z.; Mao, C.; Zhang, H. *J. Mater. Chem. C* **2015**, *3*, 4265. doi: 10.1039/c5tc00917k
- (21) Shateri-Khalilabad, M.; Yazdanshenas, M. *Cellulose* **2013**, *20*, 963. doi: 10.1007/s10570-013-9873-y
- (22) Sun, X.; Wang, H.; Lei, Z.; Liu, Z.; Wei, L. *RSC Adv.* **2014**, *4*, 30233. doi: 10.1039/c4ra03983a
- (23) Hassan, S.; Suzuki, M.; Mori, S.; El-Moneim, A. A. *RSC Adv.* **2014**, *4*, 20479. doi: 10.1039/c4ra01132e
- (24) Chen, W.; Rakhi, R. B.; Hu, L. B.; Xie, X.; Cui, Y.; Alshareef, H. N. *Nano Lett.* **2011**, *11*, 5165. doi: 10.1021/nl2023433
- (25) Li, C. C.; Yu, H.; Yan, Q.; Hng, H. H. *J. Power Sources* **2015**, *274*, 310. doi: 10.1016/j.jpowsour.2014.10.056
- (26) Hongtao, L.; Lei, Z.; Yunlong, G.; Cheng, C.; Lianjiang, Y.; Lang, J.; Gui, Y.; Wenping, H.; Yungi, L.; Daoben, Z. *J. Mater. Chem. C* **2013**, *1*, 3104. doi: 10.1039/c3tc00067b
- (27) Pei, S. F.; Zhao, J. P.; Du, J. H.; Ren, W. C.; Cheng, H. M. *Carbon* **2010**, *48*, 4466. doi: 10.1016/j.carbon.2010.08.006
- (28) Szabo, T.; Berkesi, O.; Forgo, P.; Josepovits, K.; Sanakis, Y.; Petridis, D.; Dekany, I. *Chem. Mater.* **2006**, *18*, 2740. doi: 10.1021/cm060258
- (29) Shin, H. J.; Kim, K. K.; Benayad, A.; Yoon, S. M.; Park, H. K.; Jung, I. S.; Jin, M. H.; Jeong, H. K.; Kim, J. M.; Choi, J. Y.; Lee, Y. H. *Adv. Funct. Mater.* **2009**, *19*, 1987. doi: 10.1002/adfm.200900167
- (30) Zhu, J.; Tang, S.; Xie, H.; Dai, Y.; Meng, X. *ACS Appl. Mater. Interfaces* **2014**, *6*, 17637. doi: 10.1021/am505622c