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Wire-shaped Flexible Asymmetric Supercapacitor based on

Carbon Fiber coated with Metal oxide & Polymer

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Abstract

Due to the high capacitance of the redox character of MnO_2 -PPy-carbon fiber composite and the V₂O₅-PANI-carbon fiber composite, a flexible wire-shaped fiber asymmetric supercapacitor (WFASC) was fabricated using these materials as the positive and negative electrodes, respectively. Especially, the large work function difference between MnO₂ and V₂O₅ help the device to exhibit a wide potential window of 2.0 V and a high areal capacitance of 0.613 F cm⁻². As a result, the WFASC showed a maximum energy density of 0.340 mWh cm⁻² at a power density of 1.5 mW cm⁻² and a maximum power density of 30 mW cm⁻² at an energy density of 0.294 mWh cm⁻². Furthermore, the device exhibited a perfect stability after 5000 cycles at a current density of 30 mA cm⁻², meanwhile, it could withstand the bending test and drive a LED under bending states. All of the above results prove the potential application of the WFASC device.

Introduction

Recently, wire-shaped fiber (WF) devices have been developed and applied in the field of optoelectronic device. As a new concept of device, they can improve the mechanical flexibility and provide a breakthrough in wearable devices. WF electronic devices also show perfect bending properties which could meet the requirements of wearable electronic devices and can be woven into any shape and placed anywhere, which open up a path for design innovation. Owing to these superiorities, WF electronic devices have attracted people's attention, and several kinds of WF electronic devices have been designed including WF logic circuits,¹ WF display,² and WF nanogenerators.³

The development of WF electronic devices has inspired people to find efficient, lightweight, highly flexible and wearable energy storage devices such as WF lithium ion batteries,⁴⁻⁶ WF solar cells,⁷⁻⁹ and WF supercapacitors (WFSCs).¹⁰⁻¹² Among them, WFSCs have an advantage of high power density, long cycling life and easy operation,

so WFSCs have become a kind of promising energy storage devices. For example, Wang, *et al.* first reported WFSCs made from ZnO nanowires.¹³ Peng, *et al.* designed WFSCs by twisting two aligned MWCNT fibers.¹⁴ Shen, *et al.* fabricated WFSCs based on Mn₂O₃ cube-arrays/carbon wire.¹⁵ Fan, *et al.* developed successfully using graphene/MnO₂ composite as positive electrode and activated carbon nanofibers (ACN) as negative electrode.¹⁶ However, all of the above WFSCs are either symmetric supercapacitor or asymmetric supercapacitor with the negative electrode

made by activated carbon. According to the equation: $E = 0.5 \times C \times V^2$, the increase

of energy (E) can be achieved by maximizing the specific capacitance (C) and the operation potential (V). Symmetric supercapacitors usually suffer from narrow operation potential window of less than 1 V in water electrolyte. Generally, asymmetric supercapacitors can make full use of two different electrodes to exhibit two different potential windows in the same electrolyte. As a result, working voltage window can be increased and thus the energy density of the device could be improved significantly. Because the work function of the electrode material is directly related to electrochemical oxidation/reduction potential, the operation voltage can be increased simply by choosing the large work function difference of metal oxides for asymmetric supercapacitor.¹⁷ Then the energy density of the supercapacitor could be improved ultimately in turn. So to develop a novel WFSCs, it is better that the two electrodes are composed of two kind of metal oxide with large work function difference.

Herein, we present a novel WFASCs using MnO₂-PPy-carbon fiber and V₂O₅-PANIcarbon fiber materials which have a large work function difference as the positive and negative electrodes, respectively. As known, MnO₂ is a relatively inexpensive,¹⁸ natural abundance and environmentally friendly electrode material with high theoretical capacitance,¹⁹ which is very suitable for fabricating supercapacitor,²⁰ but shows poor electrical conductivity. To improve the conductivity of MnO₂, many good conductive materials such as grapheme,²¹ metal nanostructures,²² carbon nanotubes ²³⁻²⁷ and conductive organic matter ²⁸ have been composited with MnO₂. In our work, we chose polypyrrole (PPy) as the conductive material wrapped on MnO₂, which can enhance the conductivity of MnO₂ and prevent the MnO₂ from erosion. Among various transition-metal oxides, V2O5 arising from its various vanadium oxidation states (V²⁺, V³⁺, V⁴⁺, and V⁵⁺) ²⁹ possesses the advantages of high energy density, natural abundance, low cost, unique layered structures and wide potential windows,³⁰ and then has been applied in supercapacitors.³¹⁻³³ Especially, the work function difference between it and MnO₂ is as large as 2.45 eV, which makes it a very good choice to match MnO₂ as another electrode material. However, the poor structural stability, low conductivity, and slow electrochemical kinetics of V₂O₅ are still a big challenge.³⁴⁻³⁵ Additionally, we found that pure V₂O₅ gained by electrodeposition forms large particles and these particles easily pile up, which limit the electrochemical performance. As previously literature reported, ³⁶ V₂O₅ & Polyaniline (PANI) can grow in a one-dimensional direction to form nanofibers by electro-codeposition. Generally, nanostructured PANI,³⁷ with good electroconductivity, easy synthesis and high capacitance, has been widely studied in fabricating organic-inorganic composite materials for supercapacitor.³⁸ Besides these advantages, nanostructure composites of V_2O_5 -PANI can also provide channels for charges transport and prevent the V_2O_5 from erosion. Based on the above reason, we believe that PANI is an ideal material to match with V_2O_5 . Therefore, by using MnO₂-PPy-carbon fiber and V_2O_5 -PANI-carbon fiber to assemble a WFASC, a large operation potential of 2.0 V and high energy density has been demonstrated.

Experimental

Preparation

Preparation of electrodes: Firstly the carbon fibers were divided into several sections by PDMS to avoid their disperse; Secondly the carbon fibers were cut into several parts; Thirdly the carbon fibers were cleaned by acetone, ethanol and deionized water for several times; Finally the carbon fibers dried at 80 °C in oven for 12 hours.

Fabricate the electrodes and WFASCs

MnO₂ was grown on carbon fibers via an electrochemical deposition process which was conducted on Autolab PGSTAT302N (Metrohm AG) connected to a computer. A three-electrode configuration was employed, in which a carbon fiber (diameter of 0.04 cm) was used as working electrode, Ag/AgCl as a reference electrode and platinum foil as a counter electrode. MnO₂ was electrodeposited onto a carbon fiber in an aqueous solution of 20 mM Mn(NO₃)₂ and 100 mM NaNO₃ by 30 scans at room temperature. During the electrodeposition, the potential sweep rate was 10 mV s⁻¹, ranging from 0.4 V to 1.3 V *versus* saturated calomel electrode (SCE). After that, the MnO₂ coated carbon fiber electrode was thoroughly rinsed by deionized water and dried in ambient air. An PPy film was deposited with a constant voltage of -0.8 V in a solution of 0.2 M NaClO₄ and 5% (V:V) pyrrole monomer and formed a conductive wrapping on the MnO₂-carbon fiber nanostructures.

 V_2O_5 -PANI (VP) composite nanowires were electrochemically deposited on carbon fibers at a scan rate of 20 mV s⁻¹ in an aqueous solution of 0.1 M VOSO₄ and 0.1 M aniline by 30 scans between -0.2 and 0.9 V. The pH value of solutions for electro-polymerized was adjusted to 1.8 using concentrated H₂SO₄. Then the as-grown sample was washed in deionized water and dried in vacuum at 50 °C for 24 h.

To fabricate the WFASC, two functionalized carbon fibers were used as electrodes, one wrapped by MnO_2 -PPy was used as positive electrode and the other enclosed by V_2O_5 -PANI as negative electrode, a slice of cylindrical cotton wrapped on one of functionalized carbon fiber acted as a separator to prevent short circuits, a piece of transparent silicone tube was used as a package shell, 4 M LiCl was used as an electrolyte. Then the asymmetric supercapacitor was fabricated well.

Results and discussion

Fig. 1 reveals the fabrication process of the WFASC. First, a bundle of commercially

available pure carbon fiber was cut into proper length (Fig. 1a), then a carbon fiber was welded on a copper chip by silver paste and the copper chip was fixed on a teflon substrate. To fabricate positive electrode, a layer of cross-linked MnO_2 whiskers was electrodeposited on the prepared carbon fiber (Fig. 1b). In order to enhance the conductivity of MnO_2 whiskers, PPy was electro-polymerized and wrapped on the MnO_2 -carbon fiber, and then the positive electrode was prepared (Fig. 1c). When it comes to negative electrode, V_2O_5 & PANI were grown on the prepared carbon fiber together in the same way mentioned before (Fig. 1d). Fig. 1e depicts a piece of cylindrical pristine cotton textile wrapped around the V_2O_5 and PANI composite structure electrode as a separator to prevent short circuits. When the two functional carbon fibers and 4 M LiCl were assembled together into a transparent silicone pipeline, a WFASC was fabricated (Fig. 1f).



Fig. 1 Fabrication process of Wire-shaped Fiber Asymmetric Supercapacitor: (a) a pure carbon fiber; (b) MnO_2 was electrodeposited onto carbon fiber; (c) PPy was electro-polymerized on MnO_2 -carbon fiber; (d) V_2O_5 and PANI composite structure were grown on carbon fiber; (e) a piece of cylindrical pristine cotton textile wrapped around the V_2O_5 and PANI composite structure; (f) A Wire-shaped Fiber Asymmetric Supercapacitor was fabricated.

Scanning electron microscopy (SEM, FEI Nova Nano-SEM 450) images of Fig. S1a shows a pure carbon fiber. The carbon fiber wire has a good conductivity with a line resistance of less than 25 Ω cm⁻¹, which makes it suitable as a substrate. Fig. 2a illustrates the noodle-like MnO₂ nanostructures grown on the carbon fiber in low-magnification. It can be seen that the MnO₂ nanostructures uniformly grow on the carbon fiber. The growth of MnO₂ make the originally slick carbon fiber rough and echinate with nanostructures, and this hierarchical nanostructures is convenient for charges and ions transport.³⁹ The pores constructed by the cross-linked whiskers are clearly exhibited in Fig. 2b in high-magnification, the noodle-like whiskers are estimated to be about 200-500 nm in length and 10-30 nm in width. In order to improve the electrical conductivity of MnO₂-based electrodes for optimized electrochemical performance, PPy was uniformly electro-polymerized and wrapped

on the whole MnO_2 -carbon fiber structure, as shown in Fig. 2c and 2d. Transmission electron microscopy (TEM, Tecnai G² 20 U-TWIN) image of Fig. 2e further confirms that the cross-linked whiskers of MnO_2 are highly porous, which is good for exchange and transport of ions and charges. Furthermore, the cross-linked MnO_2 whiskers are polycrystalline as prevented by a HRTEM image together with a selected area electron diffraction (SAED) pattern (Fig. 2f and inset), clear lattice fringes demonstrate that the cross-linked MnO_2 whiskers are well-crystallized structure. To confirm the ingredients of the positive electrode, the EDX spectrum analysis was shown in Fig. S1b. From it we can see that the signals of C, O and Mn were very strong.



Fig. 2 (a) and (b) SEM images of MnO_2 nanostructures grown on carbon fiber; (c) and (d) PPy wrapped on MnO_2 -carbon fiber; (e) TEM image of highly porous MnO_2 nanostructures; (f) HRTEM image (the inset is a SAED pattern) of MnO_2 with polycrystalline characteristic.

In order to evaluate the electrochemical performance of the PPy-MnO₂-carbon fiber hybrid structure, three-electrode configuration was used in the electrochemical measurement. The cyclic voltammetry (CV) curves of pure carbon fiber are illustrated in Fig. 3a, it can be judged that the carbon fiber devices were operated by scan rates ranging from 5 to 100 mV s⁻¹ within a potential window of 0.8 V. The CV curves had enclosed area and good symmetrical rectangular shape, showing that the capacitive behavior of the carbon fiber device, but the pure carbon fiber device only has a negligible areal capacitance of 0.027 F cm⁻² at the scan rate of 5 mV s⁻¹. Here we use areal capacitance as a standard for characterization (by using the area of the active electrode, just as other literature reported ⁴⁰⁻⁴¹). Fig. 3b reveals the CV curves of MnO₂-carbon fiber electrode with a well-defined capacitive behavior. In order to improve the electrical conductivity of the MnO₂-carbon fiber configuration, the PPy was further immobilized onto the MnO₂ surface. The CV curves of PPy-MnO₂-carbonfiber electrode are shown in Fig. 3c. The perfect CV curves tell us that PPy indeed facilitates the ions and charges transfer. The areal capacitance with

respect to different scan rates of PPy-MnO₂-carbon fiber were calculated from CV curves and plotted in Fig. S1c. Fig. 3d shows the CV curves obtained from carbon fiber, MnO₂-carbon fiber and PPy-MnO₂-carbon fiber electrodes at the same scan rate of 50 mV s⁻¹, respectively. The area of the CV curve enclosed from the PPy-MnO₂-carbon fiber electrode was about 9 times larger than that of the MnO₂-carbon fiber and the CV curve area of the MnO₂-carbon fiber was 23 times larger than that of the pure carbon fiber, indicating that the electrochemical performance of the positive electrode has been greatly improved through the active materials and conductive wrapping method. Galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were also used to further evaluate the electrochemical performances of the device. Nyquist plots of the positive electrode is investigated in Fig. 3e, the low combined series resistance obtained from crossing of the high-frequency domain end and the real component axis suggesting the positive electrode has a good capacitive behavior and a low diffusion resistance for ions. The EIS of pure carbon fiber and MnO₂-carbon fiber are also shown in Fig. S1e and f. When MnO2 was deposited onto pure carbon fiber, the diffusion resistance of MnO₂-carbon fiber increased, and after Ppy was deposited onto MnO₂-carbon fiber, the diffusion resistance of MnO₂-Ppy-carbon fiber decreased. This result can demonstrate our previously assumption. The GCD curves at different current densities ranging from 50 to 200 mA cm⁻² are shown in Fig. 3f, the good linear potential-time profiles of GCD, demonstrating a good capacitance performance of the positive electrode. The positive electrode presented a high areal capacitance of 3.95 F cm^{-2} at a current density of 50 mA cm⁻² and also kept 2.98 F cm⁻² at 200 mA cm⁻².



Fig. 3 (a), (b) and (c) CV curves of pure carbon fiber, MnO₂-carbon fiber composite and PPy-MnO₂-carbon fiber composite at different scan rates; (d) CV curves of pure carbon fiber, MnO₂-carbon fiber composite and PPy-MnO₂-carbon fiber composite at the same scan rate of 50 mV s⁻¹ for comparison; (e) Nyquist plot of PPy-MnO₂-carbon fiber composite;(f) GCD curves of PPy-MnO₂-carbon fiber composite at different current densities.

For the negative electrode materials, we agree with Liu's work and find out that the best molar ratio of VOSO₄ and aniline is one to one.³⁶ To further optimize the performance of the V₂O₅-PANI-carbon fiber composite, we investigated the CV cycles at the same scan rate. Fig. 4a and 4b exhibit the electrochemically deposited on carbon fibers by 20 scans, the images show that the V₂O₅-PANI composite nanostructure have not fully grown, when the CV cycles increased to 30, the V₂O₅-PANI composite nanostructure present a good nanostructures configuration as shown in the Fig. 4c and 4d.The nanostructure increases the specific surface area of the negative electrode materials and provide the transport channel of ions. Fig. S2a displays the EDX spectrum of V₂O₅-PANI-carbon fiber composite, and the peeks of main elements were investigated.



Fig. 4 (a) and (b) SEM images of V_2O_5 -PANI composite with 20 cycles; (c) and (d) SEM images of V_2O_5 -PANI composite with 30 cycles; (e) TEM image of V_2O_5 -PANI composite; (f) HRTEM image (the inset is a SAED pattern) of V_2O_5 -PANI composite with polycrystalline characteristic.

The V₂O₅-PANI composite electrode was also analyzed by CV, GCD and EIS. Fig. 5a shows the CV curves of V₂O₅-PANI composite electrode recorded at different scan rates. The V₂O₅-PANI composite electrode exhibits a wide potential window of 1.6 V which is believed to be due to the combination of the high hydrogen together with high oxygen overpotential when PANI is used as an electrode. The areal capacitance with respect to different scan rates of V₂O₅-PANI-carbon fiber were obtained from CV curves and plotted in Fig. S2b. To further evaluate the capacitance of V₂O₅-PANI composite electrode, the Nyquist plot for V₂O₅ and PANI in the frequency range of 0.01 Hz to 100 KHz is revealed in the Fig. 5b. The Nyquist plots of the electrodes all show the form with a semicircle in the higher frequency region and spike in the lower frequency region which is characteristic of the capacitive behavior. For the V₂O₅-PANI composite electrode, the combined series resistance of the electrolyte and the electrode materials is 0.38Ω cm², which is the intercept of the semicircle in the high frequency region. The interfacial charge transfer resistance is 0.49 Ω cm², which

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is the intersection of the curve at the real part. The GCD experiment was conducted from -0.9 to 0.7 V at different current density from 25 mA cm⁻² to 100 mA cm⁻², as shown in the Fig. 5c. Calculated from the data, the V₂O₅-PANI composite electrode possesses the specific capacitance of 3.07 F cm⁻² at the current density of 25 mA cm⁻².



Fig. 5 V_2O_5 -PANI-carbon fiber composite: (a) CV curves of the composite at different scan rates; (b) Nyquist plot; (c) GCD curves at different current densities.

Consid To test the advantage of the WFASC, a variety of electrochemical measurements have been performed using two-electrode configuration. ering the high capacitance of the redox character over carbon MnO₂-PPy composite and the carbon V_2O_5 -PANI composite, a WFASC was fabricated using these materials as the positive and negative electrodes, respectively. Fig. 6a reveals the CV measurements, which indicates that the device can not only work at a large potential window of 0-2.0 V, but also keep similar shape with 0-0.8 V. Generally, the large potential window means a high power density for supercapacitors. This is a major advantage compared to common symmetric supercapacitors ⁴²⁻⁴³ and one of very important factors to meet the demand of applications. Fig. 6b shows the CV curves at different scan rates in the potential window of 0-2.0 V, the curves have good symmetrical and almost rectangular shapes even at a high scan rate of 100 mV s⁻¹, meaning that the WFASC device also has good capacitive performance. To further estimate the stable potential windows of asymmetric supercapacitor, a comparison of CV curves of negative and positive electrodes performed in a three-electrode cell are tested and exhibited in Fig. S3a.¹⁶ Fig. S3b presents the relationship between the areal capacitance and scan rates. Fig. 6c and its inset exhibit the impedance spectrum of the as-fabricated WFASC, it shows a negligible 45° Warburg region, implying the fast ions transport at the active material-electrolyte interface. Fig. 6d shows the profiles of the Galvanostatic discharge curves with different current densities, further proving the perfect electrochemical behavior of the as-fabricated WFASC. The as-fabricated WFASC presented a high areal capacitance of 0.613 F cm⁻² (19.517 F cm⁻³) at a discharge current density of 1.5 mA cm⁻² and still kept 0.530 F cm⁻² at 30 mA cm⁻², being higher than others,⁴⁴⁻⁴⁵ The wider operation window of asymmetric supercapacitor compared to symmetric supercapacitor ⁴² means certain advantage of improving the energy density of the device. Power density and energy density are also used to characterize the performance of supercapacitors.⁴⁶⁻⁴⁷ Fig. S3c reveals the energy density and power density of the as-fabricated WFASC, the as-fabricated WFASC exhibited a high energy density of 0.340 mWh cm⁻² (10.828 mhW cm⁻³) at a power density of 1.5 mW cm^{-2} . Even at a high power density of 30 mW cm^{-2} , the energy density still kept 0.294





Fig. 6 Electrochemical performance of the WFASC: (a) CV curves of the device at different potential windows with a scan rate 20 mVs^{-1} ; (b) CV curves of the device at different scan rates; (c) Nyquist plot; (d) Galvanostatic discharge curves of the device at different current densities.



Fig. 7 Cycle life of the WFASC, the inset reveals the GCD curves from 4990^{th} to 5000^{th} cycles at a current density of 30 mA cm⁻²; (b) CV curves of the WFASC at straight and bend states; (c) the WFASC used to drive a LED.

The GCD test Fig. 7a shows the long-term cycle stability at a current density of 30 mA cm⁻² for 5000 cycles. From it we can see the as-fabricated WFASC only has a slight fluctuation in the whole process, proving the stability of the device is quite well, as other literature reported.⁴⁸ This illustrates a good charge-discharge reversibility of the nanostructure composite electrode and a very low leakage current of the as-fabricated WFASC. In order to testify the flexibility of the as-fabricated WFASC, CV tests at straight and bend states were conducted, as presented in Fig. 7b, we can see that there is just a little change between two states. Furthermore, as shown in Fig. 7c, a commercial LED can be driven by only one WFASC, illustrating the superior capacitive performance of our device.

Conclusions

In summary, a wire-shaped flexible asymmetric supercapacitor has been fabricated

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successfully through simple electrodeposition process. Due to the large work function difference of two electrode materilas (MnO₂ and V₂O₅), the device could work at a wide potential window of 2.0 V and showed excellent electrochemical performances. The device exhibited a high areal capacitance of 0.613 F cm⁻² at a discharge current density of 1.5 mA cm⁻² and a high energy density of 0.340 mWh cm⁻² at a power density of 1.5 mW cm⁻². The device showed very good flexibility, for example, it could withstand the bending test and drive LED even under severe bending state. In addition, the device also kept stability after 5000 cycles even at a current density of 30 mA cm⁻². These results make the WFASC as a promising candidate for widespread application.

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References

- 1 M. Hamedi, R. Forchheimer, O. Inganas, Nature materials, 2007, 6, 357.
- 2 B. O'Connor, K. H. An, Y. Zhao, K. P. Pipe, M. Shtein, Adv. Mater., 2007, 19, 3897.
- 3 Y. Qin, X. Wang, Z. L. Wang, Nature, 2008, 451, 809.
- 4 H. Lin, W. Weng, J. Ren, L. Qiu, Z. Zhang, P. Chen, X. Chen, J. Deng, Y. Wang, H. Peng, *Adv Mater*, 2014, *26*, 1217.
- 5 Y. H. Kwon, S. W. Woo, H. R. Jung, H. K. Yu, K. Kim, B. H. Oh, S. Ahn, S. Y. Lee, S. W. Song, J. Cho, H. C. Shin, J. Y. Kim, *Adv Mater*, 2012, *24*, 5192.
- 6 J. Ren, Y. Zhang, W. Bai, X. Chen, Z. Zhang, X. Fang, W. Weng, Y. Wang, H. Peng, Angew Chem Int Ed Engl, 2014, 53, 7864.
- 7 X. Fan, Z. Z. Chu, F. Z. Wang, C. Zhang, L. Chen, Y. W. Tang, D. C. Zou, Adv. Mater., 2008, 20, 592.
- 8 W. Guo, C. Xu, X. Wang, S. Wang, C. Pan, C. Lin, Z. L. Wang, J Am Chem Soc, 2012, 134, 4437.
- 9 T. Chen, L. Qiu, Z. Cai, F. Gong, Z. Yang, Z. Wang, H. Peng, Nano Lett, 2012, 12, 2568.
- 10 C. Agnès, M. Holzinger, A. Le Goff, B. Reuillard, K. Elouarzaki, S. Tingry, S. Cosnier, *Energy & Environmental Science*, 2014, **7**, 1884.
- 11 X. Dong, Z. Guo, Y. Song, M. Hou, J. Wang, Y. Wang, Y. Xia, Adv. Funct. Mater., 2014, 24, 3405.
- 12 P. Yang, W. Mai, Nano Energy, 2014, 8, 274.
- 13 J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. Liu, Z. L. Wang, Angew Chem Int Ed Engl, 2011, 50, 1683.
- 14 J. Ren, L. Li, C. Chen, X. Chen, Z. Cai, L. Qiu, Y. Wang, X. Zhu, H. Peng, Adv Mater, 2013, 25, 1155.
- 15 B. Liu, B. Liu, X. Wang, D. Chen, Z. Fan, G. Shen, Nano Energy, 2014, 10, 99.
- 16 Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Adv. Funct. Mater., 2011, 21, 2366.
- 17 J. Chang, M. Jin, F. Yao, T. H. Kim, V. T. Le, H. Yue, F. Gunes, B. Li, A. Ghosh, S. Xie, Y. H. Lee, *Adv. Funct. Mater.*, 2013, *23*, 5074.
- 18 H. Y. Lee, J. B. Goodenough, J. Solid State Chem., 1999, 144, 220.
- 19 M. Toupin, T. Brousse, D. Belanger, Chem. Mater., 2004, 16, 3184.

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- 20 J. Tao, N. Liu, L. Li, J. Su, Y. Gao, Nanoscale, 2014, 6, 2922.
- 21 G. Zhou, D.W. Wang, F. Li, L. Zhang, N. Li, Z.S. Wu, L. Wen, G. Q. Lu, H.M. Cheng, *Chem. Mater.*, 2010, *22*, 5306.
- 22 X. Lang, A. Hirata, T. Fujita, M. Chen, Nature nanotechnology, 2011, 6, 232.
- 23 S.B. Ma, K.W. Nam, W.S. Yoon, X.Q. Yang, K.Y. Ahn, K.H. Oh, K.B. Kim, J. Power Sources, 2008, 178, 483.
- 24 J. Tao, N. Liu, J. Rao, L. Ding, M. R. Al Bahrani, L. Li, J. Su, Y. Gao, Nanoscale, 2014, 6, 15073.
- 25 N. L. S. Wang, J. Tao, C. Yang, W. Liu, Y. Shi, Y. Wang, J. Su, L. Li and Y. Gao, *J. Mater. Chem. A*, 2015, 2407.
- 26 L. H. Du, P. H. Yang, X. Yu, P. Y. Liu, J. H. Song, W. J. Mai, J Mater Chem A, 2014, 2, 17561.
- 27 P. Yang, Y. Chen, X. Yu, P. Qiang, K. Wang, X. Cai, S. Tan, P. Liu, J. Song, W. Mai, *Nano Energy*, 2014, 10, 108.
- 28 G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui, Z. Bao, Nano Lett, 2011, 11, 4438.
- 29T. Qian, N. Xu, J. Q. Zhou, T. Z. Yang, X. J. Liu, X. W. Shen, J. Q. Liang, C. L. Yan, *J Mater Chem A*, 2015, *3*, 488.
- 30 H. Y. Li, K. Jiao, L. Wang, C. Wei, X. L. Li, B. Xie, J Mater Chem A, 2014, 2, 18806.
- 31 B. Saravanakumar, K. K. Purushothaman, G. Muralidharan, CrystEngComm, 2014, 16, 10711.
- 32 S. Boukhalfa, K. Evanoff, G. Yushin, Energy & Environmental Science, 2012, 5, 6872.
- 33 A. Ghosh, E. J. Ra, M. Jin, H.K. Jeong, T. H. Kim, C. Biswas, Y. H. Lee, Adv. Funct. Mater., 2011, 21, 2541.
- 34 S. D. Perera, B. Patel, N. Nijem, K. Roodenko, O. Seitz, J. P. Ferraris, Y. J. Chabal, K. J. Balkus, Advanced Energy Materials, 2011, 1, 936.
- 35 Z. Chen, V. Augustyn, J. Wen, Y. Zhang, M. Shen, B. Dunn, Y. Lu, Adv Mater, 2011, 23, 791.
- 36 M.H. Bai, T.Y. Liu, F. Luan, Y. Li, X.X. Liu, J Mater Chem A, 2014, 2, 10882.
- 37 B. K. Kuila, B. Nandan, M. Bohme, A. Janke, M. Stamm, Chem Commun (Camb), 2009, 5749.
- 38 V. Gupta, N. Miura, Electrochem. Solid-State Lett., 2005, 8, A630.
- 39 W. Chen, R. B. Rakhi, L. Hu, X. Xie, Y. Cui, H. N. Alshareef, Nano Lett, 2011, 11, 5165.
- 40 N. Liu, W. Ma, J. Tao, X. Zhang, J. Su, L. Li, C. Yang, Y. Gao, D. Golberg, Y. Bando, *Adv Mater*, 2013, *25*, 4925.
- 41 Y. Fu, X. Cai, H. Wu, Z. Lv, S. Hou, M. Peng, X. Yu, D. Zou, Adv Mater, 2012, 24, 5713.
- 42 X. Wang, B. D. Myers, J. Yan, G. Shekhawat, V. Dravid, P. S. Lee, Nanoscale, 2013, 5, 4119.
- 43 J. Tao, N. Liu, W. Ma, L. Ding, L. Li, J. Su, Y. Gao, Scientific reports, 2013, 3, 2286.
- 44 P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhou, C. P. Wong, Z. L. Wang, ACS nano, 2013, 7, 2617.
- 45 P. Yang, Y. Ding, Z. Lin, Z. Chen, Y. Li, P. Qiang, M. Ebrahimi, W. Mai, C. P. Wong, Z. L. Wang, Nano Lett, 2014, 14, 731.
- 46 A. Zolfaghari, F. Ataherian, M. Ghaemi, A. Gholami, Electrochim. Acta, 2007, 52, 2806.
- 47 J. Yan, Z. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. Song, M. Zhang, J. Power Sources, 2009, 194, 1202.
- 48 Y. Hou, Y. Cheng, T. Hobson, J. Liu, Nano Lett, 2010, 10, 2727.



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