# Highly Flexible Full Lithium Batteries with Self-Knitted $\alpha$ -MnO<sub>2</sub> Fabric Foam

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**Supporting Information** 

**ABSTRACT:** Flexible/bendable electronic equipment has attracted great interest recently, while the development is hindered by fabricating flexible/ bendable power sources due to the lack of reliable materials that combine both electronically superior conductivity and mechanical flexibility. Here, a novel structure of manganese oxide, like fabric foam, was constructed, which was then cocooned with a carbon shell via chemical vapor deposition. Serving as a binder-free anode, the self-knitted MnO<sub>2</sub>@Carbon Foam (MCF) exhibits high specific capacitance (850–950 mAh/g), excellent cycling stability (1000 cycles), and good rate capability (60 C, 1 C = 1 A/g). Moreover, a flexible full



lithium battery was designed based on an MCF anode and a LiCoO<sub>2</sub>/Al cathode, and the outstanding performance (energy density of 2451 Wh/kg at a power density of 4085 W/kg) demonstrates its promising potential of the practical applications. **KEYWORDS:** *flexible devices, full cell, \alpha-MnO<sub>2</sub> fabric foam, lithium-ion battery, high energy density* 

# INTRODUCTION

Recently, there has been stronger interest in flexible/bendable electronic equipment such as smart mobile devices, paper-like gadgets, wearable devices, wireless sensors, and rollup displays,<sup>1–5</sup> which is an emerging and promising technology for the next-generation electronic products.<sup>6</sup> Compared with conventional electronics, the strong points of flexible electronics are portable, lightweight, bendable, and even wearable or implantable.<sup>7–12</sup> Lithium-ion batteries, because of their relatively high energy and power densities, power a wide range of electronic devices including mobile phones, laptop computers, electric vehicles, etc.<sup>13,14</sup> However, the use of traditional rigid battery packs as a power source remains a bottleneck hindering the progress of wearable electronics due to a lack of reliable materials that combine electronically superior conductivity, high mechanical flexibility, and high stability in electrochemical environments.<sup>15,16</sup>

Manganese dioxide (MnO<sub>2</sub>), a traditional metallic oxide material, has received considerable attention<sup>17</sup> because of its low-cost, environmental benignity, high theoretical capacity of ~1230 mAh/g,<sup>18</sup> and relatively low electrochemical motivation force in comparison with other metal oxides such as Fe<sub>2</sub>O<sub>3</sub>,<sup>19</sup> CoO<sub>x</sub>,<sup>20</sup> and Cu<sub>2</sub>O;<sup>21</sup> these make it a promising anode material for application in lithium-ion batteries.<sup>22,23</sup> Therefore, MnO<sub>2</sub> has been studied widely, which mostly focuses on various morphologies (such as nanowires, nanorods, nanosheets, and nanotubes) and different crystalline phases (such as  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ).<sup>24–29</sup> However, few of them are applied to flexible devices without binder resulting from the absence of ideal structural flexibility and integrity.

In this paper, distinguished from common nanowires, a novel structure of manganese oxide, like fabric foam, was synthesized.

The structural integrity of ultralong  $MnO_2$  nanowires was well preserved and exhibited excellent mechanical flexibility, which met the needs of a binder-free flexible electrode. Furthermore, a carbon shell was designed via chemical vapor deposition (CVD) to improve the electrical conductivity and structural integrity of the inner wires greatly, which have limited  $MnO_2$ from use in high-performance lithium-ion batteries before.<sup>30,31</sup> Therefore, the constructed unique  $MnO_2(@C \text{ core-shell Foam}$ structure can endow it with high specific capacitance and maintain excellent cycle stability as a binder-free anode.

# EXPERIMENTAL SECTION

Synthesis of Self-Knitted  $\alpha$ -MnO<sub>2</sub> Fabric Foam. The fabric foam consisting of ultralong  $\alpha$ -MnO<sub>2</sub> nanowires was synthesized via a hydrothermal method.<sup>32</sup> In a typical process, a homogeneous solution of KMnO<sub>4</sub> (0.8 mmol) and NH<sub>4</sub>Cl (0.8 mmol) in 40 mL of H<sub>2</sub>O was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 20 h; it was then allowed to cool down at room temperature. The product was collected and rinsed with deionized water for several times, followed by drying overnight.

Synthesis of  $\alpha$ -MnO<sub>2</sub> Nanowires@Carbon Core-Shell Nanostructures. The as-prepared  $\alpha$ -MnO<sub>2</sub> nanowires were coated with carbon by the CVD method at 450 °C for 1.5 h, using argon gas 100 standard cubic centimeters per minute (SCCM) and acetylene10 SCCM.

**General Characterization.** The morphology of the materials was observed by field emission scanning electron microscopy (FESEM, SU8010, Japan) and field emission transmission electron microscopy (FETEM, FEI Tecnai G2 F20 S-TWIN TMP, Hongkong). Elemental analysis was performed on an X-ray photoelectron spectrometer (XPS,

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Figure 1. (A, B) Digital images of MF. (C) Typical FESEM images of MF. (D) Schematic illustration of MF nanowires.



Figure 2. (A, B) SEM images of MF and MCF, respectively. (C) XPS spectrum of MCF. (D, E) TEM and high-resolution TEM images of MCF. (F) XRD pattern of MCF.

Kratos Axis Ultra Dld, Japan) and a Powder X-ray Diffractometer (XRD, X'Pert-Pro MRD, Philips). Thermogravimetric-differential thermal analysis (TGA, SDT 2960, USA) was carried out on an SDT 2960, TA Instruments.

**Electrochemical Characterization.** Coin cells (CR2025) were assembled by using the as-prepared MCF as the anode, Celgard 2400 as the separator, 1 mol/L LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (4:3:3 vol %) as the electrolyte, and lithium foil as the cathode. The anodes were cut into disks with diameters of 1.2 cm, and no binder was used for preparing the electrodes. Typical electrode mass was  $1.1-1.4 \text{ mg/cm}^2$ . The battery assembly was done in an argon-filled glovebox with H<sub>2</sub>O and O<sub>2</sub> less than 0.1 ppm. The galvanostatic charge–discharge test was tested within a voltage window of 0.01–3.0 V (vs Li<sup>+</sup>/Li) by using a battery testing system (LAND CT 2001A, Wuhan, China). Cyclic voltammetry (CV) measurement was conducted at 0.6 mV/s within the range of 0.01–3.0 V on a CHI 660E (Chenhua Shanghai, China) electrochemical workstation. Electrochemical impedance spectra (EIS) measurements were

performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 to  $10^6$  Hz, using the same setup as CV tests.

Full lithium batteries were fabricated based on MCF anodes and  $LiCoO_2/Al$  cathodes.  $LiCoO_2/Al$  cathodes were purchased from HeFei Ke Jing Materials Technology Co., LDT. The single active material surface density was 22–22.5 mg/cm<sup>2</sup>, and active substances of mixed-powder proportions were 95.5%, which was more excessive than the loading density of anodes. In addition, Celgard 2400 served as the separator and 1 mol/L LiPF<sub>6</sub> dissolved in a mixture of EC, EMC, and DEC (4:3:3 vol %) served as the electrolyte. The mass of the sample was around 6.6–8.4 mg, and the loading density of the MCF active material was calculated as 1.1–1.4 mg/cm<sup>2</sup>. The whole assembly was packaged with a flexible plastic bag by an edge bonding machine.

# RESULTS AND DISCUSSION

The digital photo of  $MnO_2$  Foam (MF) is present in Figure 1A, which reveals an integrated fluffy porous structure of  $\alpha$ -MnO<sub>2</sub> nanowires and can exhibit high flexibility even in a flat shape

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Figure 3. (A) Mn 2p, (B) O 1s, and (C) C 1s XPS spectra of MCF. (D) The TGA plot between 0 and 500 °C at an increasing rate of 10 °C/min.



**Figure 4.** (A) The foundation test of the MCF electrochemical properties by the cyclic voltammetry obtained in a voltage range of 0.01-3 V (vs Li<sup>+</sup>/Li) and a potential scan rate of 0.6 mV/s. (B) Charge–discharge profiles of MCF for the 1st, 2nd, 25th, and 50th cycles in the potential range from 0.01 to 3.0 V with a low current density of 100 mA/g.

without binder (Figure 1B). Figure 1C shows a representative low-magnification FESEM image of MF, proving MF is composed of ultralong self-knitted nanowires that is in a good accordance with the schematic illustration of MF (Figure 1D). Carbon coating on  $MnO_2$  nanowires was done by CVD using  $C_2H_2$  as carbon source at a temperature of 450 °C for 1.5 h. As shown in Figure 2A,B, the surface of nanowires is rougher and the diameter becomes significantly larger, suggesting a thick layer of carbon shell. For more details, the image of TEM is provided in Figure 2D and demonstrates that the MF is covered with a well-defined carbon shell uniformly. The highmagnification TEM image (Figure 2E) reveals a crystal lattice space of 0.25 nm for the crystalline  $MnO_2$  nanostructures.

Further composition analysis of the MCF is carried out using XPS. In the survey region from 0 to 800 eV (Figure 2C), it is

evident that Mn, O, and C elements all exist. The higherresolution spectrum of Mn 2p in Figure 3A shows clearly that Mn  $2p_{3/2}$  and  $2p_{1/2}$  are found to be 642.0 and 654.0 eV, respectively. The values agree well with those reported for MnO<sub>2</sub>, indicating that the oxidation state is 4<sup>+</sup>.<sup>33</sup> The peaks at 530.4 and 531.7 eV in the higher-resolution spectrum of O 1s represent O-Mn and O-C (Figure 3B), further confirming the synergistic presence of MnO<sub>2</sub> in the composite.<sup>34</sup> The binding energy at 284.6 eV in the XPS analysis is attributed to C 1s (Figure 3C), indicating the existence of the carbon shell. The crystal phase of the sample was analyzed by powder X-ray diffraction. Figure 2F shows the XRD pattern of the MCF. All the diffraction peaks correspond to  $\alpha$ -MnO<sub>2</sub> (ICDD-JCPDS Card No. 44-0141).<sup>35,36</sup> In addition, the broad peak of the XRD pattern at about 26.5° is indexed to the (002) planes of the

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Figure 5. (A) Variation in discharge capacity vs cycle number for MCF and MF at current density of 100 mA/g. (B) EIS spectra of MF and MCF fresh cells in the frequency range of  $0.01-10^6$  Hz at room temperature. The inset is an equivalent circuit. (C) Capacity versus cycle number plot of MCF and MF at different charging rates. (D) Long-term cycling performance of MCF anode at a high current density of 1200 mA/g, and the efficiency is plotted on the right axis.

graphite carbon,<sup>37</sup> which are in accordance with the above results. Moreover, the plots of TGA are shown in Figure 3D; the initial weight loss (0–250 °C) is due to desorption of the surface adsorbed water in MCF. After the degradation of carbon, the weight loss of the MCF composites is around 25%, revealing that the content of MnO<sub>2</sub> in MCF is 75%.

The electrochemical properties of MCF and MF were directly investigated using CR2025 coin-type cells versus Li/Li<sup>+</sup>, depicted in Figure 4. The electrochemical reaction mechanism of the MF and MCF anodes is more clearly revealed using CV. The first two CV curves are shown in Figure S1 and Figure 4A between 0.01 and 3.0 V at scan rates of 0.6 mV/s. As shown in Figure S1, it is obvious that the first CV curve is somewhat different from the subsequent one. In the first cycle, a cathodic peak located at about 0.55 V corresponds to the formation of a solid electrolyte interface (SEI) layer and the reduction of MnO<sub>2</sub> with Li ions, which is described by  $MnO_2 + 4Li^+ + 4e^- \rightarrow Mn(0) + 2Li_2O$ <sup>38</sup> and another cathodic peak at about 2.15 V is attributed to the decomposed electrolyte. Meanwhile, in the first anodic sweep, two oxidation

peaks at 1.30 and 2.35 V can be observed, indicating that the electrochemical oxidation reaction may proceed by two steps. In the second cycle, the 0.55 V reduction peak disappears, indicating that formation of the SEI layer only takes place during the first cycle. After coating by a carbon shell (Figure 4A), compared with Figure S1, the area of CV curves becomes larger because the electrical conductivity is improved and the capacity of MCF increases. It can be seen that the MF characteristic peaks described above still exist in the MCF CV curves, and all reduction and oxidation peaks in the second cycle overlap well with those in the first cycle, suggesting good electrochemical reversibility and structural stability.<sup>39</sup>

The charge–discharge profiles of MCF at a current density of 100 mA/g are shown in Figure 4B. In the first cycle, the potential plateau in the range of 0.2-0.55 V corresponds to the lithiation process, while that in 1.2-1.5 V to the delithiation. It is remarkable to note that the initial discharge and charge capacities are 1411.9 and 927.0 mAh/g and the Coulombic efficiency in the initial cycle is 66% and increases to ca.100% in the subsequent cycles. The capacity loss may be caused by SEI



Figure 6. (A) Cycling performance of flexible full battery up to 80 cycles at current density of 200 mA/g. (B) Schematic illustration for the fabrication of full battery. (C-E) Practical applications of flexible full battery.

formation and decomposition of the electrolyte during the first electrochemical reaction that is in alignment to the results of the CV tests. After 50 cycles, both discharge and charge capacities of MCF are stabilized at about 840 mAh/g, which are extremely close to the 2nd and 25th cycle, further indicating that the materials are extraordinarily stable during cycling. To better understand the much-improved electrochemical performance achieved by the carbon coating, SEM was performed on the MF and MCF electrodes after cycling. From Figure S2A, obvious morphology changes of the MF electrodes are observed due to volume expansion. In contrast, the MCF nanowires are protected very well (Figure S2B), which demonstrates that the outer carbon coating prevents pulverization effectively and improved the stability of the MCF electrodes.

To evaluate the electrochemical performance of MF and MCF electrodes, the samples were tested by galvanostatic charge—discharge measurements in the voltage window of 0.01–3.0 V. The cycling performance of MCF and MF electrodes is depicted in Figure 5A at a current density of 100 mA/g. Though the initial (first cycle) irreversible discharge capacity of the MF anodes reaches up to 1298 mAh/g, the second cycle discharge capacity just remains 372 mAh/g. Moreover, the MF electrodes deliver a low reversible capacity of 190 mAh/g after 50 charge—discharge cycles, whereas that of MCF electrodes exhibit higher discharge capacity and tend to stabilize at approximately 840 mAh/g, suggesting that the MCF electrodes obtain a better stability.

Additionally, the electrochemical dynamical behaviors of MF and MCF were identified by EIS measurements. All the samples were measured at room temperature using fresh cells. As shown in Figure 5B, both MF and MCF electrodes show a semicircle at high-medium frequency and an inclined line at low frequency, which correspond to charge transfer and diffusion, respectively. The inset shows an equivalent circuit model according to the simulation. In this circuit,  $R_s$  represents the Ohmic resistance of the electrode system, including the electrolyte and the cell components. R<sub>CT</sub> represents the interfacial charge transfer resistance, which is connected to the semicircle in the high frequency region.  $R_{\rm f}$  represents the resistance of the SEI film. CPE is the double layer capacitance.  $Z_{\rm W}$  represents Warburg impedance, which is described as a diffusive resistance of the Li ion within the electrode pores.<sup>40–42</sup> The related values for resistance of Rs,  $R_p$  and  $R_{\rm CT}$  are depicted in Table S1. The very high frequency impedance is similar for each material, which is expected since this impedance is a measure of bulk electrolyte resistance in the cell. Because of a carbon layer, the  $R_{\rm CT}$  of MCF electrodes is lower than that of MF, which illustrates that the conductivity is 

Besides, the rate capability of the obtained MCF and MF electrodes is given in Figure 5C. The electrochemical properties of as-synthesized MCF were studied by charging/discharging at different current rates ranging from 0.1 to 60 C (1 C = 1 A/g). Fairly stable capacities at various rates can be observed clearly. At lower rates, the discharge capacities at 0.1, 0.3, 0.6, 0.9, 1.8, 3.6, and 6 C are 840, 690, 580, 520, 425, 320, and 240 mAh/g, respectively. Even at a high rate of 60 C, the capacity of MCF electrodes stays at about 86 mAh/g and pretty close to 36 C (100 mAh/g) with the Coulombic efficiency approaching

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almost 100%. At the first rate of 0.1 C, the capacity of 840 mAh/g can be obtained. When the cycling current was set back to 0.1 C, the electrode could still retain a large reversible capacity of 820 mAh/g. This finding reveals that almost 97.6% of the initial capacity at 0.1 C is recovered. The electrochemical studies prove that the MCF electrodes exhibit a superior reversible capacity, excellent cycling performance, and good rate capability. These results are in sharp contrast to the MF electrodes, which show continuous capacity decrease during the first 10 cycles and drop to 210 mAh/g at 0.3 C (30% of the MCF) with the same experimental conditions. Worse still, at a high current density, the discharge capacity only remains at about 30-40 mAh/g, which demonstrates that the improved rate performance is most likely due to the superior electronic conductivity of the MCF.

Furthermore, the MCF was then tested at a high current density of 1200 mA/g (Figure 5D). It can be seen that the reversible capacity increases from 300 to 480 mAh/g after 100 cycles and remains at 450 mAh/g after 1000 cycles, demonstrating strongly the extremely long cycle life and stability of MCF.

Since the synthesized self-knitted MCF as binder-free anodes for lithium-ion batteries exhibits high capacity, excellent cycling stability, and good rate capability, a highly flexible full battery was fabricated based on an MCF anode, a LiCoO<sub>2</sub>/Al cathode, a LiPF<sub>6</sub> electrolyte, and a polymer separator, respectively. The mass of the sample is around 6.6-8.4 mg, and the loading density of the MCF active material is calculated as 1.1-1.4 mg/  $cm^2$ . As shown in Figure 6A, the electrochemical behavior was studied by galvanostatic charge-discharge measurements in the voltage window of 0.01-3.7 V at a current density of 200 mA/ g. During the initial cycles, the capacity is showing an evident upward tendency from 338 to 800 mAh/g. It can be explained that the electrolyte can access this composite in depth after the lithiation and delithiation processes and offer higher electrochemical activity. In subsequent cycles, the capacity keeps rising slowly and stabilizes at approximately 825 mAh/g with a Coulombic efficiency of 99%. Besides the obtained high capacity, the MCF electrodes demonstrate satisfactory rate capability as well. As shown in Figure S3A, the specific capacity is as high as 825 mAh/g at the current rate of 0.2 C. As the current rate increases to 1.2 C, the capacity of 720 mAh/g can still be delivered. It should be noted that, after the continuous cycling with increasing current densities, a specific capacity as high as 870 mAh/g could be well recovered at a current rate of 0.2 C, which confirms the excellent Li<sup>+</sup> storage reversibility. A schematic illustration is depicted in Figure 6B to explain the structure of the full battery. The as-assembled flexible battery was used to control a light-emitting diode (LED) in a flat shape (Figure 6C). Even if the battery is bent or rolled up periodically, the LED still works normally (Figure 6D,E), which exhibits excellent mechanical flexibility of the fabricated flexible lithium-ion battery and demonstrates its practical applications in wearable electronics.

For the future potential applications such as hybrid electric vehicles and multifunctional electronics, LIBs require not only high energy density (E) but also high power density (P). The energy density and power density are calculated as

$$E = CV^2/4 \tag{1}$$

 $P = E/t \tag{2}$ 

where *C* is the total capacitance of cell, *V* is the cell voltage, and *t* is the discharge time. Ragone plots (Figure S3B) of the battery describing the relationship between energy density and power density were obtained to compare with the values reported for other flexible lithium-ion batteries.<sup>45–47</sup> At the power density of 681 W/kg, our devices show an energy density as high as 2808 Wh/kg, and when the power density increases to around 4085 W/kg, the full batteries still deliver an energy density of 2451 Wh/kg, which is much higher than most of the reported flexible lithium-ion batteries in refs 6, 46, 48, and 49 and demonstrated the potential of our flexible devices in the future applications.

#### CONCLUSION

In summary, self-knitted MnO<sub>2</sub> Foam composed of ultralong nanowires was synthesized successfully, and a carbon shell designed via CVD has improved the electrical conductivity and structural integrity of the inner wires greatly, which can endow it with high specific capacitance (850-950 mAh/g), good rate capability (60 C), and long cycle life (1000 cycles). Additionally, owing to the novel structure, the integrity is well preserved and can exhibit high mechanical flexibility, which meets the need of flexible binder-free anodes for lithium batteries. A highly flexible full battery was assembled using MCF as anode and LiCoO<sub>2</sub>/Al foil as cathode that can control an LED no matter in a flat or bent shape. The outstanding electrical and mechanical properties of flexible MCF electrodes and the corresponding power sources (energy density of 2451 Wh/kg at a power density of 4085 W/kg) will stimulate their wide use in flexible, stretchable, foldable, and wearable electronic devices.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07145.

The CV curves for MF, figures showing SEM images of the MF and MCF electrodes after five cycles, rate capability at different rates and Ragone plots of MCF// $LiCoO_2$  full lithium-ion batteries, and the table of kinetic parameters obtained from equivalent circuit fitting of experimental data from the MF and MCF lithium-ion batteries (PDF)

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#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Wang, X. F.; Lu, X. H.; Liu, B.; Chen, D.; Tong, Y. X.; Shen, G. Z. Flexible Energy-Storage Devices: Design Consideration and Recent Progress. *Adv. Mater.* **2014**, *26*, 4763–4782.

(2) Liu, J.; Buchholz, D. B.; Chang, R. P.; Facchetti, A.; Marks, T. J. High-performance Flexible Transparent Thin-Film Transistors Using a Hybrid Gate Dielectric and an Amorphous Zinc Indium Tin Oxide Channel. *Adv. Mater.* **2010**, *22*, 2333–2337.

(3) Ju, S.; Li, J. F.; Liu, J.; Chen, P. C.; Ha, Y. G.; Ishikawa, F.; Chang, H.; Zhou, C. W.; Facchetti, A.; Janes, D. B.; Marks, T. J. Transparent Active Matrix Organic Light-Emitting Diode Displays Driven by Nanowire Transistor Circuitry. *Nano Lett.* **2008**, *8*, 997–1004.

(4) Bauer, S. Flexible Electronics: Sophisticated Skin. Nat. Mater. 2013, 12, 871–872.

(5) Wang, X. F.; Liu, B.; Hou, X. J.; Wang, Q. F.; Li, W. W.; Chen, D.; Shen, G. Z. Ultralong-Life and High-Rate Web-Like  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anode for High-Performance Flexible Lithium-ion Batteries. *Nano Res.* **2014**, *7*, 1073–1082.

(6) Liu, B.; Zhang, J.; Wang, X. F.; Chen, G.; Chen, D.; Zhou, C. W.; Shen, G. Z. Hierarchical Three-Dimensional  $ZnCo_2O_4$  Nanowire Arrays/Carbon Cloth Anodes for a Novel Class of High-Performance Flexible Lithium-Ion Batteries. *Nano Lett.* **2012**, *12*, 3005–3011.

(7) Li, L.; Wu, Z.; Yuan, S.; Zhang, X. B. Advances and Challenges for Flexible Energy Storage and Conversion Devices and Systems. *Energy Environ. Sci.* **2014**, *7*, 2101–2122.

(8) Nam, K. T.; Kim, D. W.; Yoo, P. J.; Chiang, C. Y.; Meethong, N.; Hammond, P. T.; Belcher, A. M. Virus-Enabled Synthesis and Assembly of Nanowires for Lithium Ion Battery Electrodes. *Science* **2006**, *312*, 885–888.

(9) Zhou, G. M.; Li, F.; Cheng, H. M. Progress in Flexible Lithium Batteries and Future Prospects. *Energy Environ. Sci.* **2014**, *7*, 1307–1338.

(10) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414*, 359–367.

(11) Armand, M.; Tarascon, J. M. Building Better Batteries. *Nature* **2008**, *451*, 652–657.

(12) Liu, Z.; Xu, J.; Chen, D.; Shen, G. Z. Flexible Electronics Based on Inorganic Nanowires. *Chem. Soc. Rev.* 2015, 44, 161–192.

(13) Liu, B.; Wang, X. F.; Chen, H. T.; Wang, Z. R.; Chen, D.; Cheng, Y. B.; Zhou, C. W.; Shen, G. Z. Hierarchical Silicon Nanowires-Carbon Textiles Matrix as a Binder-Free Anode for High-Performance Advanced Lithium-Ion Batteries. *Sci. Rep.* **2013**, *3*, 1622.

(14) Liu, B.; Wang, X. F.; Liu, B. Y.; Wang, Q. F.; Tan, D. S.; Song, W. F.; Hou, X. J.; Chen, D.; Shen, G. Z. Advanced Rechargeable Lithium-ion Batteries Based on Bendable ZnCo<sub>2</sub>O<sub>4</sub>-Urchins-on-Carbon-Fibers Electrodes. *Nano Res.* **2013**, *6*, 525–534.

(15) Pu, X.; Li, L. X.; Song, H. Q.; Du, C. H.; Zhao, Z. F.; Jiang, C. Y.; Cao, G. Z.; Hu, W. G.; Wang, Z. L. A Self-Charging Power Unit by Integration of a Textile Triboelectric Nanogenerator and a Flexible Lithium-Ion Battery for Wearable Electronics. *Adv. Mater.* **2015**, *27*, 2472–2478.

(16) Gwon, H.; Kim, H. S.; Lee, K. U.; Seo, D. H.; Park, Y. C.; Lee, Y. S.; Ahn, B. T.; Kang, K. Flexible Energy Storage Devices Based on Graphene Paper. *Energy Environ. Sci.* **2011**, *4*, 1277–1283.

(17) Li, J. X.; Zhao, Y.; Wang, N.; Ding, Y. H.; Guan, L. H. Enhanced Performance of  $\alpha$ -MnO<sub>2</sub>-Graphene Sheet Cathode for Lithium Ion Batteries Using Sodium Alginate as a Binder. *J. Mater. Chem.* **2012**, *22*, 13002–13004.

(18) Fang, X.; Lu, X.; Guo, X.; Mao, Y.; Hu, Y. S. J.; Wang, Z.; Wang, F.; Wu, H.; Liu, L.; Chen, L. Electrode Reactions of Manganese Oxides for Secondary Lithium Batteries. *Electrochem. Commun.* **2010**, *12*, 1520–1523.

(19) Wu, M. S.; Ou, Y. H.; Lin, Y. P. Electrodeposition of Iron Oxide Nanorods on Carbon Nanofiber Scaffolds as an Anode Material for Lithium-Ion Batteries. *Electrochim. Acta* **2010**, *55*, 3240–3244.

(20) Nam, K. M.; Shim, J. H.; Han, D. W.; Kwon, H. S.; Kang, Y. M.; Li, Y.; Song, H.; Seo, W. S.; Park, J. T. Syntheses and Characterization of Wurtzite CoO, Rocksalt CoO, and Spinel  $Co_3O_4$  Nanocrystals: Their Interconversion and Tuning of Phase and Morphology. *Chem. Mater.* **2010**, *22*, 4446–4454.

(21) Xiang, J. Y.; Tu, J. P.; Yuan, Y. F.; Huang, X. H.; Zhou, Y.; Zhang, L. Improved Electrochemical Performances of Core-Shell Cu<sub>2</sub>O/Cu Composite Prepared by a Simple One-Step Method. *Electrochem. Commun.* **2009**, *11*, 262–265.

(22) Guo, C. X.; Wang, M.; Chen, T.; Lou, X. W.; Li, C. M. A Hierarchically Nanostructured Composite of MnO<sub>2</sub>/Conjugated Polymer/Graphene for High-Performance Lithium Ion Batteries. *Adv. Energy Mater.* **2011**, *1*, 736–741.

(23) Cabana, J.; Monconduit, L.; Larcher, D.; Palacin, M. R. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions. *Adv. Mater.* **2010**, *22*, E170–E192.

(24) Débart, A.; Paterson, A. J.; Bao, J.; Bruce, P. G.  $\alpha$ -MnO<sub>2</sub> Nanowires: A Catalyst for the O<sub>2</sub> Electrode in Rechargeable Lithium Batteries. *Angew. Chem., Int. Ed.* **2008**, *47*, 4521–4524.

(25) Wang, X.; Li, Y. D. Synthesis and Formation Mechanism of Manganese Dioxide Nanowires/Nanorods. *Chem. - Eur. J.* 2003, 9, 300–306.

(26) Zhang, J. T.; Chu, W.; Jiang, J. W.; Zhao, X. S. Synthesis, Characterization and Capacitive Performance of Hydrous Manganese Dioxide Nanostructures. *Nanotechnology* **2011**, *22*, 125703–125711.

(27) Sun, M.; Lan, B.; Lin, T.; Cheng, G.; Ye, F.; Yu, L.; Cheng, X. L.; Zheng, X. Y. Controlled Synthesis of Nanostructured Manganese Oxide: Crystalline Evolution and Catalytic Activities. *CrystEngComm* **2013**, *15*, 7010–7018.

(28) Wang, J. F.; Deng, L. J.; Zhu, G.; Kang, L.; Lei, Z.; Liu, Z.-H. Fluoride Anions-assisted Hydrothermal Preparation and Growth Process of  $\beta$ -MnO<sub>2</sub> with Bipyramid Prism Morphology. *CrystEng*-*Comm* **2013**, *15*, 6682–6689.

(29) Xia, H.; Feng, J.; Wang, H.; Lai, M. O.; Lu, L. MnO<sub>2</sub> Nanotube and Nanowire Arrays by Electrochemical Deposition for Super-capacitors. *J. Power Sources* **2010**, *195*, 4410–4413.

(30) Reddy, A. L. M.; Shaijumon, M. M.; Gowda, S. R.; Ajayan, P. M. Coaxial  $MnO_2/Carbon$  Nanotube Array Electrodes for High-Performance Lithium Batteries. *Nano Lett.* **2009**, *9*, 1002–1006.

(31) Hou, Y.; Cheng, Y. W.; Hobson, T.; Liu, J. Design and Synthesis of Hierarchical MnO<sub>2</sub> Nanospheres/Carbon Nanotubes/Conducting Polymer Ternary Composite for High Performance Electrochemical Electrodes. *Nano Lett.* **2010**, *10*, 2727–2733.

(32) Wang, H. Y.; Xiao, F. X.; Yu, L.; Liu, B.; Lou, X. W. Hierarchical  $\alpha$ -MnO<sub>2</sub> Nanowires@Ni<sub>1.x</sub>Mn<sub>x</sub>O<sub>y</sub> Nanoflakes Core-Shell Nanostructures for Supercapacitors. *Small* **2014**, *10*, 3181–3186.

(33) Li, B. X.; Rong, G. X.; Xie, Y.; Huang, L. F.; Feng, C. Q. Low-Temperature Synthesis of  $\alpha$ -MnO<sub>2</sub> Hollow Urchins and Their Application in Rechargeable Li<sup>+</sup> Batteries. *Inorg. Chem.* **2006**, *45*, 6404–6410.

(34) Yang, T. Z.; Qian, T.; Wang, M. F.; Liu, J.; Zhou, J. Q.; Sun, Z. Z.; Chen, M. Z.; Yan, C. L. A New Approach towards the Synthesis of Nitrogendoped Graphene/MnO<sub>2</sub> Hybrids for Ultralong Cyclelife Lithium Ion Batteries. *J. Mater. Chem. A* **2015**, *3*, 6291–6296.

(35) Cheng, F. Y.; Zhao, J. Z.; Song, W. E.; Li, C. S.; Ma, H.; Chen, J.; Shen, P. W. Facile Controlled Synthesis of MnO<sub>2</sub> Nanostructures of Novel Shapesand Their Application in Batteries. *Inorg. Chem.* **2006**, 45, 2038–2044.

(36) Qian, T.; Xu, N.; Zhou, J. Q.; Yang, T. Z.; Liu, X. J.; Shen, X. W.; Liang, J. Q.; Yan, C. L. Interconnected Three-Dimensional  $V_2O_5/$  Polypyrrole Network Nanostructures for High Performance Solid-State Supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 488–493.

(37) Hu, Y.; Jensen, J. O.; Zhang, W.; Cleemann, L. N.; Xing, W.; Bjerrum, N. J.; Li, Q. F. Hollow Spheres of Iron Carbide Nanoparticles Encased in Graphitic Layers as Oxygen Reduction Catalysts. *Angew. Chem., Int. Ed.* **2014**, *53*, 3675–3679.

(38) Wang, C.; Yin, L.; Xiang, D.; Qi, Y. Uniform Carbon Layer Coated  $Mn_3O_4$  Nanorod Anodes with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1636–1642.

# **ACS Applied Materials & Interfaces**

(39) Cai, Z. Y.; Xu, L.; Yan, M. Y.; Han, C. H.; He, L.; Hercule, K. M.; Niu, C. J.; Yuan, Z. F.; Xu, W. W.; Qu, L. B.; Zhao, K. N.; Mai, L. Q. Yolk-Shell Nanorod Anodes for High Capacity Lithium Batteries. *Nano Lett.* **2015**, *15*, 738–744.

(40) Mai, L. Q.; Dong, F.; Xu, X.; Luo, Y. Z.; An, Q. Y.; Zhao, Y. L.; Pan, J.; Yang, J. N. Cucumber-Like  $V_2O_5/Poly(3,4-ethylenedioxythiophene) \& MnO_2$  Nanowires with Enhanced Electrochemical Cyclability. *Nano Lett.* **2013**, *13*, 740–745.

(41) Chen, H. W.; Wang, C. H.; Dong, W. L.; Lu, W.; Du, Z. L.; Chen, L. W. Monodispersed Sulfur Nanoparticles for Lithium-Sulfur Batteries with Theoretical Performance. *Nano Lett.* **2015**, *15*, 798– 802.

(42) Han, J. B.; Dou, Y. B.; Zhao, J. W.; Wei, M.; Evans, D. G.; Duan, X. Flexible CoAl LDH@PEDOT Core/Shell Nanoplatelet Array for High-Performance Energy Storage. *Small* **2013**, *9*, 98–106.

(43) Xiao, Z.; Xia, Y.; Ren, Z. H.; Liu, Z. Y.; Xu, G.; Chao, C. Y.; Li, X.; Shen, G.; Han, G. R. Facile Synthesis of Single-Crystalline Mesoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> Nanorods as Anode Materials for Lithium-Ion Batteries. *J. Mater. Chem.* **2012**, *22*, 20566–20573.

(44) Evers, S.; Yim, T.; Nazar, L. F. Understanding the Nature of Absorption/Adsorption in Nanoporous Polysulfide Sorbents for the Li-S Battery. J. Phys. Chem. C 2012, 116, 19653–19658.

(45) Wang, C.; Wu, L. X.; Wang, H.; Zuo, W. H.; Li, Y. Y.; Liu, J. P. Fabrication and Shell Optimization of Synergistic  $TiO_2$ -MoO<sub>3</sub> Core-Shell Nanowire Array Anode for High Energy and Power Density Lithium-Ion Batteries. *Adv. Funct. Mater.* **2015**, *25*, 3524–3533.

(46) Balogun, M. S.; Yu, M. H.; Huang, Y. C.; Li, C.; Fang, P. P.; Liu, Y.; Lu, X. H.; Tong, Y. X. Binder-Free  $Fe_2N$  Nanoparticles on Carbon Textile with High Power Density as Novel Anode for High-Performance Flexible Lithium Ion Batteries. *Nano Energy* **2015**, *11*, 348–355.

(47) Balogun, M. S.; Li, C.; Zeng, Y. X.; Yu, M. H.; Wu, Q. L.; Wu, M. M.; Lu, X. H.; Tong, Y. X. Titanium Dioxide@Titanium Nitride Nanowires on Carbon Cloth with Remarkable Rate Capability for Flexible Lithium-Ion Batteries. *J. Power Sources* **2014**, *272*, 946–953.

(48) Wang, X. H.; Guan, C.; Sun, L. M.; Susantyoko, R. A.; Fan, H. J.; Zhang, Q. Highly Stable and Flexible Li-Ion Battery Anodes Based on TiO<sub>2</sub> Coated 3D Carbon Nanostructures. *J. Mater. Chem. A* **2015**, *3*, 15394–15398.

(49) Balogun, M. S.; Yu, M. H.; Li, C.; Zhai, T.; Liu, Y.; Lu, X. H.; Tong, Y. X. Facile Synthesis of Titanium Nitride Nanowires on Carbon Fabric for Flexible and High-Rate Lithium Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 10825–10829.