Synthesis of Metal Oxide/Carbon Nanofibers via Biostructure Confinement as High-Capacity Anode Materials

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ABSTRACT: For applications in energy storage and conversion, many metal oxide (MO)/C composite fibers have been synthesized using cellulose as the template. However, MO particles in carbon fibers usually experience anomalous growth to a size of >200 nm, which is detrimental to the overall performance of the composite. In this paper, we report the successful development of a generic approach to synthesize a fiber composite with highly dispersed MO nanoparticles (10–80 nm) via simple swelling, nitrogen doping, and carbonization of the cellulose microfibril. The growth of the MO nanoparticles is confined by the structure of the microfibrils. Density functional theory calculation further reveals that the doped N atoms supply ample nucleation sites for size confinement of the nanoparticles. The encapsulation structure of small MO nanoparticles in the conductive carbon matrix improves their electrochemical performance. For example, the formed SnO_x/carbon nanocomposite exhibits high specific capacities of 1011.0 mA h g⁻¹ at 0.5 A g⁻¹ and 581.8 mA h g⁻¹ at 5 A g⁻¹. Moreover, the



fiber-like nanocomposite can be combined with carbon nanotubes to form a flexible binder-free electrode with a capacity of ~ 10 mA h cm⁻², far beyond the commercial level. The process developed in this study offers an alternative approach to sophisticated electrospinning for the synthesis of other fiber-like MO/carbon nanocomposites for versatile applications.

KEYWORDS: cellulose, nanofiber, metal oxide/carbon composite, nitrogen doping, anode material

■ INTRODUCTION

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Electrical vehicles, clean-energy storage, and various portable devices require lightweight, compact, and low-cost lithium-ion batteries (LIBs).^{1–3} Hence, great efforts have been made to explore highly reversible anodes with large capacities.^{4,5} Metal oxides (MOs) are considered promising anode materials for next-generation LIBs because of their high theoretical capacity, abundance, and environmental friendliness.^{6–12} Nevertheless, practical application of MO-based anodes is limited by their low initial Coulombic efficiency (CE), large volume change, and poor cyclability.^{5,13–16} For instance, SnO₂ has a high theoretical specific capacity of 1494 mA h g⁻¹ but suffers from poor conductivity and severe pulverization caused by a 358% volume change during the charge/discharge process.^{10,17–19}

To enhance the electrochemical performance of MOs, various methods were explored, such as reducing the particle size and fabricating carbonaceous composites.^{20,21} In the composite, advanced carbon sources such as graphene and carbon nanotubes (CNTs) were used as highly conductive agents. For example, Mn_3O_4 nanoparticles were grown on graphene via a two-step reaction. The capacity of the synthesized Mn_3O_4 /graphene could reach the theoretical value of the oxide.²² Dong et al. reported SnO_2 particles fixed on graphene nanosheets with a polyaniline layer, for

which a reversible capacity of 700 mA h g⁻¹ was achieved at 200 mA g^{-1,23} An ultrafine and highly dispersed nano-SnO₂/ CNT hairball composite was prepared by spray drying and the subsequent solvothermal treatment, demonstrating a capacity of 809.2 mA h g⁻¹ after 100 cycles at 200 mA g⁻¹.²⁴ Although these nanocomposites can reach high capacities, the unprotected MO might agglomerate on the surface of the graphene or nanotube, which is detrimental to its long-term stability. Liu et al. described an ultrasonication-assisted process used to encapsulate SnO₂ nanoparticles in the channels of CNTs. The formed composite delivered a capacity of 400 mA h g⁻¹ at 1 A g^{-1,25} but loading of SnO_2 is limited to 30 wt % by the channel volume. Electrospinning offered a versatile and powerful tool to synthesize MO/C nanocomposites. For example, a Ni-added SnO₂/carbon nanofiber composite was synthesized via electrospinning, showing a stable capacity of 447.6 mA h g⁻¹ at 50 mA g⁻¹ over 100 cycles.²⁶ Zhou et al.

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Figure 1. Schematic illustration of the preparation process of SnO_x/N -CF. (a) Cellulose fiber, (b) microfibril, (c) microfibril/ $SnCl_2$, (d) microfibril/ $Sn(OH)_2$ /urea, and (e) SnO_x/N -CF.



Figure 2. Characterization of SnO_x/N -CF and SnO_x/CF . (a,b) SEM and (c) TEM images of SnO_x/N -CF, (d) HRTEM image of SnO_x/N -CF, (e) STEM of SnO_x/N -CF and the corresponding element mapping images of (ii) carbon, (iii) nitrogen, (iv) tin, and (v) oxygen, and (f,g) SEM and (h) TEM images of SnO_x/CF .

reported the synthesis of hollow core—shell SnO_2/C fibers by electrospinning that delivered a capacity of 833 mA h g⁻¹ at 0.6 A g⁻¹ after 500 cycles.²⁷ However, the scale-up of the process was hindered by the sophisticated electrospinning devices. Herein, we demonstrate a general facile process for the synthesis of a $\text{SnO}_x/\text{carbon}$ nanocomposite. The SnO_x nanoparticles (<25 nm) are evenly encapsulated in the nitrogen-doped carbon fiber (N-CF) because of structure confinement of the cellulose microfibrils. As the anode of LIBs, the obtained $\text{SnO}_x/\text{N-CF}$ has a remarkable electrochemical performance, exhibiting ultrahigh capacities of 1011.0 mA h g⁻¹ at 0.5 A g⁻¹ and 581.8 mA h g⁻¹ at 5 A g⁻¹. This material can retain 100.7% capacity after 900 cycles at 5 A g⁻¹. In addition, this strategy is effective for the synthesis of other MO/carbon nanofibers, such as Fe_2O_3 and MnO_2 , for use as high-performance anode materials.

RESULTS AND DISCUSSION

Synthesis, Characterization, and Structural Analysis. The synthesis process of the $\text{SnO}_x/\text{N-CF}$ nanocomposites is illustrated in Figure 1. In the process, cellulose fibers (Figure 1a), a low-cost and eco-friendly bioresource, are chosen as the carbon source. First, the cellulose fibers in commercially available filter paper were mechanically stirred into flat microfibrils (Figure 1b). In the stirring process, the primary and secondary walls of the plant fiber were exfoliated to liberate the microfibrils.²⁸ After exfoliation, the thickness of the microfibrils was dramatically reduced, as was manifested by the



Figure 3. Schematic illustration of the formation mechanism of SnO_x nanoparticles in SnO_x/N -CF (a) and in SnO_x/CF (b). The absorbing process of SnO_2 on the N-doped carbon surface (c) and carbon surface (d).

notable expansion after the filter papers were exfoliated and freeze-dried into a microfibril sponge, as shown in Figure S1. The microfibril is composed of cellulose nanofibers with crystalline (60-70%) and amorphous regions (30-40%),^{29,30} and the latter can easily swell in solvents such as water, ethanol, and dimethylformamide (DMF). The in situ morphologies (Figures S2 and S3) of the microfibrils before and after swelling in the abovementioned solvents were revealed using an optical microscope. The width of the microfibril underwent 134, 115, and 104% expansion after swelling in DMF, water, and ethanol, respectively. Among these solvents, DMF had the highest swelling rate, and thus, DMF was chosen as the swelling agent. To incorporate the MO, the obtained microfibrils were swelled in the DMF solution with SnCl₂ for 40 min at 70 °C. After hydrolyzation in water, the microfibril/ $Sn(OH)_2$ composite (Figure 1d) was obtained. The swelled microfibrils were then further soaked in a urea (CH_4N_2O) solution,³¹ and after they were dried and carbonized, Sn(OH)₂ turned into SnO_x particles encapsulated in the CF. Additionally, nitrogen was doped into the CF because of the decomposition of urea. As a result, SnO_x/N -CF (Figure 1e) was obtained.

The morphology of the SnO_x/N-CF nanocomposite is revealed in its scanning electron microscopy (SEM) image (Figure 2a,b). Most of the morphological features are flat fibers with a typical thickness of ~ 100 nm (Figure S4). Only a few nanoparticles appear on the surface of the fibers. The transmission electron microscopy (TEM) image (Figure 2c) indicates that the fiber is filled with 10-25 nm nanoparticles. The high-resolution TEM (HRTEM) image (Figure 2d) further shows that the nanoparticles with lattice fringes of 0.33 and 0.30 nm are SnO₂ and SnO, respectively. This observation is consistent with the X-ray diffraction (XRD) pattern which indicates that SnO₂ and SnO coexist (Figure S5). However, a small amount of metallic Sn is also detected because of the reduction of carbon.²¹ The average crystallite size of SnO_r in SnO_{x}/N -CF is ~12 nm, as determined with the Scherrer equation based on the peak width of the XRD pattern.³² To investigate the ratio of Sn, SnO, and SnO₂ in the composite, Xray photoelectron spectroscopy (XPS) tests were conducted. The XPS analyses (Figure S6) indicate that the $SnO_x/N-CF$ sample contains the elements Sn, N, O, and C. The content of N elements is calculated as approximately 2.44 wt %. The peaks of 495.65 and 487.15 eV are ascribed to Sn 3d_{3/2} and $3d_{5/2}$ of Sn^{2+} , respectively, and the peaks of 495.1 and 486.65 eV can be assigned to Sn $3d_{3/2}$ and $3d_{5/2}$ of Sn⁴⁺, respectively. The Sn⁰/Sn²⁺/Sn⁴⁺ ratio is estimated as 15:62:23 with XPS

analysis. Thermogravimetric analysis (TGA) was conducted to estimate the percentage of SnO_r in the SnO_r/N -CF composite. A weight loss of ~8.5% below 100 °C may be caused by chemisorbed water, and a loss of \sim 46.3% within a temperature range of 100-580 °C is due to oxidation of carbon by air (Figure S7). The weight slightly increases from 580 to 690 $^{\circ}$ C, which might be ascribed to the oxidation of SnO or Sn.³³ Therefore, the SnO_x content in the SnO_x/N-CF is estimated as ~44.5 wt %. Furthermore, the scanning TEM (STEM) image and related elemental mapping (Figure 2e) of the SnO_x/N-CF indicate that Sn, N, O, and C elements are evenly distributed in the composite fibers. These results confirm that nitrogen is successfully doped into the carbon structure. For comparison, a SnO_x/CF nanocomposite (SnO_x/CF) without nitrogen doping was also synthesized, and Figure 2f,g shows the SEM images of the nanocomposite. It can be clearly observed that ~500 nm SnO_x particles are scattered on the surface of the CF, and nanoparticles are minimally observed inside the CFs, as shown in its TEM image (Figure 2h). This "sweating" phenomenon was also observed in previous studies in which the cellulose fiber without nitrogen doping was used as the template.³⁴ Thus, nitrogen doping dramatically influences the morphology of the nanocomposite. The mechanism for the formation of homogenous SnO_x nanoparticles inside the fiber-like SnO_x/N -CF is illustrated in Figure 3. During the swelling process, urea and the oxide precursor enter the amorphous region of the cellulose nanofiber. After carbonization, nitrogen atoms (as heteroatoms in the carbon structure) can easily absorb SnO_x because of the interaction between N and Sn atoms, thus supplying plenty of active sites for the nucleation and growth of SnO_x nanoparticles.^{13,35–37} In addition, the growth of SnO_x particles is partially limited by the size of the amorphous region among the cellulose nanofibers. Thus, the growth of SnO_r nanoparticles is somehow confined by the biostructure of the nanofiber. SnO_x nanoparticles with a small size are formed inside the fiber, as shown in Figure 3a. However, in an allcarbon structure, such active sites do not exist. The surface energy between the carbon layer and oxide nanoparticles is large. As a result, the nanoparticles with large size are expelled out of the carbon structure, as illustrated in Figure 3b. To further understand the growth of SnO₂ molecules on the Ndoped carbon, the absorption energy of SnO₂ on carbon or N4-doped carbon, as a typical defect, is calculated as follows

$$\Delta E = E_{\text{C.nNSnO}_2} - E_{\text{SnO}_2} - E_{\text{C.nN}} \tag{1}$$

where $E_{C_{1}NN_{SnO_{2}}}$ is the total energy of C_0N_SnO₂ and C_4N_SnO₂, $E_{SnO_{2}}$ is the energy of the SnO₂ molecule, and

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Figure 4. Electrochemical performance of $\text{SnO}_x/\text{N-CF}$ compared with that of the SnO_x/CF composite. (a) CV curves at 0.1 mV/s from 0.01 to 3 V, (b) charge/discharge curves at 0.2 A g⁻¹ at the first, second, third, and fifth cycles of the $\text{SnO}_x/\text{N-CF}$ electrode, (c) rate cycle performance of $\text{SnO}_x/\text{N-CF}$ and SnO_x/CF composites at various current rates from 0.2 to 15 A g⁻¹, (d) cycling performance of $\text{SnO}_x/\text{N-CF}$ and SnO_x/CF composites at a current density of 0.5 A g⁻¹, and (e) long-term cycling performance of $\text{SnO}_x/\text{N-CF}$ at 5 A g⁻¹. (f) Nyquist plots of SnO_x/CF and SnO_x/CF at 5 A g⁻¹. (f) Nyquist plots of SnO_x/CF and SnO_x/CF at 5 A g⁻¹. (f) Nyquist plots of SnO_x/CF and SnO_x/CF and SnO_x/CF at SnO_x/CF at SnO_x/CF and SnO_x/CF at SnO_x/CF and SnO_x/CF and SnO_x/CF at SnO_x/CF and SnO_x/CF and SnO_x/CF and SnO_x/CF at SnO_x/CF at SnO_x/CF and SnO_x/CF and SnO_x/CF at SnO_x/CF at SnO_x/CF and SnO_x/CF and SnO_x/CF and SnO_x/CF and SnO_x/CF at SnO_x/CF at SnO_x/CF at SnO_x/CF at SnO_x/CF and SnO_x/CF at SnO_x/CF at SnO_x/CF at SnO_x/CF at SnO_x/CF and SnO_x/CF at SnO_x/CF

 $E_{C nN}$ is the energy of C_0N and C_4N, where n = 0 and n = 4indicate the carbon surface with and without 4N doping, respectively. Herein, we chose the P-N4 model for calculation because the defect model is generally accepted and used in density functional theory (DFT) studies for single-atom catalysts,^{38,39} which are prepared via a route similar to our methods. The ΔE of SnO₂ on the 4N-doped carbon surface is -0.98 eV. The binding energy of SnO₂ on carbon-N4 is negative, indicating that this reaction is exothermic and occurs spontaneously. SnO₂ seeds form on the N-doped carbon surfaces via chemical bonding. The chemical bonds make the N-Sn bonds shorter than 2.38 Å, as indicated in Figure 3c. Density of states (DOS) is also used to identify the features of C-Sn and N-Sn bonds. For C 0N SnO₂ without Nsubstitution, only the DOSs of Sn and O are superimposed, which means that only the Sn-O bond can be detected and no reaction occurs between C and Sn atoms, as shown in Figure S8b. Moreover, the states near the Fermi level come from the carbon atoms. For C_4N_SnO₂ with 4N doping (Figure S8a), the DOSs of N, O, and Sn are highly overlapping, which indicates the transfer of electrons between these three atoms and the formation of covalent bonds between N and Sn. Furthermore, the N atoms contribute to the states near the Fermi level as well, which means that the lone-paired N atoms can be used to increase the conductivity and absorption

activity, while the ΔE of SnO₂ on the carbon surface is calculated as 0.48 eV. The positive energy implies that the adsorption of SnO₂ on carbon without defects is endothermic, resulting in metastable states that only belong to the van der Waals force or polar effect. The distance between the C and Sn atoms is ~3.28 Å, which is too long for chemical bonds, and only physical adsorption can be expected.⁴⁰ This weak bonding makes the formation of SnO₂ seeds impossible on the carbon surface at high temperature. The Sn content in the SnO_x/CF is estimated to be higher than that in SnO_x/N-CF based on XRD analyses (Figure S5). The existence of urea suppresses the formation of Sn and might also be helpful in promoting the even distribution of annealed products in the SnO_x/N-CF composite.

Electrochemical Performance. Figure 4a shows the cyclic voltammetry (CV) curves of the $\text{SnO}_x/\text{N-CF}$ electrode for the initial five cycles from 0.1 to 3.0 V at 0.2 mV s⁻¹. Two distinct peaks at 0.7 and 0.2 V appear during the initial cycle but vanish in the following cycles, which is normally the result of solid electrolyte interphase (SEI) film formation, the reduction of SnO_x to metallic Sn, and partial irreversibility of lithium oxide.^{5,41,42} In the subsequent cycles, the well-defined cathodic peaks at 0.27 and 0.56 V are related to lithium alloying with Sn. The distinct anodic peaks at 0.67, 0.75, and 0.82 V correspond to the delithiation process of Li_xSn.^{24,43,44}



Figure 5. (a) SEM image of SnO_x/N-CF/CNT and (b) cycling performance of the SnO_x/N-CF/CNT electrode at 0.2 C.

The anodic peaks at 1.23 and 1.88 V are attributed to the partially reversible reaction of Sn to SnO_2 .^{45,46} The entire process is described by eqs 2 and 3. Near 2.95 V, an intense peak occurs in the CV curves of the first oxidation cycle, which might be on account of the side reactions between the electrolyte and the surface of the amorphous carbon.⁴⁷ The peak at approximately 0.27 V becomes more dominant during the following cathodic process, which indicates an activated electrochemical process.¹⁷ In addition, the CV curves of the second to the fifth cycles are consistent with each other, demonstrating the excellent reversibility of the charge/ discharge process in the SnO_{*}/N-CF electrode.

$$\text{SnO}_{x} + 4\text{Li}^{+} + 4e^{-} \rightleftharpoons \text{Sn} + 2\text{Li}_{2}\text{O}$$
 (2)

$$\operatorname{Sn} + \operatorname{Li}^{+} + x e^{-} \rightleftharpoons \operatorname{Li}_{x} \operatorname{Sn} \qquad (0 \le x \le 4.4)$$
(3)

The galvanostatic charge/discharge curves of the SnOx/N-CF electrodes at 0.2 A g^{-1} are displayed in Figure 4b. Voltage plateaus corresponding to the oxidation and reduction peaks in the CV curves can be attributed to the lithiation/delithiation processes. The charge and discharge capacities of the first cycle are 1182.6 and 1428.7 mA h g⁻¹, respectively, resulting in an initial CE of 82.8%. The large irreversible capacity loss of the SnO_v/N-CF can be related with the SEI film's formation and the partial irreversibility of lithium oxide. The charge and discharge capacities in the fifth cycle decrease to 922.1 and 960.7 mA h g^{-1} , respectively, which corresponds to a CE of 95.98%. Figure 4c displays the rate performance of the $SnO_x/$ N-CF and the SnO_x/CF composite electrodes at various current densities. The SnO_x/N-CF electrode delivers rate capacities of 1049.5, 856.5, 733.6, 656.2, 618.4, 508.3, 366.7, and 256.6 mA h g^{-1} at 0.2, 0.4, 1, 1.6, 2, 5, 10, and 15 A $g^{-1},$ respectively. Obviously, SnOx/N-CF exhibits a much higher reversible capacity than the SnO_x/CF composite (220.9 mA h g^{-1}) at a current density of 5 A g^{-1} . However, at a lower current density of 0.5 Å g^{-1} , SnO_x/N-CF delivers a higher capacity of 715.9 mA h g^{-1} . Figure 4d shows the cyclic performance of the SnO_x/N-CF and the SnO_x/CF composites at 0.5 A g^{-1} . SnO_x/N-CF exhibits a high specific capacity of 1011.0 mA h g^{-1} and excellent cycling stability after 230 cycles. Because the N-CF remains at approximately 380 mA h g⁻¹ after 200 cycles at 0.5 A g^{-1} , as shown in its long-term cycling performance (Figure S9), it contributes ~21% of the overall capacity. Although the SnO_x/CF composite also exhibits good cycling stability, it displays a lower specific capacity of 369.1 mA h g^{-1} . The long-term performance of the electrode is also investigated. The electrode was cycled at a specific current of 0.5 A g^{-1} for 95 cycles followed by 900 cycles at a specific current of 5 A g^{-1} (Figure 4e). Under these conditions, the electrode shows a discharge capacity of 721.6 mA h g^{-1} with 110.0% (793.5 mA h g^{-1}) capacity retention after 95 cycles at 0.5 A g^{-1} . Remarkably, the specific capacity can reach 581.7 mA h g^{-1} at 5 A g^{-1} and remain at 100.7% (577.7 mA h g^{-1}) after 900 cycles. The increasing capacity of the SnO_x/N-CF nanocomposite might be ascribed to the following reasons. The activation process of the electrode materials facilitates penetration of the electrolyte into N-CF and supplies additional interfacial charge storage between SnO_x and carbon. Additionally, SnO_x serves as an electrocatalyst which promotes the decomposition of the electrolyte and the reversible reaction, offering additional capacity during charge/discharge ⁻⁵⁰ Figure S10 shows a TEM image of the cycling.⁴ morphologies of the electrodes after cycling. The particles in the electrode become small and more amorphous because of the conversion reaction and alloying/dealloying.

To explore additional details of the electrode kinetic process, electrochemical impedance spectroscopy (EIS) analyses were performed. Figure 4f shows the EIS curves of the Nyquist plots of the SnO_x/N -CF and the SnO_x/CF composite electrodes, which were fitted with the equivalent circuit (inset in Figure 4f). The intercept with the Z (Ω) -axis at high frequency is related with the Ohmic resistance (R_s) , including the resistances of the electrolyte and electrical contact.¹⁴ The semicircle at the high and middle frequency ranges is ascribed to the charge-transfer resistance (R_{ct}) of the SEI film and the internal SnO_x products. A smaller semicircle for SnO_x/N-CF than SnO_x/CF indicates that the $SnO_x/N-CF$ has faster reaction kinetics (Table S2). The specific capacity and capacity retention for the SnO_x/N -CF electrode are much larger than the previously reported values (Table S1) on SnO_2/CNF and SnO_2/C microfibers.^{5,18,23,25,44,51-53} This result could be ascribed to the following reasons: (i) the size of the SnO_r nanoparticle is less than 25 nm, ensuring high kinetics during lithiation. Together with its intimate contact with the conductive carbon matrix, it can exhibit excellent rateperformance. (ii) Because of the encapsulation of the SnO_r nanoparticle in the matrix, it is difficult to lose contact from the collector, but it is easy to form the stable SEI layer. Thus, longterm stability can be maintained. (iii) N doping enhances the conductivity of carbonaceous materials and improves the ion permeability of the carbon layer, contributing to the stability of the SEI film. We also explored the possibility of using the SnO_x/N-CF nanocomposite as the high-loading electrode. A mixture of cellulose microfibrils with urea, SnO_x precursor, and CNT suspension was vacuum-filtered to obtain the film, which was subsequently carbonized to form the SnO_x/N-CF/CNT nanocomposite. The ratio of active materials to CNT is estimated as \sim 9:1, and the SEM image of its microstructure is

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shown in Figure 5a. SnO_r/N -CF is intertwined with CNTs to form a conductive network. The nanocomposite is flexible, as shown in Figure S11. The areal loading of the nanocomposite can reach 13.3 mg cm⁻². The cross-sectional view of SnO_x/N -CF/CNT reveals that the thickness of the electrode is approximately 360 μ m (Figure S12), and at 0.2 C, its capacity can reach 751.7 mA h g^{-1} , equivalent to an areal capacity of 10 mA h cm⁻², as shown in Figure 5b. The capacity can be retained for 30 cycles without obvious decay. These capacities are far beyond the commercial level $(3-4 \text{ mA h cm}^{-2})$. The fibrous CF with diameters of several hundred nanometers and CNTs with diameters of 10-20 nm form the hierarchical interpenetrating network. The structure not only enhances the mechanical flexibility of the electrodes but also facilitates the transport of electrons. Meanwhile, the macropores among the network provide the rapid path for the diffusion and transport of Li^+ in the thick electrode.^{54–56} Thus, the active materials in the electrode can be fully utilized and high areal capacity can be achieved in the composite electrode.

The biostructure confinement strategy is extended to the synthesis of other MO/N-CF. For example, $SnCl_2$ was substituted with ferric nitrate as the MO precursor. The XRD pattern (Figure S13) of the obtained product confirms the formation of the hematite Fe_2O_3 phase. TEM images (Figure 6a,b) further reveal Fe_2O_3 nanoparticles with an average size of 55 nm dispersed in the N-doped CF. These nanoparticles are surrounded by a graphitized carbon layer with an interlayer distance of approximately 0.36 nm (Figure



Figure 6. (a) TEM image of Fe_2O_3/N -CF, (b) HRTEM image of Fe_2O_3/N -CF, (c) STEM image (i) of Fe_2O_3/N -CF and the corresponding element mapping images of (ii) carbon, (iii) nitrogen, (iv) iron, and (v) oxygen, and (d) long-term cycling performance of Fe_2O_3/N -CF at 5 A g⁻¹.

6b).⁵⁷ The formation of the graphitic carbon layer is due to the catalytic effect of the Fe element. The STEM image (Figure 6c) indicates that nitrogen and carbon elements are distributed homogenously in the composite. In addition to solid particles (Figure S14b,c), hollow particles (Figure S14a,d) also exist. The hollow particles might form due to the Kirkendall effect during oxidation of the composite, as suggested in the literature.^{58,59} The formation of such an inhomogeneity should be further investigated. However, these particles are still confined in the carbonized fibers, with the sizes far below those in Fe_2O_3/CF (Figure S15a). Thus, biostructure confinement still works in this case. Fe₂O₃ nanoparticles are absent from the surface of the fiber, as shown in the SEM image (Figure S15b). In contrast, large Fe_2O_3 particles are observed in Fe_2O_3/CF without nitrogen doping. The Fe₂O₃/N-CF electrode shows excellent cycling stability, and it retains a specific capacity of 401.2 mA h g^{-1} at 5 Å g^{-1} after 3000 cycles (Figure 6d). MnO₂/N-CF was also synthesized with a similar biostructure confinement process. As shown in Figure S16, MnO₂/N-CF electrodes exhibit large reversible capacities of 682.4, 530.3, 440.7, 370.1, 298.6, and 247.2 mA h g⁻¹ at 0.2, 0.5, 1, 2, 5, and 10 A g⁻¹, respectively. Although this process can be applicable to the synthesis of many MO/C nanocomposites, the carbon content in the nanocomposite is relatively high, and further work is needed to decrease the carbon content. Thus, the Li storage capacity of the composite can be further increased.

CONCLUSIONS

In summary, we developed a biostructure-confinement approach for the synthesis of fiber-like SnO_x/C nanocomposites using cellulose microfibrils as the template. Because of the space confinement of the amorphous region in the microfibril and the ample nucleation sites supplied by the doped N heteroatom, the size of the SnO_x nanoparticles was confined to below 25 nm. Such homogenously distributed SnO_x encapsulated in a conductive nitrogen-doped carbon matrix contributed to its excellent Li storage capacity. The approach reported in this study can be further extended to the preparation of other fiber-like MO/carbon nanocomposites for potential applications in energy storage and conversion and catalysis.

EXPERIMENTAL SECTION

Synthesis of Cellulose Microfibrils. Filter paper (10 g, Newstar Hangzhou, China) was soaked in deionized water (500 mL) overnight and stirred in a blender for 70 min to form a pulp. The obtained pulp was freeze-dried into microfibrils.

Synthesis of SnO_x/**CF Nanocomposites.** For production of the SnO_x/CF composite, the prepared microfibrils (1 g) were swelled in a homogeneous SnCl₂ DMF solution (40 mL, 0.2 mol L⁻¹) for 40 min at 70 °C. The swollen microfibrils were dipped in acetone for 2 min. After filtering, the microfibrils were hydrolyzed. After washing and freeze-drying at -50 °C in vacuum, the microfibrils/Sn(OH)₂ was obtained. The microfibril/Sn(OH)₂ was preoxidized at 240 °C for 8 h in air.⁶⁰ The resultant composite was heated to 600 °C in nitrogen at 5 °C min⁻¹ and held at this temperature for 5 h to obtain the SnO_x/ CF nanocomposite.

Synthesis of SnO_x/N-CF Nanocomposites. To produce the SnO_x/N-CF composite, the prepared microfibrils (1 g) were swelled in a homogeneous SnCl₂ DMF solution (40 mL, 0.2 mol L⁻¹) for 40 min at 70 °C. The swollen microfibrils were dipped in acetone for 2 min. After filtering, the microfibrils were hydrolyzed. The swelling-treated microfibril/Sn(OH)₂ was subsequently soaked in a 30 wt % urea (CH₄N₂O) aqueous solution for 2 h.³¹ After filtering, washing, and freeze-drying at -50 °C in vacuum, the microfibrils/Sn(OH)₂/

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urea was obtained. The microfibril/Sn(OH)₂/urea was then preoxidized at 240 °C for 8 h in air.⁶⁰ The resultant composite was heated to 600 °C in nitrogen at a rate of 5 °C min⁻¹ and held at this temperature for 5 h to obtain the SnO_x/N-CF nanocomposite. Fe₂O₃/N-CF and MnO₂/N-CF nanocomposites can be obtained by replacing SnCl₂ with ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O] or manganese chloride (MnCl₂), followed by heating at 800 °C for 2 h in a N₂ atmosphere and at 350 °C for 2 h in air.

Synthesis of the SnO_x/N-CF/CNT Nanocomposite. The microfibril/Sn(OH)₂/urea (1 g) was dispersed in a 5.5 mL singlewall CNT (SWCNT) *N*-methyl pyrrolidinone solution (5 mg/mL) under continuous ultrasonication for 3 h. Subsequently, the microfibril/Sn(OH)₂/urea/SWCNT membranes were prepared by vacuum filtration. The membranes were preoxidized at 240 °C for 8 h in air.⁶⁰ The resultant composite was heated to 600 °C in nitrogen at a rate of 5 °C min⁻¹ and held at this temperature for 5 h to obtain the SnO_x/N-CF/CNT nanocomposite. The ratio of active materials to CNT is estimated as ~9:1 because the microfibril/Sn(OH)₂/urea lost three-fourth of its weight after carbonization.

Characterization. The morphology of the product was examined by a scanning electron microscope (Philips XL30 FEG) and a transmission electron microscope (TEM (JEOL JEM-2010). XRD analyses were performed on a Rigaku D/Max-RB diffractometer with Cu K α radiation. TGA was conducted using a Mettler TGA/DSC3+ analyzer at 10 °C min⁻¹ in air. XPS analysis was performed using a Thermo Fisher Scientific K-alpha analyzer.

Theoretical Calculation. DFT analysis was applied to investigate the growth of SnO₂ on N-doped carbon surfaces. All calculations were performed using the Vienna Ab initio Simulation Package (VASP)⁶¹ in this paper, and the exchange and correlation energy functions were treated by the Perdew–Burke–Ernzerhof variant of the generalized gradient approximation.⁶² The interactions between ions and electrons were described with the projector augmented wave pseudopotential approach,^{63,64} and the energy cutoff for the plane wave basis set was set to 500 eV. All calculations were considered in the spin-unrestricted manner. The first Brillouin zone was sampled using a $5 \times 5 \times 1 \Gamma$ -centered *k*-point grid. The vacuum slab was set to 15 Å. As noted in a previous paper,³⁵ pyridinic N carbon is the most possible structure for N-doped carbon. Therefore, in this paper, the structure of N-doped carbon also used 4 pyridinic N doping, as shown in Figure 3c. The lattice parameters of carbon and N-doped carbon were optimized to 9.861 Å (four times 2.645 Å).

Electrochemical Measurement. The electrochemical performance of MO/N-CF was characterized in Li half-cells. The electrode was prepared by mixing 80 wt % active material MO/N-CF, 10 wt % Super P (conductive additive), and 10 wt % sodium alginate (SA, binder) dissolved in the deionized water to form a uniform slurry. The mixture slurry was pasted on copper foil and dried at 80 °C under vacuum for 12 h. The average loading of active materials was 0.6-1 mg cm⁻². The dried electrodes were loaded into an argon-filled glovebox for battery assembly. The counter electrode was lithium foil, and the electrolyte was a 1.0 M LiPF₆ solution in ethylene carbonate/ diethyl carbonate (v/v = 1:1) with 10 wt % fluoroethylene carbonate as the additive. The galvanostatic discharge/charge electrochemical performance was assessed on an automatic battery testing system (LAND CT2001A) at 25 °C. EIS from 1 MHz to 0.1 Hz was recorded at the electrochemical workstation (AutoLab 302N). The specific capacity of the electrode was calculated on the basis of the total weight of the MO/N-CF composites.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c03390.

Detailed information on the digital photograph of the filter paper and microfibril sponge; optical microscopy image of the microfibril before and after swelling; TEM image of $SnO_x@N$ -CF after cycling; XRD pattern of

SnO_x@N-CF and SnO_x@CF; XPS spectrum of SnO_x/ N-CF; TGA curve of SnO_x@N-CF; DOS of N, O, and Sn in C 4N SnO₂ and of C, O, and Sn atoms in C 0N SnO₂; digital photograph of the SnO_x/N-CF/ CNT flexible electrode; SEM images of the cross section of the SnO_x/N-CF/CNT electrode; long-term cycling performance of N-CF at 0.5 A g⁻¹; XRD pattern of Fe_2O_3/N -CF; TEM image of Fe_2O_3/N -CF after cycling; SEM image of Fe₂O₃/CF and Fe₂O₃/N-CF; HRTEM image of nanoparticles in Fe₂O₃/N-CF; rate cycle performance of MnO₂/N-CF; comparison of specific capacity at different rates for the SnO2@N-CF composite electrode with those of the $SnO_2@C_1$ SnO₂@CNT, and SnO₂@graphene composite anodes reported; and simulation values of parameters in an equivalent circuit of the Nyquist plots of the SnO_r/CF and SnO_{*}/N -CF anodes before and after cycling (PDF)

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Author Contributions

Z.B., Y.M., G.W., and G.G. conceived the idea and planned the experiment. D.C., Y.D., R.W., and X.H. conducted the materials synthesis and characterization. All authors co-wrote the manuscript.

The authors declare no competing financial interest.

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