**Fabrication of ultrafine manganese oxide-decorated carbon nanofibers for
high-performance electrochemical capacitors**

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Abstract Ultrafine manganese oxide-decorated carbon nanofibers ($\text{MnO}_n\text{-CNF}$, $1.3 < n < 2.0$) as a new type of electrode materials are facilely fabricated by direct conversion of Mn, Zn-trimesic acid (H_3BTC) metal organic framework fibers (Mn-ZnBTC). The construction and evolution of Mn-ZnBTC fibers are investigated by SEM and *in situ* high-energy XRD. The manganese oxides are highly dispersed onto the porous carbon nanofibers formed simultaneously, verified by TEM, X-ray absorption fine structure (XAFS), Raman, ICP-AES and N_2 adsorption techniques. As expected, the resulting $\text{MnO}_n\text{-CNF}$ composites are highly stable, and can be cycled up to 5000 times with a high capacitance retention ratio of 98% in electrochemical capacitor measurements. They show a high capacitance of up to 179 F g^{-1} per mass of the composite electrode, and a remarkable capacitance of up to 18290 F g^{-1} per active mass of the manganese(IV) oxide, significantly exceeding the theoretical specific capacitance of manganese(IV) oxide (1370 F g^{-1}). The maximum energy density is up to 19.7 Wh kg^{-1} at the current density of 0.25 A g^{-1} , even orders higher than those of reported electric double-layer capacitors and pseudocapacitors. The excellent capacitive performance can be ascribed to the joint effect of easy accessibility, high porosity, tight contact and superior conductivity integrated in final $\text{MnO}_n\text{-CNF}$ composites.

Keywords: Manganese oxide; Carbon nanofiber; Assembly; *In situ* synthesis; Supercapacitor

1. Introduction

The increasing demand on environmentally benign, high-performance energy-storage systems has stimulated intense research interest in areas such as batteries and capacitors [1]. Supercapacitors have emerged as one of the most promising candidates for energy storage as they can provide a higher power density than batteries, and a higher energy density than conventional dielectric capacitors. And thereby their applications are widely shown in consumer electronics, energy management, memory back-up system, industrial power and mobile electrical systems [2]. To be competent for these applications, the improvement of the capacitive performance, as well as the decrease of the fabrication cost for electrode materials, is the essential criteria. In the search for appropriate materials for supercapacitor electrodes, various carbons, conducting polymers and transition metal oxides have been extensively investigated [3]. Among them, the manganese oxides prove to be promising for next generation supercapacitors owing to its low cost, environmental compatibility and high specific capacitance [4]. However, the capacitance of manganese oxides cannot be achieved intrinsically due to **their** large size and poor dispersion, and they usually suffer from inferior stability, low conductivity and large volume change during the charge/discharge processes. To overcome these drawbacks, fabrication of ultrafine manganese oxides and combination of them with porous carbons would be the solution.

Among various carbonaceous materials, one-dimensional (1D) nanostructured

carbon nanofibers (CNF) exhibit superior thermal and electrical conductivity, and shorter diffusion paths for electrons and ions during the electrochemical process [5]. And therefore the metal oxide composites based on the strengthened carbon nanofibers have been widely investigated. Recent advances in the fabrication of metal oxide-carbon nanofiber composites focus on a *post*-synthetic procedure, in which the carbon nanofibers are *pre*-synthesized by a chemical vapor deposition (CVD), catalytic CVD (CCVD) or electrospinning method, followed by impregnation and reduction of metal salts [6-8]. Such a tedious synthesis renders loosely attached metal oxides, which are randomly distributed on the external surface or near the pore mouth, eroding the reactivity and stability of composite materials finally. To replace such “low efficient” preparations, pyrolysis of electrospun fibers within metal and carbon precursors proves to be effective to construct evenly dispersed metal oxides firmly attached onto the carbon nanofibers [9-10]. However, the resulting composites often possess an extremely low surface area and porosity, though some pore-forming reagents, including surfactants and silica assistants, are often involved [11-13], which largely limits the power capacity. Facile fabrication of high-performance ultrafine metal oxide-carbon nanofiber composites still remains challenging.

Herein, we report ultrafine manganese oxide-decorated carbon nanofibers (MnO_n-CNF) as a new type of electrode materials fabricated by a facile synthesis. By optimizing the assembly time, Mn, Zn-containing metal organic framework fibers were skillfully constructed by assembly of MnCl₂·4H₂O and Zn(Ac)₂·2H₂O and trimesic acid (H₃BTC) in the presence of N,N-dimethylformamide (DMF), and were

then directly converted to $\text{MnO}_n\text{-CNF}$ after pyrolysis. This facile fabrication integrates some merits, including easy accessibility, high porosity, tight contact and superior conductivity in final $\text{MnO}_n\text{-CNF}$ composites. And thus the $\text{MnO}_n\text{-CNF}$ composites exhibit an ultra-high specific capacitance up to 18290 F g^{-1} per active mass of manganese(IV) oxide, and can be cycled up to 5000 times with a high capacitance retention ratio of 98% during the electrochemical capacitor test. Meanwhile, the high energy density are comparable to or higher than high-end commercially available supercapacitors. These results demonstrate that the $\text{MnO}_n\text{-CNF}$ composite exhibits great potentials as an efficient electrode material for supercapacitors.

2. Experimental section

2.1. Preparation of manganese oxide-decorated carbon nanofibers.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and H_3BTC were used as precursors for the synthesis of Mn, Zn-containing metal organic framework fibers in the presence of DMF. The molar ratio of the precursor mixture used in the preferred preparation is 6 H_3BTC : 5(1-x) $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$: 5x $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$: 650 DMF, where x represents the Mn molar percentage in **total metals of Mn and Zn in the synthetic mixture**, and was set to be 0, 0.025, 0.050, 0.100 and 0.500%. Typically, a certain amount of metal salts combined with 1.25 g of H_3BTC were dissolved in 50 mL of DMF under constant agitation, and were then solvothermally treated at 140°C for 750 min. The resulting precipitate was collected after decanting the mother liquor, rinsing with DMF and drying under vacuum, and was denoted as 100xMn-ZnBTC. Then the

100xMn-ZnBTC fiber was placed in a quartz boat, flushing with N₂ flow, and heated in a tube furnace up to 950 °C at a rate of 5 ° min⁻¹ and maintained at this temperature for 2 h, yielding the manganese oxide-carbon nanofiber composite, 100xMnO_n-CNF. In addition, the *post-synthetic* 0.100MnO_n-CNF-p and mechanically mixed 0.100MnO₂+CNF were also prepared for comparison (Supporting Information).

2.2. Characterization

SEM analysis was performed on a FEI-Quanta 200F field-emission scanning microscope operated at 15 kV with an EDS detector. The TEM images, selected area electron diffraction (SAED) patterns, high angle annular dark field scanning TEM (HAADF-STEM) images and elemental maps were recorded using a FEI Tecnai G2 F20 transmission electron microscope equipped with an energy dispersive X-ray spectroscopic analyzer operated at a voltage of 200 kV. Samples were sonicated in EtOH for 5 min, and one drop of the suspended sample was dripped in a holey carbon microgrid supported on a 300 mesh copper grid. N₂ adsorption/desorption isotherms were recorded at 77 K using a JW-BK222 static volumetric gas adsorption instrument manufactured by Beijing JWCB Sci. & Tech. Co., Ltd. Before measurements, the samples were de-gassed at 300 °C for 3 h in vacuum. The specific surface area was determined by using the Brunauer-Emmett-Teller (BET) method and the mesopore size distribution was measured by using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms. *In situ* synchrotron X-ray diffraction measurements were performed at the 11-ID-C beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. High-energy X-rays

of 115 KeV energy and $0.6 \text{ mm} \times 0.6 \text{ mm}$ beam size were used to obtain two-dimensional (2D) diffraction patterns in the transmission geometry using a Perkin-Elmer large area detector placed at 1.6 m from the sample. X-ray absorption fine structure (XAFS) was carried out on the 12-BM-B beamline of APS at Argonne National Laboratory. The XAFS data were obtained in the fluorescence mode at the Mn K-edge (6539.0 eV). The XAFS data were processed using the Athena software for background removal, *post*-edge normalization and X-ray absorption near edge structure (XANES) analysis. The oxidation states were determined by comparing the inflection point of the edge to that of standards with a known oxidation state. The extended X-ray absorption fine structure (EXAFS) was analyzed using Artemis software, which implemented FEFF. The EXAFS data reduction was conducted by utilizing the standard procedures. The EXAFS function, χ , was obtained by subtracting the *post*-edge background from the overall absorption and then normalized with respect to the edge jump step. Subsequently, k^3 -weighted $\chi(k)$ data in k space were Fourier transformed to those in r space to separate the EXAFS contributions from different coordination shells. However, fitting the Mn local structure was not successful because the error of coordination numbers is always larger than 10%. Raman spectra were recorded using a HORIBA Jobin Yvon HR800 instrument with a microscope attachment. A laser wavelength of 633 nm wavelength was focused using a diffraction limited spot, and the scan time was 2 s for each sample.

The Mn dosage was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis conducted on a Perkin Elmer emission spectrometer.

Certain amount of vacuum-dried sample was placed in a crucible and heated at 600 °C for 8 h in air. The residue was then dissolved in 3 mL of aqua fortis solution, and each solution was filtered through a 0.45 µm polyethersulfone filter and set the constant volume to be 10 mL, and then submitted for analysis.

2.3. Electrochemical test

Electrochemical measurements were performed *via* a conventional three-electrode system in a 6 M KOH-distilled water electrolyte, which were performed using a CHI660D electrochemical workstation. The Hg/Hg₂Cl₂ electrode was used as a reference electrode, and Pt as a counter electrode. The working electrode slurries containing the MnO_n-CNF composite synthesized, acetylene black and polytetrafluorethylene at a weight ratio of 7: 2: 1 were painted on a nickel foam for electrochemical characterization. The Ni foam has a surface area of 1 cm² and then the pressure of 3 MPa was applied. The electrochemical properties were tested by cyclic voltammetry (CV) and galvanostatic charge-discharge (the potential window in the range of -1.0 to 0 V *versus* Hg/Hg₂Cl₂ electrode), and electrochemical impedance spectroscopy (frequency range between 1 mHz and 10³ kHz). The electrochemical specific capacitance (C_m) of the electrode material was determined as follows:

$$C_m = \frac{C}{m} = \frac{S}{2UVm}$$

in which C_m is the gravimetric specific capacitance of electrode material (F g⁻¹), C is the capacitance (F), m is the mass of electrode material (g), S is the integrated area of the CV curve, V is the scan rate (mV s⁻¹) and U is the potential window (V). The

pseudocapacitance due to the manganese(IV) oxide (C_{MnO_2}) in the composite has been calculated by subtracting the electrochemical double layer capacitor (EDLC) capacitance contributed by the pure CNF substrate according to the following equation:

$$C_{MnO_2} = (C_m - C_c \times C\%)/Mn\%$$

Where C_c is the specific capacitance of pure CNF, and $C\%$ and $Mn\%$ are the weight percentages of CNF and MnO_2 in the composites.

The energy density and power density were estimated, using the following equations:

$$E = \frac{1}{2} \times C_m \times (\Delta V)^2$$

$$P = \frac{E}{\Delta t}$$

where ΔV (V) refers to the potential change within the discharge time Δt (s), E ($J g^{-1}$) refers to the energy density, P ($W g^{-1}$) corresponds to the average power density.

3. Results and discussion

3.1. Synthesis

The schematic diagram in Fig. 1 shows the preparation process of MnO_n -CNF composites. To illustrate the growth progress of Mn, Zn-containing metal organic framework fibers (Mn-ZnBTC), SEM was employed to monitor the time-dependant morphology of the representative 0.100Mn-ZnBTC (0.100% of Mn molar percentage). In terms of uniform hexagonal plates crystals (seed crystals, 1 min) displayed in Fig. 2, the size of these plates increases when the reaction time is prolonged to 5 min. When the reaction is proceeded for 10-60 min, these plates become smooth and compact,

and their size is further increased. As the reaction time is extended to 240 min, prism-like fibers with a length of up to 10 μm start to form, originated from the piled hexagonal plates along the (100) direction. However, these hexagonal plates are loosely connected because the gap between two plates exists. Longer fibers are produced as the reaction time is extended to 480 min, and the hexagonal cross-section is transformed to a circular one. Based on these observations, the initially formed 2D hexagonal plates are stacked up to 1D fibers, and further grow into smooth and uniform fibers when prolonging the reaction time. So in our experiment, the Mn-ZnBTC fibers were successfully constructed by assembly of metal salts with H_3BTC struts in DMF for 750 min. And then *one-pot* conversion was employed to transform Mn-ZnBTC fibers to MnO_n -CNF composites under N_2 atmosphere (Fig. 1).

To determine the proper temperature for this *one-pot* conversion, the transformation of Mn-ZnBTC fibers during pyrolysis was investigated by *in situ* high-energy X-ray diffraction (XRD) study. As illustrated in Fig. 3a, the starting material displays a set of *rutile*-structured ($P4_2/mnm$) diffractions in the 2θ range of $0.3\text{--}3^\circ$ [14]. These diffractions become weak at 150°C , indicating the initial decomposition occurred. And they are completely vanished at *ca.* 500°C , suggesting the decomposition was completed. At 500°C , the graphitic carbon starts to form (JCPDS No. 41-1487), showing the characteristic diffractions at 0.4° [15]. Meanwhile, the wurtzite ZnO (JCPDS No. 36-1451) is initially formed, showing a series of diffractions ranging from 2.0° to 4.5° [16], represented by the filled cycles (Fig. 3b). The increased intensity below 700°C indicates more ZnO formed, while the decreased

intensity above 700 °C implies the reduction of ZnO to metallic Zn and its further volatilization occurred (Fig. 3a). A fraction of ZnO still remains because the rapid cooling was employed once the temperature reaches to 950 °C, which can be completely removed by prolonging the pyrolysis time. It is noteworthy that the lattice parameters of ZnO are temperature dependent, and the increase in temperature leads to the expansion of lattice (Fig. 3b), as reported by Banerjee and coworkers [17]. Moreover, the manganese oxides, mainly Mn₃O₄ and MnO₂ (unified into MnO_n, $1.3 < n < 2.0$), start to emerge at *ca.* 650 °C, as illustrated by the presence of diffraction peaks of Mn₃O₄ (JCPDS No. 24-0734) at 2.5° and MnO₂ (JCPDS No. 44-0141) at 3.2°, 3.8° and 4.5° [18]. The intensity of these diffraction peaks increases as the temperature was elevated from 650 to 950 °C (Fig. 3b), implying the growth of manganese oxides. Based on these investigations, the strategy of pyrolysis at 950 °C for 2 h was carried out to transform Mn-ZnBTC fibers to MnO_n-CNF composites. This fabrication is quite facile without the need of expensive apparatus or the assistance of pore-forming reagents and extra carbon precursors.

The above results help us understand the fabrication process for MnO_n-CNF composites. First, Mn²⁺ and Zn²⁺ ions coordinated with H₃BTC struts in the presence of DMF, and they assembled into 2D hexagonal plates and then were stacked up into 1D fibers under solvothermal conditions. During the assembly process, the fibrous morphology and the metal dispersion are preset in the Mn-ZnBTC fibers. The following high-temperature pyrolysis at 950 °C is a unique “one stone, three birds” strategy for transformation of Mn-ZnBTC fibers to MnO_n-CNF composites. Gradual

loss of hydrogen, oxygen and carbon occurred when heated, and the H₃BTC struts were converted to inorganic carbons. The anchored Mn species, which bind several oxygens from H₃BTC struts, were *in situ* reduced in the presence of the liberated gas (H₂, CO, *etc.*) and the formed carbon, yielding manganese oxides (MnO_n). Meanwhile, the *in situ* formed ZnO acted as a template to consolidate the carbonaceous network, which was reduced to Zn metal above 700 °C in the presence of carbon, and was then removed when heated to 908 °C (b.p. of Zn). It is worth mentioning that Zn²⁺ species are more inclined to reduce than Mn²⁺ species, because Zn²⁺/Zn has a higher electrode potential (-0.7618 eV) than Mn²⁺/Mn (-1.185 eV). In this case, ZnO is easily reduced to Zn, while the formed manganese oxide remains. Moreover, the vaporization of Zn metals, and the decomposition of crystalline MOFs would create carbon nanofibers within high porosity.

3.2. SEM and TEM studies

SEM and TEM observations were first employed to verify the formation of Mn-ZnBTC fibers, which is the prerequisite to fabricate MnO_n-CNF composites. As illustrated in Fig. 4a, the SEM image of representative 0.100Mn-ZnBTC exhibits uniform fibers, and displays an average diameter of *ca.* 100 nm and a length of 5-10 μm. These fibers have a prism-like shape, showing some defects on the surface (Fig. 4b). TEM, HAADF-STEM and elemental maps show that these fibers are stuffed (Fig. 4c) and uniform (Fig. 4d), and C, O, Zn and Mn elements are evenly distributed throughout the whole fiber (Fig. 4e), further confirming that the formed 0.100Mn-ZnBTC fibers are homogeneous. It is noteworthy that O and Zn elements

are more dense, in accordance with the SEM-EDX result (Fig. S1), suggesting the predominance of Zn_4O secondary building units in 0.100Mn-ZnBTC fibers. By varying the Mn molar percentage in the range of 0.025-0.500%, different Mn, Zn-containing metal organic framework fibers can be synthesized, showing essentially similar appearance and dimensions (Fig. S2a-d) to 0.100Mn-ZnBTC. They are well separated without agglomeration, and have lengths ranging from several to tens of micrometers and diameters from tens to several hundred nanometers.

Being pyrolyzed, the parent fibrous morphology is inherited in the resulting 0.100MnO_n-CNF composite (Fig. 4f). However, these fibers are slightly contracted, and their cross-sections are fluffy (Fig. 4g). No aggregation can be observed, implying a well-dispersed configuration. TEM observation reveals that these nanofibers display a dark and bright appearance, and are intercrossed into a web (Fig. 4h). The HAADF-STEM image of a single nanofiber shows that the surface is rugged, and the manganese oxides are hardly observed (Fig. 4i), though the elemental maps demonstrate the presence of evenly distributed Mn species (Fig. 4j). The above observations lead to a tentative postulation that the Mn species were inserted into the carbon nanofiber in the form of ultrafine MnO_n. High-magnification TEM image shows the nanonodules (*ca.* 5 nm) are periodically distributed on the carbon nanofiber network (Fig. 4k), implying that the tiny MnO_n particles are interconnected. However, only bright diffraction rings assigned to graphitic carbons (Fig. 4l) are shown in the selected area electron diffraction (SAED) pattern [19,20], further confirming the formation of ultrafine MnO_n. Other Mn-ZnBTC fiber derived MnO_n-CNF composites

also show similar appearance and dimensions (Fig. S2e-h) to 0.100MnO_n-CNF. This suggests that the MnO_n-CNF composites can be successfully fabricated from Mn-ZnBTC fibers by tailoring the Mn molar percentage ranging from 0.025 to 0.500%.

3.3. XAFS study

To further reveal the formation of ultrafine MnO_n, the elemental specific X-ray absorption fine structure (XAFS) was employed to investigate the transition and local structure of Mn species. The Mn dosage in final MnO_n-CNF composites is ultra-low, estimated to be 0.09-1.36 wt% by ICP-AES analysis (Table S1). Investigation of such low concentrated Mn species is extremely difficult using lab characterization techniques. XAFS can be competent for this analysis profiting from high flux and intensity of synchrotron radiation light. As illustrated in Fig. 5A, the 0.100Mn-ZnBTC precursor exhibit a extremely strong white line intensity as compared to MnCl₂·4H₂O and MnO₂ standards, implying that the introduced Mn²⁺ species bind to several oxygens from H₃BTC struts, corresponding to the coordination of O→Mn. When pyrolysis, the resulting 0.100MnO_n-CNF composite exhibits a *pre*-edge feature and a negative shift in the adsorption edge position as compared to 0.100Mn-ZnBTC, suggesting that the Mn species are mostly reduced after pyrolysis. These reduced species still carry some positive charges because the edge position shifted positively as compared to that of Mn foil [21]. And the positive charges are larger than +2, since 0.100MnO_n-CNF shows a stronger white line intensity than MnCl₂·4H₂O. Fig. 5B shows the radial distribution curves obtained by Fourier

transformation of the $k^3\chi(k)$ EXAFS spectra. The 0.100MnO_n-CNF composite shows one prominent peak at 1.3 Å from Mn-O pairs and an additional peak at 2.6 Å from Mn-Mn contributions [22], confirming the formation of manganese oxides. The observation that the Mn-O bonding distance is close to that in MnO₂ suggests the strong metal-support interaction, linking to the tight contact between MnO_n and CNF.

3.4. Raman spectroscopy

The amount of graphitic carbons is the indication of conductivity of MnO_n-CNF composites, which affects the electrochemical performance significantly. So Raman spectroscopy was performed to investigate the local structure of carbons (Fig. 6). In the first order Raman spectra of the sp²-carbons, two conspicuous peaks emerge at approximately 1321 cm⁻¹ (D band) and 1591 cm⁻¹ (G band), arising from the disordered carbon structures and the vibration mode to the movement in opposite directions of two carbon atoms in a single graphene sheet [23]. It is generally accepted that the integral area ratio of the “G band” to the “D band” (I_G/I_D) is the indication of graphitization degree. The 0.100MnO_n-CNF shows a largest I_G/I_D value of 0.372 (Table S1), implying the existence of most graphitic components in the carbonaceous network. The variation of I_G/I_D value demonstrates the role of Mn dosage on the conductivity of MnO_n-CNF composites.

3.5. N₂ adsorption study

Low temperature N₂ adsorption was performed to reveal the pore structure. An IV type isotherm with a distinct H₄ type hysteresis loop is observed for both pure CNF and MnO_n-CNF composites (Fig. 7A), implying the mesoporous arrays within slit

pores [24,25]. It is found that the surface area and pore volume vary depending on the Mn dosage. The pure CNF exhibits a BET specific surface area of $1234 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.916 \text{ cm}^3 \text{ g}^{-1}$, lower than those of $\text{MnO}_n\text{-CNF}$ composites (Table S1). This implies that the introduction of Mn species facilitates the improvement of pore structure. The porous parameters are Mn dosage dependent. When increasing the Mn dosage from 0.09 to 1.36 wt%, the surface area and pore volume decrease from $1507 \text{ m}^2 \text{ g}^{-1}$ and $1.129 \text{ cm}^3 \text{ g}^{-1}$ for 0.025 $\text{MnO}_n\text{-CNF}$ to $1366 \text{ m}^2 \text{ g}^{-1}$ and $0.961 \text{ cm}^3 \text{ g}^{-1}$ for 0.500 $\text{MnO}_n\text{-CNF}$ (Table S1). In spite of this, it is noteworthy to mention that our fabricated $\text{MnO}_n\text{-CNF}$ composites exhibit the extremely high surface area and porosity, nearly 10 times of those reported [9-13]. Moreover, all $\text{MnO}_n\text{-CNF}$ composites show a similar pore size around 4.0 nm (Fig. 7B), implying that the manganese oxides are mainly inserted into the carbonaceous network, corresponding to a tight contact. According to these findings, large surface area, high porosity and uniform mesopores are integrated in $\text{MnO}_n\text{-CNF}$ composites, which are expected to be beneficial to the adsorption and diffusion of electrolyte ions.

3.6. Capacitive performance

To explore the energy-storage application of the $\text{MnO}_n\text{-CNF}$ composite, the sample was fabricated into a supercapacitor electrode, and the performance was evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. Fig. 8a shows the CV curves of various samples at a scan rate of 1 mV s^{-1} . The *quasi*-rectangular shapes at potential window ranging from 0 to -1.0 V were observed, suggesting an ideal pseudocapacitive behavior [26]. The absence of redox

peaks suggests that the supercapacitor is charged-discharged at a pseudo-constant rate over the complete voltammetric cycle [4]. The gravimetric specific capacitance is proportional to the integrated CV area. The 0.100MnO_n-CNF composite exhibits a higher specific capacitance of up to 179 F g⁻¹, while CNF, 0.025MnO_n-CNF, 0.050MnO_n-CNF and 0.500MnO_n-CNF have a lower specific capacitance of 116, 140, 158 and 142 F g⁻¹, respectively. This strongly suggests the important role of Mn dosage in the capacitance enhancement. Compared to 0.100MnO_n-CNF, the *post*-synthetic 0.100MnO_n-CNF-p and mechanically mixed 0.100MnO₂+CNF exhibit a much lower specific capacitance of 134 and 114 F g⁻¹, respectively. The superior dispersion of manganese oxides realized by *in situ* synthesis should be responsible for a larger capacitance. The pseudo-capacitance based on manganese(IV) oxide (C_{MnO₂}), calculated based on the literature method [27,28], increases from 16501 F g⁻¹ for 0.025MnO_n-CNF to 18290 F g⁻¹ for 0.050MnO_n-CNF, and then decreases to 1329 F g⁻¹ for 0.500MnO_n-CNF (Table S2). The largest pseudo-capacitance of any MnO_n-based materials was achieved in this study [4,18,26], nearly 14 times of the theoretical specific capacitance of manganese(IV) oxide (1370 F g⁻¹). The highly dispersed MnO_n can be fully utilized due to their ultra-small size and extremely low loading. And thus in such a hybrid configuration, manganese oxides offer an extremely high specific capacitance.

To further investigate the capacitive performance of our samples, galvanostatic charge-discharge (GCD) experiments were performed at a current density of 0.25 A g⁻¹ (Fig. 8b). These curves are linear and symmetric, implying good reversibility and high

charge-discharge efficiency. The discharge time of 0.100MnO_n-CNF is significantly increased as compared to other composites, corresponding to a larger charge capacity. The change of capacitance based on the GCD curves is consistent with that from the cyclic voltammograms (Table S3). Figure S3 shows the GCD curves of 0.100MnO_n-CNF at different current densities. The potential-time profiles maintain a triangular shape even at a high current density, implying that the 0.100MnO_n-CNF is suitable for applications in supercapacitors in which the rapid charge-discharge is required.

The superior 0.100MnO_n-CNF was then subjected to further CV investigation under different scan rates. As shown in Fig. 8c, the specific capacitance decreases by 40% (from 179 to 108 F g⁻¹) as the sweep rate increases from 1 to 100 mV s⁻¹, indicating the excellent mesoporosity. The 0.100MnO_n-CNF composite shows a large surface area and a uniform mesopore size distribution. These properties have allowed a high rate of solution infiltration and facilitated the ion insertion/extraction and electron transportation. The relationship between the capacitance retention ratio and potential scan rate is plotted (Fig. 8d). The minimized capacitance at high scan rate originates from the decreased ion accessible surface areas. The higher the capacitance retention ratio is, the better the ion transport behavior will be. The capacitance retention ratios at 100 mV s⁻¹ are above 60% for both pure CNF and MnO_n-CNF composites, suggesting that such a high capacitance can be maintained under very high power operation.

Electrochemical impedance spectroscopy (EIS) provides important information

about the interfacial properties of electrodes, which was used to examine their conductive and diffusion behavior. The equivalent circuit fitting of the Nyquist plot of 0.100MnO_n-CNF is shown in Fig. 9a. The slope of the curves at a low frequency is called Warburg impedancue (W), which is induced by ion diffusion/transport from the electrolyte to the electrode surface. The low-frequency segment of the impedance spectrum was nearly vertical except for CNF and 0.050MnO_n-CNF, indicating ideal capacitor behavior. The semicircular part in the higher frequency corresponds to the charge transfer at the electrode/electrolyte interface, and its diameter is equivalent to the Faradaic charge transfer resistance (R_{ct}). Comparing the Nyquist plots of various samples (Fig. 9b), it is clear that 0.025MnO_n-CNF, 0.050MnO_n-CNF and 0.100MnO_n-CNF show a smaller diameter of semicircle as compared to 0.500MnO_n-CNF, implying a higher conductivity was achieved. Solution resistance (R_s) is the intersection of the curve at real part Z' . It is a combinational resistance of ionic resistance of electrolyte, intrinsic resistance of substrate, and contact resistance between electrode and current collector. Considering that the same electrolyte, current collector and assembling technique for the electrode were used during the test, the intercept shown in the high frequency semicircle essentially reveals the conductivity of MnO_n-CNF composites. Correspondingly, the solution resistance ranges from 0.45 to 0.52 Ω , smaller than that (0.73 Ω) of 0.500MnO_n-CNF (Fig. 9b, inset), confirming the superior conductivity. The conductance of MnO_n-CNF electrode material decays faster at Mn levels greater than 0.39 wt%. Excess introduction of metal oxides erodes the composite conductivity, which agrees with that reported for V₂O₅ film/carbon

nanofiber paper electrode [28].

The cycling stability of 0.100MnO_n-CNF was examined at a current density of 5 A g⁻¹ (Fig. 9c). The capacitance remains almost constant with a slight fluctuation, and 98% of the initial capacitance (149 F g⁻¹) is retained when cycling up to 5000 cycles. The fading rate is only 0.00071% per cycle, which makes the MnO_n-CNF composite highly stable during the repeated charge-discharge process. Such a high stability can be ascribed to the tight contact between manganese oxides and carbon nanofibers rendered by *in situ* synthesis. The cycling performance of 0.100MnO_n-CNF is much better than those of previously reported MnO₂-NiO hybrid array (12% loss after 1500 cycles) [29], MnO₂ coaxially coated on a CNT array (decreased by *ca.* 11% after only 500 cycles) [30], and electrodeposited MnO₂ film (13% loss after 2000 cycles) [31].

In order to completely determine the electrochemical performance of our materials, energy density and power density were further estimated. The Ragone plot for the 0.100MnO_n-CNF capacitor in 6 M KOH is presented in Fig. 9d, showing that the specific energy density is about 19.7 Wh kg⁻¹ at a current density of 0.25 A g⁻¹, even orders higher than those of reported electric double-layer capacitors and pseudocapacitors [32,33]. It is noteworthy to mention that specific energy still is 17.0 Wh kg⁻¹ at a high current density of 2 A g⁻¹. The power density is 0.89 kW kg⁻¹ at a current density of 2 A g⁻¹, comparable to or higher than high-end commercially available supercapacitors [34]. All the above results clearly reveal the exceptional capability of the 0.100MnO_n-CNF electrode to meet the requirements for high capacitance, good rate capability and long cycling life, which are crucial factors for

high-performance energy-storage devices.

4. Conclusions

In summary, ultrafine manganese oxide-decorated carbon nanofibers have been successfully developed by skillful construction and evolution of Mn, Zn-containing metal organic framework fibers. This facile and economic synthesis renders ultrafine manganese oxides, which are evenly dispersed, and are firmly inserted into the porous carbon nanofibers formed simultaneously. Some merits, such as easy accessibility, high porosity, tight contact and superior conductivity, are integrated in final MnO_n -CNF composites. And thus a remarkable specific capacitance up to 18290 F g^{-1} of per mass of MnO_2 , and an excellent cycling up to 5000 times, as well as a high energy density of 19.7 Wh kg^{-1} have been achieved using such MnO_n -CNF composites. Therefore, supercapacitors based on this novel hybrid composite are of low cost but high performance, which would accelerate their adoption in practical applications.

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Fig. 1. Illustration of the MnO_n -CNF fabrication process.

Fig. 2. High-resolution SEM images of 0.100Mn-ZnBTC synthesized at different reaction time.

Fig. 3. (a) Contour map of the temporal *in situ* synchrotron high energy X-ray diffraction patterns recorded by pyrolysis of 0.100Mn-ZnBTC in temperature range of 30-950 °C with a ramp rate of 5 °C min⁻¹ in Ar atmosphere, and (b) the corresponding high energy X-ray diffraction patterns.

Fig. 4. (a) SEM image and (b) the corresponding high-resolution SEM image, (c) TEM image, (d) HAADF-STEM image and (e) elemental maps of 0.100Mn-ZnBTC; (f) SEM image and (g) the corresponding high-resolution SEM image, (h) TEM image, (i) HAADF-STEM image and (j) elemental maps of 0.100MnO_n-CNF; (k) the enlarged image for a single nanofiber shown in (h); and (l) SAED pattern of 0.100MnO_n-CNF.

Fig. 5. (A) Mn K-edge XANES and (B) Mn K-edge EXAFS of (a) 0.100Mn-ZnBTC, (b) 0.100MnO_n-CNF, (c) Mn foil, (d) MnCl₂·4H₂O and (e) MnO₂.

Fig. 6. Raman spectra of (a) CNF, (b) 0.025MnO_n-CNF, (c) 0.050MnO_n-CNF, (d) 0.100MnO_n-CNF and (e) 0.500MnO_n-CNF.

Fig. 7. (A) N₂ adsorption/desorption isotherms and (B) the corresponding pore size distribution curves of (a) CNF, (b) 0.025MnO_n-CNF, (c) 0.050MnO_n-CNF, (d) 0.100MnO_n-CNF and (e) 0.500MnO_n-CNF.

Fig. 8. Capacitive performance: (a) CV curves at 1 mV s⁻¹, (b) galvanostatic charge-discharge curves at 0.25 A g⁻¹, (c) CV curves at different scans for 0.100MnO_n-CNF and (d) capacitance retention ratios as a function of scan rates in 6 M KOH.

Fig. 9. Capacitive performance: (a) measured and simulated EIS impedance for 0.100MnO_n-CNF, and the equivalent electrical circuit (inset), (b) Nyquist plots, (c) cycling durability of 0.100MnO_n-CNF, and (d) Ragone plot performed in 6.0 M of KOH aqueous solution for 0.100MnO_n-CNF.

Morphology controlled synthesis of Mn, Zn-containing metal organic framework fibers was carried out by varying the assembly time. Such a fiber precursor was converted to a new type of ultrafine manganese oxide-decorated carbon nanofiber upon pyrolyzed. This synthesis integrates excellent accessibility, high porosity, tight contact and superior conductivity in the final products, and thus exhibits a remarkable capacitance of up to 18290 F g⁻¹ per active mass of the manganese(IV) oxide, high stability of cycling up to 5000 times, as well as the maximum energy density is up to 19.7 Wh kg⁻¹ at the current density of 0.25 A g⁻¹.