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High-performance flexible supercapacitors based on mesoporous carbon nanofibers/Co$_3$O$_4$/MnO$_2$ hybrid electrodes†

Yunpeng Huang, Yue-E Miao, Weng Weei Tjiu and Tianxi Liu*

In this work, self-standing Co$_3$O$_4$ doped CNF (CNFs/Co$_3$O$_4$) membranes were prepared through a facile sol–gel electrospinning and high-temperature carbonization process, followed by a subsequent in situ redox reaction in KMnO$_4$ solution to obtain mesoporous MnO$_2$ sheets coated CNFs/Co$_3$O$_4$/MnO$_2$ composite membranes. The as-fabricated flexible CNFs/Co$_3$O$_4$/MnO$_2$ membrane electrodes exhibit superior capacitive performance compared to CNFs/MnO$_2$ membranes, with a high specific capacitance of 840 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ (based on the mass of MnO$_2$) which is ascribed to the electrochemically active and electrically conductive CNF backbone contributed by Co$_3$O$_4$ doping and the efficient electron transportation and ion diffusion derived from the highly dispersed mesoporous MnO$_2$ nanosheets. Furthermore, a flexible supercapacitor device using CNFs/Co$_3$O$_4$/MnO$_2$ membranes as two symmetric electrodes has also been demonstrated, which exhibits good flexibility and remarkable capacitive performance as well.

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†Electronic supplementary information (ESI) available: Cross-sectional image and digital photographs of CNFs/Co$_3$O$_4$ and CCMs membranes; comparison on the total capacitance between CCMs and CMs. Detailed calculation process of MnO$_2$ loading percentage and specific capacitance. See DOI: 10.1039/c4ra17312k

Introduction

In recent years, flexible and environmentally friendly energy-storage devices have attracted much attention due to the growing requirement for sustainable and cost-effective energy.\textsuperscript{1,2} The supercapacitor has emerged as one of the most promising energy-storage devices due to its higher energy density than conventional physical capacitors, higher charge/discharge rate capability and longer life-cycles than Li-ion batteries.\textsuperscript{3–5} According to the charge/discharge process, supercapacitors can be divided into electrical double-layer capacitors (EDLCs) based on carbon-active materials, and pseudocapacitors based on redox-active materials. Compared with EDLCs, pseudocapacitors using conducting polymers or transition metal oxides possess higher specific capacitance because of the utilization of fast and reversible surface Faraday redox reactions for charge storage. Thus, most of the recent research interests on supercapacitors are focused on the development of pseudocapacitors derived from redox-active materials with high specific capacitance and stability.\textsuperscript{6–8}

Among transition metal oxides, RuO$_2$ is generally recognized as the best electrode materials for pseudocapacitors owing to its high specific capacitance, but the rarity and high-cost limit its vast application.\textsuperscript{9–10} Other low-cost transition metal oxides such as Co$_3$O$_4$,\textsuperscript{11} Fe$_2$O$_3$,\textsuperscript{12} NiO,\textsuperscript{13} and V$_2$O$_5$\textsuperscript{14} also have been extensively studied as potential electrode materials with excellent capacitive performance. Especially, MnO$_2$ is the most thoroughly investigated electrode materials for the next generation supercapacitors on the basis of its intriguing characteristics, such as low cost, environmental friendliness, natural abundance and high theoretical specific capacitance of 1370 F g$^{-1}$.\textsuperscript{15} However, being limited by its poor electrical conductivity (10$^{-5}$ to 10$^{-6}$ S cm$^{-1}$), such high theoretical specific capacitance has not been achieved in those reported works. To address this problem, considerable research efforts have been dedicated to improve the electrical conductivity of MnO$_2$ based electrode materials. Some materials have been loaded on MnO$_2$ serving as conducting additives, such as metal nanostructures,\textsuperscript{16} carbon nanotubes,\textsuperscript{17,18} graphene,\textsuperscript{19} and conductive polymers.\textsuperscript{20,21} 

\textit{Vice versa}, coating MnO$_2$ onto other materials with good electrical conductivity such as Zn$_2$SnO$_4$,\textsuperscript{22} WO$_3$,\textsuperscript{23} SnO$_2$,\textsuperscript{24} graphene,\textsuperscript{25} carbon fiber paper\textsuperscript{26} has also been demonstrated to be a promising approach to improve its electrical conductivity and capacitive performance. Despite all these achievements, developing efficient approaches to obtain high-performance MnO$_2$-based electrode materials still remains a great challenge.

Carbon nanofibers (CNFs) have always been applied in electrodes of supercapacitors, secondary batteries, low-temperature fuel cells, and sensors,\textsuperscript{27,28} owing to their high...
mechanical strength, electrical conductivity, and chemical stability. Electrospinning is a simple and versatile method for fabricating nanofibers with diameters in the range of nanometers to a few microns, as well as a quite straightforward method for preparing free-standing and flexible CNFs membranes which could meet the urgent global demand for flexible and wearable energy storage devices. Furthermore, metal oxides, e.g., VO₂, Fe₂O₃, can be easily incorporated with electrospun CNFs through a sol–gel process combined with post annealing treatment, which can serve as additives to improve the conductivity or electrochemical activity of CNFs. Kang et al. presented a rational synthesis of hierarchical MnO₂/conducting polypyrrole (PPy)@CNF triaxial nano-cables via in situ interfacial redox reaction, which exhibit good rate capability and long-term cycling stability. In the work of Wu et al., ultrathin hierarchical MnO₂ coated electrospun CNFs were synthesized and directly used as electrode for supercapacitor. The specific capacitance based on MnO₂ mass was evaluated to be 900 F g⁻¹ at a scan rate of 2 mV s⁻¹. Nevertheless, few works have been reported on the utilization of electrospun CNFs for MnO₂-based flexible supercapacitors.

In this work, we present the design and fabrication of ultrathin MnO₂ nanosheets coated Co₃O₄ doped self-standing electrospun CNFs membrane as flexible electrode material for supercapacitors. CNFs/Co₃O₄ nanofibers with a mean diameter of 250 nm are first prepared through a facile sol–gel electrospinning and high-temperature carbonization, where nano-sized Co₃O₄ particles are uniformly dispersed in CNF backbone. Ultrathin MnO₂ nanosheets/nanowhiskers are further deposited on CNFs/Co₃O₄ template via a facile in situ redox reaction in KMnO₄ solution under mild conditions. The self-standing CNFs/Co₃O₄ nanofiber membrane matrix not only works as a conducting substrate for the full utilization of MnO₂ but also actively participates in the charge storage process by virtue of the electroactive Co₃O₄. Electrochemical measurements show that the specific capacitance of CNFs/Co₃O₄/MnO₂ nanofiber membrane reaches 840 F g⁻¹ at a scan rate of 5 mV s⁻¹ (based on the mass of MnO₂), and the composite electrode materials also exhibit excellent rate capability and long-term cycling stability. Furthermore, they are used to construct a simple flexible supercapacitor with high flexibility and good capacitive performance, demonstrating the potential applications of transition metal oxides incorporated electrospun CNFs membranes in flexible energy storage devices.

Experimental

Materials

Polyacrylonitrile (PAN, Mw = 150 000 g mol⁻¹) was purchased from Sigma-Aldrich. Cobalt acetate (Co(Ac)₂·4H₂O), potassium permanganate (KMnO₄) and sodium sulfate (Na₂SO₄) were supplied by Sinopharm Chemical Reagent Co. Ltd. N,N-Dimethylformamide (DMF) and ethanol were obtained from Shanghai Chemical Reagent Company. All aqueous solutions were prepared with doubly distilled water.

Preparation of CNFs/Co₃O₄/MnO₂ composite membrane

The preparation procedure of CNFs/Co₃O₄/MnO₂ composite is schematically described in Scheme 1. First of all, PAN nanofibers containing Co(Ac)₂ were prepared through a facile sol–gel electrospinning. Briefly, 1 g of PAN powder was first dissolved in 8 mL of DMF at room temperature under vigorous stirring. Afterwards, 2 mL of Co(Ac)₂ DMF solution was prepared and dropwise added into the above transparent PAN solution and stirred overnight to obtain a homogeneous red solution for electrospinning. The freshly prepared precursor solution was then transferred into a 5 mL plastic syringe and injected with a feeding rate of 0.2 mm min⁻¹ through a no. 21 stainless steel needle connected to a high-voltage DC power supply. A rotating aluminum drum was grounded and set as the collector with a distance of 12 cm to the needle tip. When a fixed voltage of 20 kV was applied to the system, nanofibers were generated and deposited on the aluminum drum. After 30 min of electrospinning, non-woven PAN/Co(Ac)₂ composite membrane was formed and easily peeled off from the collector.

Pre-oxidation and carbonization treatments of the as-obtained PAN/Co(Ac)₂ membrane were then performed according to our previous report. Typically, the dried PAN/Co(Ac)₂ membranes were first pre-oxidized in an air atmosphere under 250 °C for 1 h with a heating rate of 1 °C min⁻¹. Then, samples were heated up to 900 °C at a rate of 5 °C min⁻¹ and carbonized for 1 h under N₂ atmosphere. During the carbonization process, PAN fibers were carbonized to CNFs while Co(Ac)₂ was transformed into Co₃O₄ simultaneously. The self-standing CNFs/Co₃O₄ membrane thus prepared at a given weight was soaked into KMnO₄ solution and kept under 80 °C for reaction according to the well-known mechanism:

$$3C + 4MnO_4^- + H_2O = 4MnO_2 + 2HCO_3^- + CO_3^{2-} \quad (1)$$

With the dark purple solution turned into transparent, the products were rinsed with DI water for several times and absolute ethanol for one time to remove the byproduct. Then, the as-prepared CNFs/Co₃O₄/MnO₂ hybrid membranes were vacuum dried before further measurements. For the synthesis of CNFs/
CoO$_2$/MnO$_2$ composite membranes with different loading amount of MnO$_2$, the weight ratio of CNFs/Co$_3$O$_4$ membrane to KMnO$_4$ was varied from 10 : 1, 10 : 5, 10 : 10 to 10 : 20, with the resulted products denoted as CCM-1, CCM-5, CCM-10 and CCM-20, respectively. For comparison, CNFs/MnO$_2$ membranes without Co$_3$O$_4$ doping were also synthesized under the same conditions, with CNFs/MnO$_2$ composite membranes denoted as CM-1, CM-5, CM-10 and CM-20, respectively.

Characterization

Morphology of the samples was investigated using field emission scanning electron microscope (FESEM, Zeiss) at an acceleration voltage of 5 kV. All samples were coated with a thin layer of gold prior to FESEM observations. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were performed under an acceleration voltage of 200 kV with a JEOL JEM 2100 TEM. Thermogravimetric analysis (Pyris 1 TGA) was performed under nitrogen flow from 100 to 800 °C at a heating rate of 20 °C min$^{-1}$. X-ray diffraction (XRD) experiments were conducted from 2θ = 10$^\circ$ to 80$^\circ$ on an X’Pert Pro X-ray diffractometer with CuKα radiation (λ = 0.1542 nm) under a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectroscopy (XPS) analyses were made with a VG ESCALAB 220i-XL device. All XPS spectra were corrected using C 1s line at 284.6 eV.

Electrochemical measurements

The electrochemical properties of the as-prepared electrode materials were performed using a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a standard three-electrode setup, where a platinum wire was used as the counter electrode, a Ag/AgCl electrode as the reference electrode and the modified glass carbon electrode (GCE) as the working electrode. Prior to all measurements, GCE was carefully polished with alumina powders (1.0, 0.3 and 0.05 μm) on a polishing cloth, rinsed thoroughly with DI water between each polishing step, sonicated in ethanol and water, and then allowed to dry at room temperature. The working electrode was prepared by attaching a piece of precut CNFs/Co$_3$O$_4$/MnO$_2$ hybrid membrane (typically 3 × 3 mm$^2$) onto GCE using Nafton as conductive binder. Afterwards, the modified electrode was left to dry at room temperature in a desiccator. Cyclic voltammetry (CV) curves at different scan rates and galvanostatic charge/discharge curves were collected in a potential range from 0 to 0.9 V. AC impedance measurements were carried out from 10$^{-2}$ to 10$^6$ Hz with an amplitude of 5 mV. All the tests were performed in a N$_2$ saturated 0.5 M Na$_2$SO$_4$ solution.

In full cell tests, the flexible supercapacitor was assembled. In detail, the flexible CNFs/Co$_3$O$_4$/MnO$_2$ self-standing composite membranes (1 × 1 cm$^2$) were used as both electrodes, and separated by a filter paper soaked with electrolyte (0.5 M Na$_2$SO$_4$). Two copper foils were used as the current collectors. All of the components were assembled into a layered structure and sandwiched between two pieces of PET film.$^{35,39}$

Results and discussion

Morphological and structural characterization

PAN is the most commonly used precursor polymer for carbon fiber production, which usually involves two processes of pre-oxidation and carbonization.$^{40}$ During the pre-oxidation in air at 250 °C, PAN undergoes cyclization and partial dehydrogenation which makes it denser and more stable to keep fibrous structure during the subsequent high temperature carbonization. During the carbonization process, polymers begin to pyrolyze with a considerable amount of volatile by-products be released.

In this work, Co$_3$O$_4$ was introduced into CNFs to improve their electrochemical activity, with the doping amount controlled by varying the solid content of Co(AC)$_2$ in PAN solution as 1 wt% and 3 wt% (with respect to PAN mass). Fig. S1† show the digital photographs of CNFs/Co$_3$O$_4$ membranes derived from different contents of Co(AC)$_2$. It can be seen that CNFs/Co$_3$O$_4$ membrane obtained from 1 wt% Co(AC)$_2$ is highly flexible (Fig. S1A†). Upon increasing the content of Co(AC)$_2$ to 3 wt%, the resulted CNFs/Co$_3$O$_4$ membrane becomes quite fragile (Fig. S1B†), which can hardly meet the requirement for flexible electrodes. Fig. 1A presents the PAN/Co(AC)$_2$ nanofibers before heat treatment, where smooth and randomly orientated nanofibers with a mean diameter of 350 nm can be observed. After carbonization, the surface of fibers becomes rough and the mean diameter reduces to 250 nm (Fig. 1B) resulting from the decomposing of polymer during heat treatment. It is also worth noting that there are a considerable amount of Co$_3$O$_4$ nanoparticles uniformly distributed in/on CNFs (Fig. 1B), which will improve the electrochemical activity of CNFs without sacrificing the porosity and flexibility. Compared to pure CNFs, the fiber diameter of CNFs/Co$_3$O$_4$ is almost unchanged, which is ascribed to the relatively low doping amount of Co$_3$O$_4$. In addition, the thickness of CNFs/Co$_3$O$_4$ membrane was controlled at about 31 μm by limiting the electrospinning time within 30 min for the consideration of lightweight, as shown in Fig. S2A†.

Coating of MnO$_2$ on CNFs/Co$_3$O$_4$ membranes is performed via a simple in situ redox reaction. As shown in Fig. 2, small sheet-like MnO$_2$ nanostructures can be clearly observed on the surface of CCM-1 (Fig. 2A). After increasing the KMnO$_4$ amount, a full coverage of MnO$_2$ nanosheets is more uniformly formed on CCM-5 nanofibers (Fig. 2B). Further increasing the mass ratio of CNFs/Co$_3$O$_4$ : KMnO$_4$ to 10 : 10, the MnO$_2$ layer

![Fig. 1 FESEM images of (A) electrospun PAN/Co(AC)$_2$ nanofibers, (B) CNFs/Co$_3$O$_4$ nanofibers derived from 1 wt% of Co(AC)$_2$ in PAN and (C) pure CNFs.](image-url)
becomes denser and more homogeneous (Fig. 2C), with the thickness estimated to be 70 nm (Fig. 2E). When the KMnO$_4$ amount was raised to a high value of 10 : 20, the MnO$_2$ shell on CCM-20 becomes extremely thick as 130 nm (Fig. 2D and F). More seriously, with the excessive coating of MnO$_2$, the inner part of MnO$_2$ becomes compact and unaccessible by electrolyte, which is unhelpful for the better utilization of active materials and would lead to inferior capacitive performance. Worse still, as the deposition of MnO$_2$ would consume the carbon backbone, excessive MnO$_2$ loading will definitely deteriorate the flexibility of the resulted composite membrane. As displayed in Fig. S2B and S2C,† CCM-10 film is intact and quite flexible, while on the contrary the product of CCM-20 is a pile of fragments.

From the TEM images presented in Fig. 3, a well-defined core–shell structure can be observed on CCM-10 (Fig. 3A). The porous MnO$_2$ shell is composed of numerous ultrathin outwards positioned sheet-like nanostructures (Fig. 3B). HRTEM image in Fig. 3C reveals the interplanar spacing of 0.66 nm for MnO$_2$ nanosheets, corresponding to the (001) plane of birnessite type MnO$_2$. It is notable that Co$_3$O$_4$ nanoparticles are almost invisible in Fig. 3A, which may be caused by the small amount of Co$_3$O$_4$ doping and the relatively large fiber diameter.

Crystal structures of the obtained composite materials were examined by XRD (Fig. 4A). The well-defined peak of the red curve at 2θ value of 44.7° corresponds to the crystal plane of (400), which indicates the existence of Co$_3$O$_4$ (JCPDS card no. 42-1467). The diffraction peaks of CCM-10 at around 12°, 25.3° and 37° can be readily indexed to the (001), (002) and (021) crystal planes of birnessite type of MnO$_2$ (JCPDS card no. 18-0802). XPS
characterization was used to examine the chemical composition of CNFs/Co3O4/MnO2 composites. As shown in Fig. 4B, the spectra of Co 2p reveals the 2p3/2 peak positioned at 781.0 eV, which is identified to be elemental Co in Co3O4, further confirming the presence of Co3O4 in CNFs/Co3O4/MnO2 composites. Moreover, the two peaks centered at 642.8 and 655.0 eV in Mn 2p spectrum can be designated to the binding energy of Mn 2p3/2 and Mn 2p1/2, respectively, revealing the dominance of MnO2 in the product.

TGA was used to characterize the loading percentage of MnO2 in the composites. As shown in Fig. 5, at the temperature above 400 °C, carbon is burned out in air, with the residue being a mixture of Mn3O4 and Co3O4. Based on this, mass loading of MnO2 in all the samples was calculated and presented in Table S1 (the detailed calculation was provided in ESI†).

Electrochemical properties

Electrochemical measurements were performed with a standard three-electrode system in 0.5 M Na2SO4 solution to evaluate the electrochemical performance of CNFs/Co3O4/MnO2 composites. For a comparison, CNFs/MnO2 composites without Co3O4 doping were also studied. CV was used to investigate the electrochemical charge storage capacity of the modified electrodes. Fig. 6A shows CV curves of CNFs/Co3O4, CCM-1, CCM-5, CCM-10, CCM-20 at a scan rate of 100 mV s−1, with all of the CCM membranes showing nearly symmetrical rectangle shape, indicating a good capacitor characteristic. Especially, CCM-10 electrode shows the highest specific current density with a moderate distorted rectangular shape. Fig. 6B presents CV curves of composites without Co3O4 doping. Predictably, CM membranes exhibit relatively same rectangular shapes as CCMs derived from the capacitive nature of MnO2. It can also be observed from Fig. 6A and B that pure CNFs and CNFs/Co3O4 without MnO2 coating show nearly no electrochemical capacitive performance. The specific capacitance from CV based on the mass of MnO2 was calculated according to the literature, and the results are shown in Fig. 6C. The specific capacitance of CCM-1 reaches 559 F g−1 at a scan rate of 5 mV s−1, while that of CM-1 is just 349 F g−1. Additional comparison on the total capacitance between CCMs and CMs also displays the same trend (Fig. S3†). This relatively higher value is ascribed to the conductive and electroactive CNF/Co3O4 fibrous backbone which could endow the full utilization of MnO2. Further increasing the loading amount of MnO2, the resulting specific capacitance jumps to as high as 840 F g−1 for CCM-10 and drops to 351 F g−1 for CCM-20, indicating that excessive MnO2 loading would deteriorate the capacitive behavior of the electrodes. As aforementioned, the compact MnO2 coating would surely block the diffusion pathway of ions and electrolyte for energy storage, thus leading to the lower specific capacitance for CCM-20 and CM-20. In addition, the specific capacitances of CCMs are all higher than those of CMs with the same MnO2 loading, which is ascribed to the synergetic effect of mesoporous MnO2 and nano-sized Co3O4.

The electrochemical impedance spectroscopy (EIS) analysis is a powerful and informative technique to evaluate the properties of conductivity and charge transport in the electrode/electrolyte interface. Nyquist plots of CCM-10 and CM-10 electrodes are displayed in Fig. 6D. Both of the plots show a nearly vertical line in the low-frequency region, exhibiting excellent capacitor behavior for MnO2 coated composite materials. The high frequency loop is related to the electronic resistance inside the electrode materials. Thus, it can be observed that CM-10 shows a much lower Faradaic charge transfer resistance compared to CCM-10, indicating that Co3O4 doping could not only increase the electrochemical activity but also significantly improve the electrical conductivity of CNFs.

Fig. 7A shows CV curves of CCM-10 electrode at different scan rates in 0.5 M Na2SO4 aqueous solution. The shapes of these curves are quasi-rectangular, indicating the ideal electrical double-layer capacitance behavior and fast charging/discharging process characteristic. The variation in the specific capacitance of CCM-10 as a function of the scan rates is
plotted in Fig. 7B. Under a high scan rate of 100 mV s\(^{-1}\), the specific capacitance still retains 401 F g\(^{-1}\) (based on MnO\(_2\)), revealing good capacitive behavior and high-rate capability for CNFs/Co\(_3\)O\(_4\)/MnO\(_2\) electrodes. The self-standing conductive CNFs/Co\(_3\)O\(_4\) backbone and porous sheet-like MnO\(_2\) nanostructures can not only provide a shorter electron transportation and ion diffusion pathway, but also facilitate the reaction of active species, hence resulting in a good rate capability. Current density is one important factor influencing the capacitive behavior of supercapacitors. Fig. 7C shows the constant current charge/discharge curves of the CCM-10 composite at different current densities. It is obvious that the charging curves are very symmetric with their corresponding discharging counterparts, and the voltage loss is low even at a high current density of 10 A g\(^{-1}\), indicating the low internal resistance which is in good agreement with the EIS results.

To further test the feasibility of CNFs/Co\(_3\)O\(_4\)/MnO\(_2\) composite membranes for flexible capacitance applications, a simple flexible in-board supercapacitor based on CCM-10 was presented for a demo. The flexible device was fabricated using two pieces of self-standing CNFs/Co\(_3\)O\(_4\)/MnO\(_2\) membranes as both electrodes. As shown in Fig. 8A, the as-prepared supercapacitor is lightweight and highly flexible, which can even endure folding and twisting without destroying its construction. The CV curves in Fig. 8B demonstrate that fluctuation of the electrochemical performance of the flexible supercapacitor is subtle and acceptable under different bending angles. Additionally, the symmetric and rectangular-shaped CV curves show the ideal pseudocapacitive nature of MnO\(_2\) and fast redox reaction in the flexible device. Fig. 8C displays the charge/discharge curves of this device at different current densities ranging from 0.2 to 2.0 mA cm\(^{-2}\). A small sloping potential profile with a potential plateau can be observed at lower current density, indicating a typical Faradaic reaction. The long-term cycling stability of the flexible supercapacitor was tested through CV cycles at a scan rate of 100 mV s\(^{-1}\), which is shown in Fig. 8D. After 3000 cycles, the specific capacitance of the device still retains 95.9% of its initial value, suggesting that the as-fabricated supercapacitor has a good cyclic performance and is quite promising as a flexible energy storage device.

Power density and energy density are two important parameters for evaluating the electrochemical performance of
the supercapacitors. Fig. 9 presents the Ragone plots of assembled flexible CNFs/Co$_3$O$_4$/MnO$_2$ supercapacitor. The highest power and energy densities for the hybrid electrodes are 10.8 kW kg$^{-1}$ at energy density of 23.1 W h kg$^{-1}$ and 49.8 W h kg$^{-1}$ at power density of 1.1 kW kg$^{-1}$, respectively. These values are comparable to those of the reported MnO$_2$ based composites, demonstrating the potential applications of CNFs/Co$_3$O$_4$/MnO$_2$ composite membranes in efficient and flexible energy storage devices.

Conclusions
In summary, a novel flexible electrode of CNFs/Co$_3$O$_4$/MnO$_2$ composite nanofiber membranes for supercapacitors has been prepared through a facile sol–gel electrosprning combined with subsequent carbonization and in situ redox reaction. The as-fabricated self-standing CNFs/Co$_3$O$_4$/MnO$_2$ membranes exhibit superior capacitive performance of 840 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ (based on the mass of MnO$_2$) compared to CNFs/MnO$_2$ membranes, which is ascribed to the improved electrical conductivity and electrochemical activity of CNF backbone benefiting from Co$_3$O$_4$ doping and fast electron transportation and ion diffusion. Furthermore, a flexible supercapacitor device using CNFs/Co$_3$O$_4$/MnO$_2$ membranes has also been demonstrated, which exhibits remarkable flexibility and capacitive performance. This unique flexible electrode holds great potential in the application of flexible and lightweight energy storage devices.

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