Nickel Metallized Nanofibers Based MnO_2//PPy as Electrodes for All-in-One Ultrathin Flexible Asymmetric Supercapacitors

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***Abstract*—As the fast development of lightweight and wearable electronic products, high-performance ultrathin flexible supercapacitors have become a promising type of energy storage devices which are attracting great attention. Integrating all the components of supercapacitor into the two sides of a porous film could avoid displacement and delamination between component layers which contributes to enhancing device flexibility. Such an "all-in-one" integration would also simplify manufacturing process compared with traditional sandwich-like laminated process. Herein, we propose a convenient and scalable fabrication method for all-in-one ultrathin supercapacitor with table electrochemical performance and excellent flexibility. The supercapacitor is prepared by integrating current collector, cathode, and anode into one piece of ultrathin electrospinning polyacrylonitrile (PAN) nanofibers membrane. Firstly, the membrane is metalized with Ni by two sides as current collectors, leaving the middle part as the separator. Subsequently, MnO_2 and polypyrrole (PPy) are loaded on the two conductive sides of the membrane by electrochemically deposition respectively to form MnO_2//separator//PPy all-in-one structure which drastically minimizes the proportion of inactive materials. The assembled all-in-one supercapacitors exhibited enhanced capacitive performance (28.48 F/g at 50 mV/s), good cycling stability (68.5% capacity retention after 3200 cycles at 50 mV/s), and excellent flexibility. It displays great potential in broad market of emerging various flexible, wearable, and portable energy electronic devices.**

Keywords—All-in-One, Ultrathin, Flexible, Supercapacitors

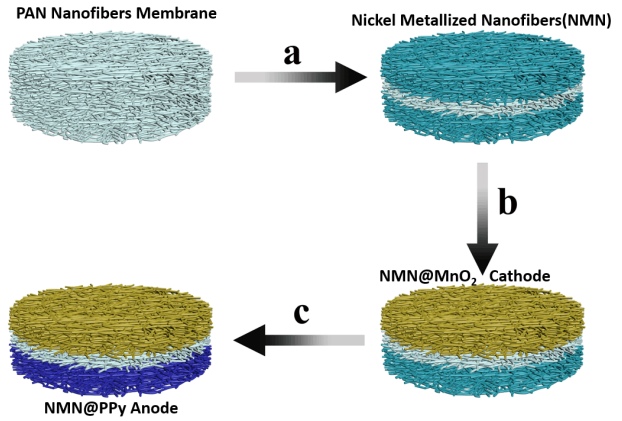
I. INTRODUCTION

As the fast development of lightweight and wearable products, the energy storage devices with high performance, ultrathin thickness, and excellent mechanical flexibility, become more and more important and urgent [1,2]. Supercapacitors, prized for high-power density and long cyclic life, are particularly promising for achieving reliable energy storage [3-5]. Therefore, high-performance, ultrathin, and flexible supercapacitors have become a promising candidate which has attracted great attention [6-8]. Despite enormous advancements have been made for fabricating high-performance flexible supercapacitors, the devices still face challenges from architectural design [9]. Generally, supercapacitors predominantly are assembled into a sandwich architecture, where anode, cathode, current collector, and separator are separately prepared and then stacked together [10,11]. However, this discrete stacking approach will cause displacement and delamination between component layers and increase additional ineffective weight and volume which could lead to poor mechanical flexibility and a low gravimetric or volumetric capacity [12-15].

Recently, many mechanically flexible energy storage devices with all-in-one architecture, which can enable all components to be monolithically integrated into one film, are reported [16]. The seamless and continuous connection of the all-in-one devices not only drastically minimize the proportion of inactive material to achieve efficient electron and ion transport but also avert detachment from the neighboring components and the relative multilayer delamination under long-term mechanical deformation[11]. Such "all-in-one" integration would also simplify manufacturing process compared with traditional sandwich-like laminated process, and make supercapacitors to be able to keep a compact architecture to reach the requirement of next generation flexible wearable electronic devices.

Herein, we reported a convenient and scalable fabrication method for an all-in-one ultrathin supercapacitor with excellent mechanical flexibility and stable electrochemical performance. The supercapacitor was prepared by integrating current collector, cathode, and anode into a piece of ultrathin nanofibers membrane (schematic 1). Firstly, the porous polyacrylonitrile (PAN) nanofibers membrane was prepared by electrospinning. Secondly, the two sides of PAN membrane were metallized via magnetron sputtering with Ni as current collectors and the leaving middle part without metallization as separator. Thirdly, the nickel metallized nanofibers (NMN) were loaded with MnO_2 (NMN@MnO_2) as cathode and PPy(NMN@PPy) as anode, respectively. The NCM@MnO_2 cathode and NMN@PPy anode exhibited high specific capacitance of 119.7 F/g (2 mV/s) and 49.96 F/g (2 mV/s), respectively. The all-in-one ultrathin supercapacitor device was fabricated by NMN@MnO_2 and NMN@PPy electrodes showed enhanced capacitive performance (28.48 F/g, 50 mV/s), good cycling stability (68.5% capacity retention after 3200 cycles at 50 mV/s), and excellent

mechanical flexibility. Using the ways of electrospinning, magnetron sputtering, and electrodeposition, the all-in-one ultrathin flexible supercapacitors fabrication can be accomplished through conventional equipment for scalable production, which displays great potential in broad market of emerging various flexible, wearable, and lightweight energy **electronic** devices.



Schematic 1. The illustraion of fabracation process of all-in-one ultrathin flexible asymmetric supercapacitors: (a) Sputtering and electrodeposition nickel onto the two sides of electrospinning nanofibers membrane, and the middle part without metallized as separator. (b) Electrodepositing a layer MnO_2 onto upper side of metallized nanofibers as the cathode. (c) Electrodepositing a layer PPy onto lower side of metallized nanofibers as the anode.

II. Experimental Section

A. Fabracation of PAN Nanofibers Membrane

PAN nanofibers membrane was prepared through electrospinning. PAN (1.05 g, M_w = 150k g/mol) and SiO_2 (0.35 g) were mixed in dimethylformamide (12 mL) at 70 °C with magnetic stirring for 24 h to obtain the spinning solution. The electrospinning was operated with a moving speed of 0.08 mm/min through the 23 gauge needle (orifice diameter=340 μm) under a direct-current voltage of +18 kV~-2 kV. A piece of aluminum foil covered on the roller with a slow rolling speed of 40 rpm to collect PAN nanofibers. There is 20 cm distance between needle and aluminum foil.

B. Fabrication of Nickel Metallized Nanofibers(NMN) Membrane

The two sides of nanofibers membrane were metallized with nickel through magnetron sputtering. After 15 mins deposition, the depth of nickel layer was 15 μm. Then the metallized nanofibers were electrodeposited. The electrodeposition solution contained 26 g $NiSO4{\cdot}6H_2O$, 4 g $NiCl_2{\cdot}6H_2O$, 0.02 g sodium dodecyl sulfate, and 100 mL DI water. After a 10-minute electrodeposition, the obtained NMN was clean-upped and dried.

C. Synthesis of NMN@MnO_2 and NMN@PPy Electrodes

After metallizing the PAN nanofiber, MnO_2 and PPy were electrodeposited respectively in two electrodes system with a counter electrode of Ti foil.

The electrodeposition solution for MnO_2 is 0.05 M MnAc2. The NMN was connected on a DC power with a deposition time of 2 min and current density of 5 mA/cm^2. Then the obtained NMN@MnO_2 electrode was cleaned and dried. The mass change was measured by analytical balance.

The electrolyte solution for PPy was 6.9 mL/L pyrrole monomer and 18 g/L oxalic acid. The electrodeposition process and parameters were similar to the MnO_2. Then the obtained NMN@PPy electrode was cleaned and dried. The mass change was measured by analytical balance.

D. Packaging of the All-in-one Ultrathin Flexible Supercapacitor

The structure of all-in-one supercapacitor was NMN@MnO_2//nanofibers//NMN@PPy. PI film was used as the package materials for the supercapacitor package. Then two Cu sheets were connected with the cathode and anode of the supercapacitor respectively as tabs.

E. Characterizations

The microscopic morphologies of nanofibers were observed under a SEM (scanning electron microscopy, HITACH S4800). The CV (cyclic voltammetry) and GCD (galvanostatic charge-discharge) curves were obtained through an electrochemical station (VMP3, Bio-Logic).

III. Results and Discussions

A. Structural and Morphological of the Nickel Metallized Nanofibers and Electrodes

For the fabrication of the all-in-one ultrathin flexible asymmetric supercapacitors, we performed six processes in sequence including electrospinning PAN, nickel magnetron sputtering, electrodepositing nickel, loading MnO_2, loading PPy, and packaging.

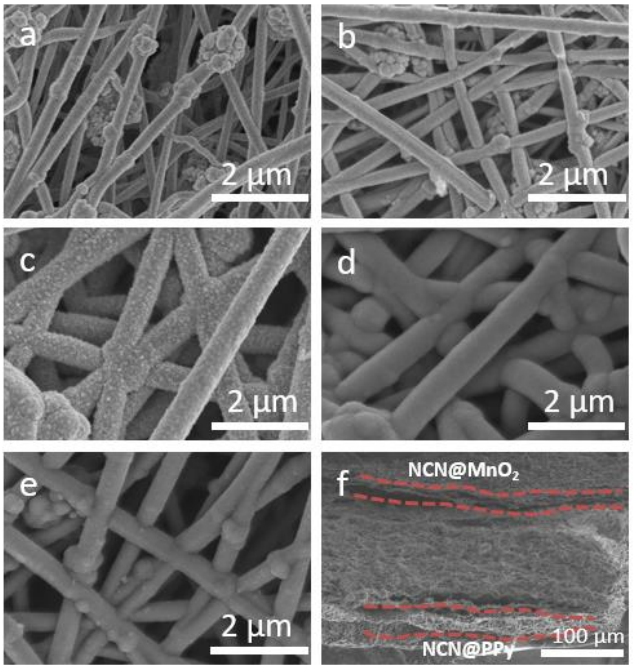


Fig. 1 (a) The SEM of PAN nanofibers; (b) The SEM of nanofibers after magnetron sputtering nicke; (c) The SEM of nanofibers after electrodeposition nickel; (d) The SEM of NMN@MnO_2; (e) The SEM of NMN@PPy; (f) The cross-sectional SEM of all-in-one ultrathin flexible asymmetric supercapacitors.

Fig. 1a shows the morphology of PAN nanofibers with the diameter of 200 nm to 350 nm. Fig. 1b is the morphology of nanofibers after magnetron sputtering nickel. The diameter of nanofibers slightly increased to 250 nm to 500 nm. To improve the electric conductivity of the metallized nanofibers membrane, the electrodeposition of nickel with a duration time of 10 min was applied. Fig. 1c shows that the

nickel layer coated on nanofibers become thinker after electrodeposition which beneficial to reducing the sheet resistance of the NMN. Fig. 1d is the NMN@MnO_2 sample with the deposition of MnO_2 for 2 min, showing the uniform distribution of MnO_2. Fig. 1e is the NMN@PPy sample with the deposition of PPy for 2 min which has a structure with sufficient macropores for ion transport. Fig. 1f shows the cross-sectional SEM of all-in-one ultrathin flexible asymmetric supercapacitors. MnO_2 was electrochemically deposited onto one side of the nanofibers membrane as cathode. PPy was electrochemically deposited onto another side of the nanofibers membrane as anode. The ultrathin asymmetric supercapacitor consist of NMN@MnO_2 cathode, PAN nanofibers membrane and NMN@PPy anode shows an all-in-one sandwiched structure with a thickness of 200 μm .

B. *Electrochemical Characterization of the NMN@MnO_2 Cathode*

The NMN@MnO_2 cathode electrochemical performance was tested in a mild aqueous 0.5 M Na_2SO_4 electrolyte to avoid the corrosion of NMN.

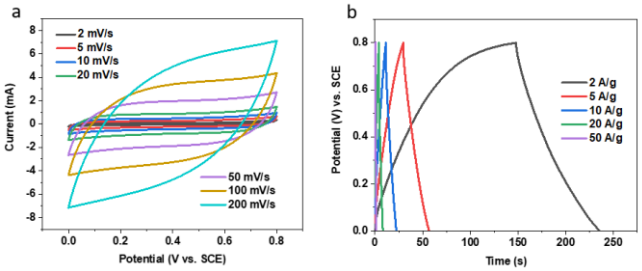


Fig. 3. The NMN@MnO_2 cathode electrochemical performance. (a) The NMN@MnO_2 cathode CV curves; (b) The NMN@MnO_2 cathode GCD curves.

After a series of testings, we found the NMN@MnO_2 cathode showed no polarization and exhibited a capacitive behavior at the working potential windows in 0~0.8 V. After 2 mins electro-deposition, the mass loading of MnO_2 was 0.27 mg/cm^2 and the rectangle-like shape CV curves of NMN@MnO_2 cathode indicates that it exhibited the typical electric double electrochemical behavior as shown in Fig. 3a. Under the various scan rates, the CV curves showed that obvious polarization did not happened. Even at the scan rate of 100 mV/s, the CV profiles also displayed rectangular which was an ideal capacitive behavior. The specific capacitance value of NMN@MnO_2 cathode was 119.7 F/g at the scan of 2 mV/s. Because of massive macropores and special PAN nanofibers conductive network coated with nickel, the NMN@MnO_2 provide an efficient channels for ions transportation and high conductive network for electrons conduction. Fig. 3b is the GCD curves of the NMN@MnO_2 cathode in different current densities which are almost symmetrical and linear with tiny voltage drop. The symmetrical charge and discharge process illustrates that the NMN@MnO_2 cathode has rate performance and good electrochemical reversibility. It considered that the excellent wettability of the nanofibers including SiO_2 nanospheres which accelerate the penetration of the electrolyte into the NMN@MnO_2 cathode and the direct contact of MnO_2 with the conductive NMN, without the involvement of any polymer binder promotes the performance. This above good results show remarkable and excellent electrochemical properties of the NMN@MnO_2 cathode for supercapacitors.

C. *Electrochemical Characterization of the NMN@PPy Anode*

To further verify the electrochemical of the NMN, PPy was selected as anode electrode materials to load onto NMN through electro-polymerization. As the same with NMN@MnO_2 cathode electrochemical test, the NMN@PPy anode was measured in the mild aqueous electrolyte.

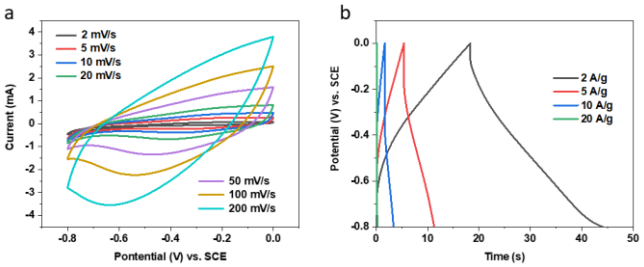


Fig. 4. The NMN@PPy anode electrochemical performance. (a) The CV NMN@PPy anode CV curves; (b) The NMN@PPy anode GCD curves.

The working potential windows of the NMN@PPy anode was 0.8~0 V, wherein the electrochemical performance was investigated. After 2 min deposition, the mass loading of PPy was 0.42 mg/cm^2. Fig. 4a is the NMN@PPy anode CV curves which showed obvious capacitance property. The specific capacitance value of the NMN@ PPy anode was 49.96 F/g at the scan of 2 mV/s. Fig. 4b is the GCD curves of NMN@ PPy anode from 2 A/g to 20 A/g, showing a typical isosceles triangle shape. The high electrochemical performance of the NMN@PPy anode can be illustrated by the three factors: the good connected architecture of the metallized nanofibers can effectively decrease the contact resistance between current collectors and active materials, the rich microporous and mesoporous film structure is beneficial to ion transport in the whole NMN@PPy anode area, and the submicron size of nanofibers makes a great contribution to increasing high special surface area of electrode for high mass loading of the PPy.

D. *Electrochemical Characterization of the All-in-One Ultrathin Flexible Asymmetric Supercapacitors*

To evaluate the feasibility of all-in-one ultrathin flexible asymmetric supercapacitors working at device level, we further assembled a coin type cell and packaged a pouch cell by matching the capacitance of the NMN@MnO_2 cathode and NMN@PPy anode, respectively. After a series testing, the asymmetric supercapacitor showed a capacitive behavior and exhibited insignificant polarization at the working potential window in 0~1.3 V. Fig. 5a shows the CV curves of the asymmetric supercapacitor at the scan rate range of 2 to 200 mV/s. The specific capacitance of the asymmetric supercapacitor was calculated as 31 F/g at the scan of 2 mV/s. The GCD curves (Fig. 5b) showed similar shapes with the single electrodes at various tested current densities, which demonstrates a typical capacitive behavior of supercapacitor. The excellent results are obtained because of the efficient transport of ions and electrons in the conductive and porous nanofibers framework. After a successive CV cycling test (3200 cycles) at the scan rate of 50 mV/s, the supercapacitor showed a capacitance retention of 68.5%, demonstrating the excellent cycling performance. To present the flexibility of the supercapacitor, we performed the bending tests. In Fig. 5d, the supercapacitor can be bent at the angles 180° without noticeable cracks, suggesting excellent flexibility. Fig. 5e is the CV curve of the supercapacitor at the scan rate of 50

mV/s in different bending angles with specific capacitance of 28.48 F/g(0°) and 29 F/g(180°), showing a high capacity. In a addition, the CV profiles of the supercapacitor in different bending angles nearly kept the same shape, showing favorable flexibility.

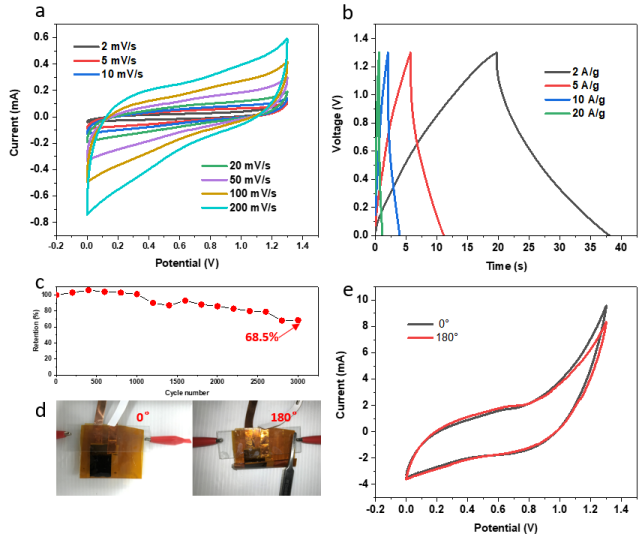


Fig. 5. The all-in-one ultrathin flexible supercapacitors electrochemical performance. (a) The coin type cell CV curves; (b) The coin type cell GCD curves; (c) The coin type cycling stability; (d) The photograph of a pouch type cell (size:6 cm×5 cm); (f) The pouch type cell CV curve at the scan rate of 50 mV/s in different bending angles.

IV. Conclusions

In summary, we prepared an all-in-one ultrathin flexible supercapacitor by convenient and scalable fabrication method of electrospinning, sputtering, and electrodeposition. The all-in-one structure of supercapacitor effectively decreases the proportion of inactive materials, avoids displacement and delamination between component layers. We found that the transport resistance of ions and electrons was reduced because of the superior interface contact of active material and current collectors. Therefore, the assembled flexible all-in-one supercapacitor exhibited great capacitive performance (28.48 F/g, 50 mV/s), good cycling stability (68.5% capacity retention after 3200 cycles at 50 mV/s), and excellent mechanical flexibility. The above-mentioned features of the supercapacitor illustrate great potential in broad market of emerging various flexible, wearable, and portable energy electronic devices.

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