High-performance Supercapacitor based on Metal Oxide Coated Fibrous Electrode

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Abstract—**Miniaturized energy storage devices with high energy density have been drawing extensive attentions owing to their promising applications in consumer electronics, such as smart phones, roll-up electronics, electronic paper, and wearable electronics etc. We have developed a three-dimension fibrous nanostructure for the fabrication of supercapacitor electrodes, which contains electrodeposited nickel nanowires covered by a thin layer of MnO_2 as the active material. The nanoporous electrode with excellent ohmic conductive structure ensures the supercapacitor devices exhibit excellent flexibility, high rate performance and high areal capacitance (up to 1.8 F/cm^2) with excellent cyclability up to 20,000 times. Due to the superior electrochemical and mechanical properties, we envisage that the new technology may find vast applications in the future wearable and miniaturized electronic devices.**

I. INTRODUCTION

With the bloom of portable electronics, miniaturized energy storage and delivery devices become more important than ever.[1-4] Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have been under intensive study due to their high energy and power density and long cycling life.[4, 5] Electrochemical performance of supercapacitor electrode has been significantly improved due to the technological advances of active materials and current collector materials.[1] Highly conductive current collectors composed of continuous nanostructures with good flexibility can provide excellent mechanical support and electrical network for active materials.[6-9] Many conductive micro-frameworks have been reported including carbon fiber network, nanopillar/nanotube arrays, nanoporous metallic films etc.[6, 9-13] For instance, nickel nanocones have been developed as ultrathin current collector for supercapacitors with significantly improved capacitance and rate performance.[10]

Inspired by these intriguing works, here we developed a novel current collector fabrication technology via a solution based electroless plating process. This metal coated fibrous thin film showed excellent conductivity and flexibility. Importantly, the 3-D metal wrapped nanofiber framework is capable to support active material for a high mass loading per area, which is critical to the enhancement of areal capacitance. Owing to its nanoporous and highly conductive performance characteristics, active materials could be deposited on the fibrous skeleton. Moreover, the rough surface of the nanofibers can provide excellent adhesion between active material and the current collector. In order to demonstrate the significant enhancement of its capacitance performance, a typical active materials---manganese dioxide (MnO_2)---is deposited on the nickel coated nanofibrous membrane through electro-deposition. Calculating from electrochemical data of the electrode, the areal capacitance of the nickel coated fibrous membrane supported MnO_2 investigated in 0.5 M Na_2SO_4 is up to 1.8 F/cm^2, which is among the best results.[14-17] Furthermore, the electrochemical electrode shows stable cycling property, with only ~12% capacitance loss after 20000 cycles.

II. EXPERIMENTAL

A. *The fabrication of nickel coated polymer microfiber*

The Ni coated fibrous microstructure was fabricated via an electroless nickel plating process. The polymer membrane was purchased from NKK Co. Inc. with a thickness of 100 μm. The polymer membrane was firstly activated via a Sn-Pd activation process. . Then, the membrane was placed into the electroless plating solution bath which contained $Ni(Ac)_2$, $Na_2C_6H_5O_7$ and $N_2H_4 \cdot H_2O$ and kept for 30 min at 70 ℃.

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B. The preparation of nickel coated microfiber membrane loaded with nanostructured MnO_2 electrode.

MnO_2 was deposited via an electrodeposition process. The nickel coated micro fibrous membrane was used as positive electrode and nickel foam was used as negative electrode. The electrodeposition process was proceeded in a 0.1 M $Mn(Ac)_2$ solution with constant positive bias of 10 V.

C. Materials characterization.

The crystalline information was obtained from the X-ray diffraction measurements (XRD, Bruker DS RINT2000/PC). The morphology of the nickel deposited fibers was observed by field emission scanning electron microscopy (FE-SEM, HITACH S4800, Japan). The electrochemical properties of the as-prepared samples were investigated on an electrochemical station (VMP3, BioLogic, France) by a typical three-electrode configuration in a Na_2SO_4 (0.5 M) aqueous electrolyte. The working electrodes were the as-prepared samples with an electrode area of 1.5 cm^2, and platinum and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The applied potential window of cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) was in the range from 0.0 V to 0.8 V. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range between 100 KHz and 0.01 Hz with an amplitude of 5 mV at the open-circuit potential. The specific capacitance was calculated from the CV curves according to the equations:

$$C = \frac{\int i(V)dV}{mv\Delta V} \qquad (1)$$

where, C is the specific capacitance of materials, m is the mass loading on the substrate, v is the scan rate, ΔV is the potential window in the CV curves, and i(V) is the volumetric current.

III. RESULTS AND DISCUSSION

Here we successfully coated the fibrous polymer membrane network continuously with a thin nickel layer by electroless deposition, achieving excellent flexibility of the polymer membrane and excellent conductivity of the metallic nanostructure. Furthermore, nanostructured MnO_2 was electrodeposited on nickel coated polymer fibers (NCP). According to the X-ray diffraction (XRD) results (Fig 1), three characteristic peaks are in good accordance with the pattern of JCPDS card (68-0380), suggesting pure nickel was deposited on the polymer membrane. Fig 2a and b display the scanning electron microscopy (SEM) images of raw polymer fibers and nickel coated polymer fibers. The polymer fibers with an average diameter of ~1 μm are cross-linked with each other, forming a continuous fibrous microstructure. With the subsequent growth of nickel nanolayer on the fibrous substrate, the conductivity of the membrane greatly improved, enabling the functional membrane to be an excellent candidate for the current collector. Importantly, the natural continuous fibrous nanostructure with excellent conductivity dramatically improved the amount of active material's mass loading per area. From Fig 2c and d, obvious roughness of the NCP could be figured out, which greatly enhanced the adhesion between the electro-deposited MnO_2 and the current collector.

The electro-deposition of nanoscaled MnO_2 is operated in $Mn(Ac)_2$ solution; the Mn^{2+} around the positive electrode (NCP) tends to lose two electrons and combines with O^{2-} to form MnO_2 solid and deposits on the surface of NCP. When NCP is coated with MnO_2, from the XRD pattern (as shown in Fig 1b), there was no obvious crystalline information about MnO_2. Fig 2d shows the morphology of NCP coated with nanoscaled MnO_2. The NCP maintained its structure without noticeable fracture of the nickel layer, owing to the excellent adhesion of the nickel and the fiber. The fibrous microstructure also facilitates the electrolyte transporting through the NCP framework.

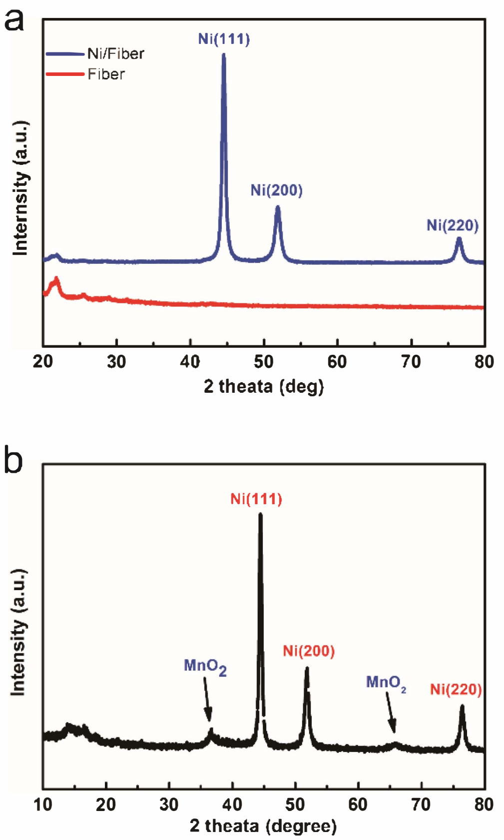

Fig. 1. (a) XRD pattern of polymer fiber and nickel coated polymer fiber membrane. (b) XRD pattern of MnO_2 deposited on NCP.

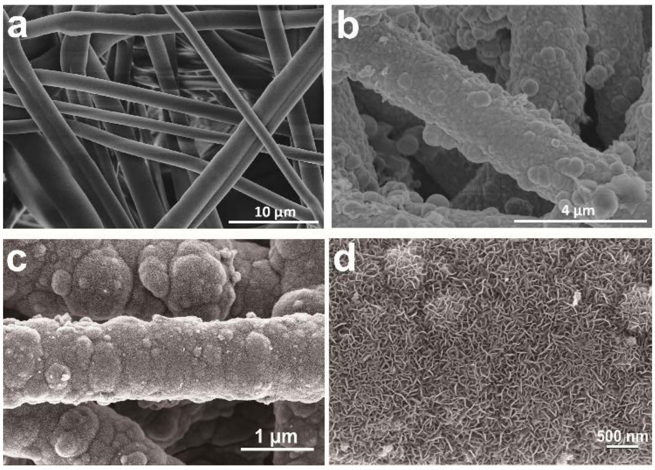

Fig. 2. (a) SEM images of polymer fiber. (b) SEM image of nickel coated polymer fiber. (c), (d) SEM image of MnO_2 deposited on nickel coated polymer fiber with different magnification.

Electrochemically, the novel NCP current collector greatly enhances the mass loading per area of active material. Fig 3a shows that the increment of the mass loading of MnO_2 manifests linear relationship with electro-deposition process. The electrodes are tested in a three-electrode configuration with aqueous 0.5 M Na_2SO_4 electrolyte, with the maximum mass loading of MnO_2 up to 11.54 mg/cm^2, which is larger than most recently reported results. The areal specific capacitance is calculated from the CV results. It is found in Fig 3b that the scan rate response increases with the increment of MnO_2 mass loading in the range of 1.7 mg/cm^2 to 11.54 mg/cm^2. The electrochemical electrodes exhibit higher areal capacitance with increased active material's mass loading, especially at slow scan rates. As a result, the areal specific capacitance is greatly enhanced to 1.8 F/cm^2 at a scan rate of 2 mV/s and a mass loading of 11.54 mg/cm^2. From Fig 3 c and d, the CV results at low mass loading presents more ideal rectangular shape, suggesting superior specific capacitive performance. Meanwhile, when the mass loading is high, the CV curves become a similarly shuttle type, indicating inferior specific capacitance but excellent areal capacitance.

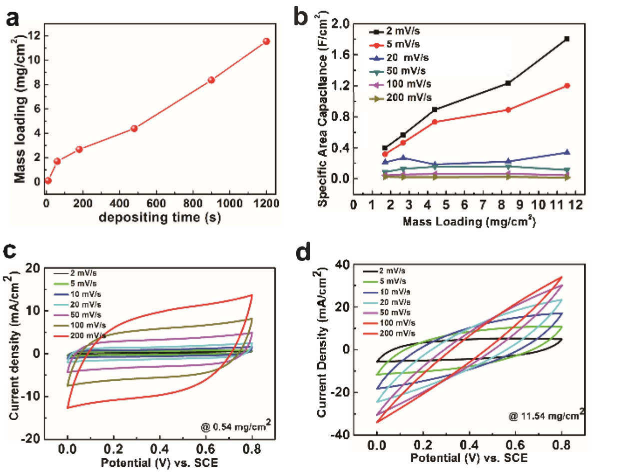

Fig. 3. (a) mass loading density of MnO_2 under gradually increasing electrodepositing duration. (b) Areal capacitance vs. mass loading for MNPC hybrid films at different scan rate. (c) Representative CV curves of MNCP hybrid film with mass loading of 1.7 mg/cm^2 (c) and 11.54 mg/cm^2 (d) at different scan rate.

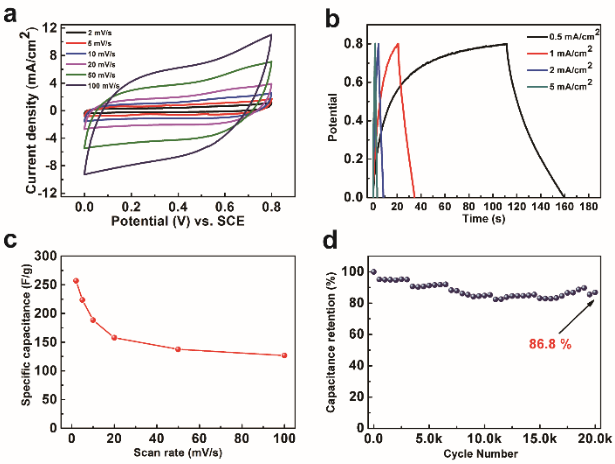

Fig. 4. (a) CV curves of MNCP electrode at different scan rate. (b) GCD curves of MNCP obtained at different current density. (c) specific capacitance of MNCP at different scan rate. (d) The cycling capability of MNCP electrode.

To further evaluate the electrochemical property of MnO_2 coated NCP (MNCP) electrode, a sample with a mass loading of 0.61 mg/cm^2 is electrochemically characterized. The CV results of MNCP electrode is manifested in Fig 1a, and the ideal rectangular shape of CV curves suggests excellent capacitive performance. Fig 4b shows the GCD curves at different current density, and the IR drop is only ~0.2 V at 2 A/g. It is known that the cyclability is a critical index for supercapacitors. The cycling performance of the electrode is shown in Fig 4c, the capacitance retention after 20,000 cycles is about 95 %, suggesting excellent stability among the best metal oxides electrochemical electrodes recently reported.[10, 18-20] The rate performance of NMNAs electrode is displayed in Fig 4d, where the specific capacitance is calculated from CV results. The specific capacitance of MNCP electrode is 256.9 F/g at a scan rate of 2 mV/s. When the scan rate increases to 100 mV/s the specific capacitance is 126.8 F/g. The excellent electrochemical performance can be attributed to the presence of NCP, which greatly enhances the conductivity of MnO_2 and the transport of electrolyte.

IV. CONCLUSION

Three-dimensional metal deposited fibrous framework for supercapacitor electrodes was developed, involved with the electroless deposition of nickel with a subsequent electro-deposition of a thin layer of MnO_2 as the active material. The nanoporous electrode displays excellent conductivity and flexibility, resulting in high areal capacitance (up to 1.8 F/cm^2) and excellent cyclability up to 20,000 cycles. This fabrication technology of metallic/polymer composite membrane may potentially find applications in future wearable energy storage and delivery devices. This work may arouse the interests of materials scientists and electronic engineers.

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