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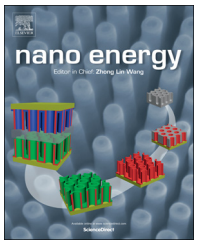

RAPID COMMUNICATION

# Constructing optimized wire electrodes for fiber supercapacitors

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**Abstract**
Fiber electronic devices are commonly built on fibrous substrates with the advantages for the direct use as weavable and embedded device units or integrated textile modules. In this work, $Mn_2O_3$ cube-arrays/carbon wire electrodes were designed for a new kind of fiber supercapacitors. To realize micro-devices with well-optimized performance, different electrode structures were designed and fabricated including the straight, bent, and coiled fiber supercapacitors (S-FSC, B-FSC, and C-FSC), among which the C-FSC showed the optimized and best performance. Our work confirmed that the performance of micro-devices can be well tuned by simply tailoring the device architectures.


## Introduction

As integration, miniaturization, flexibility, and optimization are considered as the primary features of the new generation of electronics, enormous effort has been paid on developing flexible and wearable devices in recent years [1–12]. Different from conventional two-dimensional planar electronics, fiber electronic devices are commonly built on one-dimensional fibrous/wire substrates. Fiber electronic devices usually show advantages for the direct use as wearable and embedded device units or integrated textile modules that cannot be fulfilled by conventional planar devices, which are very attractive in realizing miniaturized portable devices and

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multi-functional "smart textiles" for sensors, detectors, displays and implanted medical devices. Several kinds of fiber electronic devices have been designed including fiber logic circuits [13], fiber solar cells [14,15], fiber displays [16], and fiber nanogenerators [17], etc.

The development of fiber electronic devices inspired much interest in developing efficient, lightweight, highly flexible/wearable energy storage devices such as fiber solar cells, fiber lithium ion batteries, and fiber supercapacitors (FSC) since they are one of the key components for fully flexible electronic systems. Among the emerged fiber energy devices, fiber supercapacitors have higher power density, longer cycling life and more safe operation than fiber lithium ion batteries and thus are considered as a new class of energy storage components. Since Wang's group reported the first prototype of FSC made from ZnO nanowires [18], FSCs made of different electrodes were designed. For examples, Peng et al. designed FSC by twisting two aligned MWCNT fibers [19]. Miao et al. fabricated yarn FSCs based on CNT@PANI arrays [20]. To better prevent the twisted fiber-electrodes from electric short during bending, Zou et al. demonstrated the well-designed helical spacer wire placed in between two electrodes [21]. Our group also fabricated FSCs made of $ZnCo_2O_4$ nanowires electrode and grapheme electrode [22].

Although different kinds of FSCs with different performances were successfully designed recently, one key and crucial issue that was neglected is how to improve the performance of each FSC. As is known, $Mn_2O_3$ has many unique advantages in energy storage fields, such as low cost, environmentally friendly, and high potential performance, etc. Although many methods have been developed to synthesize various $Mn_2O_3$ electrodes for supercapacitors under different experimental conditions, such as particles, nanorods, and spheres [23-25], no information about $Mn_2O_3$ cube/carbon fiber-electrodes prepared via a low-cost/facile route was disclosed till now. Herein, with $Mn_2O_3$ cube arrays/carbon fibers as electrodes, we demonstrated that the performance of the designed FSCs can be efficiently improved by simply varying the electrode structure (straight, bent, and coiled fiber electrodes, respectively). Both experiments and theoretical simulations were carried out to demonstrate the efficient strategy to get optimized FSCs.

## Experimental section

### Synthesis of $Mn_2O_3$ cube-arrays/carbon fibers matrix

$Mn(AC)_2$ (2 mmol) and urea (2 mmol) was initially dissolved in distilled water (40 mL) and then the solution was transferred into a Teflon-lined autoclave. Pre-cleaned carbon fibers were then immersed in this solution. A typical hydrothermal reaction at 160 °C for 5 h was then performed, which resulted in the formation of the aligned $Mn_2O_3$ cube arrays grown on the carbon fibers. The morphology and microstructure of the samples were investigated by field emission scanning electron microscopy (FE-SEM; Sirion 200).

### Wire-device fabrication and characterization

After placing two as-synthesized composite fibers as working electrodes on a PET film, the silver electrodes were fixed to the two ends of the PET substrate. A gel electrolyte of PVA/$H_2SO_4$ was transferred on the composite fibers to form a thin all-solid-state device. CV characteristics of the fiber supercapacitors were evaluated by sweeping the voltage from 0 to 0.8 V at various scan rates using a CHI electrochemical station (760D). Galvanostatic charge-discharge curves of these devices were measured at different current densities between 0 and 0.8 V using a PVA/$H_2SO_4$ gel electrolyte with the electrochemical station at the room temperature.

### Computational simulations

The simulations of the capacitors were carried out by using ANSYS Maxwell. To calculate the capacity, the width of each electrode was set as 1 mm, and the length of the capacitors, the distance between two electrodes were set as 50 mm and 2 mm, respectively. In addition, the voltages on the two fiber electrodes are symmetrically set as $+0.4$ V and $-0.4$ V.

## Results and discussion

We first grew $Mn_2O_3$ cube arrays on carbon fibers to form the binder-free fiber electrodes via a simple hydrothermal method, as is shown in Figure 1a. Briefly, carbon fibers with excellent electrical conductivity were used as the templates for the in-situ growth of $Mn_2O_3$ cube-arrays (Figure S1). The experimental details can be found in Experimental section. Figure 1b shows the low-magnification scanning electron microscopy (SEM) image of the as-prepared $Mn_2O_3$ cube-arrays/carbon fibers from the hydrothermal method for 5 h, which clearly shows that the samples consist of several small fibers coated with $Mn_2O_3$ crystals. Higher-magnification SEM image shown in Figure 1c reveals that numerous microcubes grown on the carbon fibers are packed tightly, forming high density shells on the carbon fibers. Figure 1d displays that the as-prepared $Mn_2O_3$ microcubes have highly uniform size of about 2 μm and the diameter of individual core/shell composite fiber is approximately 14 μm, which is slightly larger than that of the bare carbon fibers due to the coating of $Mn_2O_3$ product. Figure 1e shows the photograph of a single as-grown composite fiber coiled around a glass rod, revealing its outstanding flexibility.

To acquire information about the composition of the as-grown product, energy dispersive spectroscopy (EDS) microanalysis was carried out on the selected area of an individual composite fiber, as shown in Figure S2a. The corresponding EDS spectrum revealed that the as-grown structures are composed of only C, Mn, and O elements, indicating formation of pure $Mn_2O_3$/carbon fibers matrix (Figure S2b). The information about the elemental distributions within the composite fiber is provided by EDS mapping and the corresponding images of C, Mn and O are shown in Figure S2(c-e) respectively. Note that all the images show that the corresponding element is distributed uniformly across the whole wire, further confirming the uniform $Mn_2O_3$/C core/shell structures are successfully prepared. In addition, the crystallographic structure of the as-prepared composites was further analyzed by X-ray diffraction (XRD) (Figure S3). All the diffraction peaks in this