Flexible fiber-shaped supercapacitors based on hierarchically nanostructured composite electrodes

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ABSTRACT

A novel all-solid-state, coaxial, fiber-shaped asymmetric supercapacitor has been fabricated by wrapping a conducting carbon paper on a MnO₂-modified nanoporous gold wire. This energy wire exhibits high capacitance of 12 mF·cm⁻² and energy density of 5.4 μW·h·cm⁻² with excellent cycling stability. Hierarchical nanostructures and coaxial architectural design facilitate effective contacts between the two core@sheath electrodes and active layers with high flexibility and high performance. This work provides the first example of coaxial fiber-shaped asymmetric supercapacitors with an operation voltage of 1.8 V, and holds great potential for future flexible electronic devices.

1 Introduction

The rapid development of flexible and portable/wearable electronic devices has aroused considerable attention due to their high flexibility and foldability [1–4] and has greatly boosted the demand for matching flexible and light-weight power sources [1–4]. As an emerging type of energy storage device, flexible solid-state supercapacitors (SCs) have many advantages—such as high flexibility and safety, small size and high power density—and offer great promise in the field of flexible and wearable electronics [5–7]. However, the currently existing flexible SCs are mostly based on two-dimensional (2D) stacked or planar structures [8, 9] which are usually heavy and bulky, and cannot meet the requirements for small and lightweight microelectronics. Recently, fiber supercapacitors in the shape of two twisted fiber electrodes have been explored extensively since they can be easily woven or knitted into electronic clothes for wearable electronics [10–16]. Nevertheless, these devices can be easily broken during bending, and the two fiber electrodes also easily separate from each other. Only very recently, have several fiber supercapacitors with a coaxial structure been developed; these can avoid the above problems [17, 18]. In addition,
compared to the parallel fiber structure, the whole size of the coaxial fiber supercapacitor device is smaller, holding great promise for practical applications [19, 20]. To our knowledge, however, all of the reported coaxial fiber supercapacitors are symmetric (assembled with two identical electrodes). The low voltage window in symmetric designs often limits their energy densities. One effective strategy to increase the energy density and the cell voltage is to construct asymmetric supercapacitors (ASCs) [21–25]. ASCs that consist of a battery-type electrode (cathode) and a capacitor-type electrode (anode) can make full use of two different potential windows [26–28]. As a result, the operating voltage of the devices can be extended, and hence the energy density can be improved. Therefore, it is highly desirable to design ASCs with a coaxial fiber structure to achieve high performances.

Among various electrode materials for ASCs, MnO2 has attracted intense attention because of its low cost, environmental friendliness, and high theoretical capacitance (1,370 F·g⁻¹) [7, 29, 30]. However, the poor electrical conductivity of MnO₂ (~10⁻⁵–10⁻⁶ S·cm⁻¹) significantly impedes its wide use [31, 32]. To address this issue, designing composite materials by depositing MnO₂ onto a conductive substance is a feasible strategy [33–35]. Recently, flexible nanoporous gold (NPG) wires have been used as supports for active materials for applications in electrochemical biosensors [36]. The nanoporous hybrid architecture, excellent conductivity and high flexibility of NPG can provide superior electronic/ionic conductivity and mass transport giving enhanced performance [36–40]. Inspired by the outstanding characteristics of NPG wires in biosensors, NPG wires should be a good candidate for application in fiber supercapacitors.

Herein, we report on a novel design of all-solid-state, highly flexible, coaxial fiber ASCs made by scrolling a carbon nanotube (CNT)/carbon paper electrode on a NPG@MnO₂ wire electrode with a polymer gel. The NPG wire possesses both high flexibility and satisfactory tensile strength. It can be used as the backbone to support MnO₂ nanoflowers, which not only enables full utilization of MnO₂ and fast electronic/ionic transfer through the electrode, but also avoids using a binder. The as-fabricated coaxial fiber ASCs can be reversibly charged/discharged at a high voltage of 1.8 V, delivering a satisfactory energy density of 5.4 μW·h·cm⁻² and maximum power density of 2,531 μW·cm⁻². Moreover, our coaxial fiber ASC device exhibits good cycling durability with 90% capacitance retention after 2,000 cycles.

2 Experimental

2.1 Synthesis of MnO₂ nanoflowers on nanoporous gold wire

NPG wires of 200 µm in diameter were prepared by a multi-cyclic electrochemical alloying/dealloying method on an electrochemical workstation (CHI660D, CHI Instruments, Shanghai) [36]. The alloying/dealloying of the gold wire was realized in a three-electrode setup, which consisted of a Zn plate and a Zn wire as the counter and reference electrode, gold wire as the working electrode, and 1.5 M ZnCl₂ dissolved in benzyl alcohol (BA) as the electrolyte. The electrolyte was prepared by dissolving anhydrous ZnCl₂ in BA at 80 °C, and the mixture stirred for several hours till the solution becomes clear. Multi-cyclic potential sweeps were applied to the working electrode at a scan rate of 10 mV·s⁻¹ and a temperature of 120 °C in the potential range 1.88 to –0.72 V (vs. Zn). The first cycle was from –0.72 to 1.88 V (vs. Zn) and the later cycles were from 1.88 to –0.72 V (vs. Zn) repeatedly.

After 50 cycles, the gold electrode was taken out and washed with BA, ethanol, and water in sequence. The resultant NPG wire was then dipped into a mixed solution of 0.1 M Mn(CH₃COO)₂ and 0.1 M Na₂SO₄. Nanostructured MnO₂ was electrodeposited on NPG with a three-electrode cell, where the NPG was used as the working electrode, a platinum plate as the counter electrode and a Ag/AgCl electrode as the reference electrode. When a constant current of 0.025 mA was applied, MnO₂ nanoflowers were conformally plated on the NPG wire. The loading of MnO₂ can be easily adjusted by changing the deposition time, and can be calculated by integrating the total plating coulombic charge over the duration of the electrolysis.