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Novel coaxial fiber-shaped sensing system integrated with an asymmetric supercapacitor and a humidity sensor

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ABSTRACT

A high-performance fiber-shaped integrated multifunctional sensing system was designed and fabricated based on flexible fiber-shaped supercapacitors (FFSCs) and humidity sensors. A facile and cost-effective method was proposed to grow three-dimensional MnO_2 nanoballs (NBs)@Ni cone/carbon nanotube (CNT) film with a high specific capacitance of 609.06 mF cm^{-2} at a current density of 0.5 mA/cm^2. In addition, asymmetric coaxial FFSCs (ACFFSCs) with a maximum operating voltage of 1.8 V were assembled by wrapping MnO_2 NBs@Ni cone/CNT film on MoS_2 nanosheet arrays/carbon nanotube fibers as the inner and outer electrodes of the ACFFSCs device, respectively, with poly(vinyl alcohol)/KOH as the gel electrolyte. The assembled ACFFSCs device embraces a high specific capacitance of 195.38 mF cm^{-2}, and a superior areal energy density of 83.59 μWh cm^{-2}. Moreover, the ACFFSCs device acts as the stable power supply for the coaxial fibrous humidity sensor, and the obtained flexible humidity sensing system possesses high sensitivity (2.483/%RH) in the detection of relative humidity (RH), with a fast response speed of 0.39 s.

1. Introduction

With the rapid development of flexible and portable electronics, wearable integrated devices with multiple function have become an important trend in modern electronics [1–5]. As advanced electronic products, flexible smart sensors can be used to gather and exchange data for monitoring ambient information, including temperature, light intensity, the presence of hazardous gases, and humidity [6–9]. Incorporated wearable electronics with flexible sensors have recently aroused abundant attention due to the appearance of smart healthcare detection systems, which can act as electronic skin that attaches to the human body to monitor ambient information [10–13]. However, flexible sensors cannot be directly used in most electronic devices because their output power is insufficient [14]. Therefore, it is necessary to use electrochemical energy storage systems to offer stable and durable output power. The most effective strategy is to construct an all-in-one flexible system; such a system, is superior to an external power supply because of the latter's lack of convenience in wearable electronic technologies. Very recently, an all-in-one, flexible, integrated system on a single piece of paper was reported [15]. However, practical applications in the wearable electronic field may be limited by planar integrated configurations because they are heavier and larger than fiber-shaped integrated configurations with multiple functions. Construction of integrated configurations is urgently needed to realize both high-performance energy storage devices and ultrasensitive sensors with multiple functions (gas sensor, pressure sensor, photodetector, humidity sensor, etc.). As highly efficient flexible energy storage devices, flexible fiber-shaped supercapacitors (FFSCs) have attracted increasing attention because of their promising characteristics of a rapid charge/discharge rate, high power density, long cycling stability, and splendid stitchability [16–23]. However, their low energy density limits their application in the flexible and wearable field. A strategy of constructing an asymmetric supercapacitor was recently studied extensively, and the devices' high energy density was obtained by improving the operating voltage window [24–26]. However, asymmetric coaxial FFSCs (ACFFSCs) with a larger specific capacitance are

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highly desirable. Therefore, our target is to amplify the device's specific capacitance by increasing the specific capacitance of the fibrous electrode materials.

As an ideal pseudocapacitive material, MnO_2 is a promising candidate for FFSCs because of its facile approach, low cost, broad electrochemical operating voltage window, high theoretical specific capacitance (1370 F/g), and environmental friendliness compared with traditional electrical double-layer capacitors [27–29]. Meanwhile, MnO_2 possesses a higher energy density due to its major active sites and its reversible and rapid redox reactions [30,31]. However, the lower specific capacitance of MnO_2 was obtained due to its facile structure and low electronic conductivity. Therefore, our strategy is to construct a hierarchical three-dimensional (3D) structure that consists of a highly conductive nickel cone as a 3D conductive scaffold and pseudocapacitive transitional metal oxide (MnO_2) as the active substance. The 3D conductive network is expected to offer a short ion diffusion path, a rapid electron/ion diffusion rate, and more active sites for pseudocapacitive reaction. In this study, 3D hierarchical MnO_2 nanoballs (NBs)@Ni cone/carbon nanotube (CNT) film heterostructures directly grown on CNT fibers (CNTFs) were fabricated by a facile and environmentally friendly method, exhibited an excellent specific capacitance of 609.06 mF/cm^2, and benefited from intriguing structural features. The technical performance and practical functionality of modern flexible wearable electronic devices are important factors in our daily lives. For example, people increasingly emphasize their health-related quality of life and have become more aware of the harmful effects of dry and moist air on their skin. Thus, it is necessary to fabricate a wearable and highly sensitive humidity sensor that will allow people to protect their health status by adjusting the air humidity.

As a conceptual exhibition, a high-performance fiber-shaped integrated multifunctional wearable electronic device was fabricated that incorporated FFSCs with a humidity sensor. In the integrated multifunctional configuration, ACFFSCs with a maximum operating voltage of 1.8 V have been assembled by wrapping MnO_2 NBs@Ni cone/CNT film on MoS_2 nanosheet arrays (NSAs)@/CNTFs as the inner and outer electrodes of ACFFSCs devices, respectively, with poly(vinyl alcohol) (PVA)/KOH as the gel electrolyte. We were encouraged to find that the as-fabricated humidity sensor operated stably after integration with an ACFFSCs device.

2. Experimental section

All the chemicals were purchased from Sigma-Aldrich and were used without further purification.

2.1. The synthesis of MnO_2 nanoballs (NBs)@Ni cone/carbon nanotube (CNT) film (MnO_2 NBs@Ni/CNT film)

First, before use, CNT films were treated in O_2 plasma for 5 min at 150 W. The Ni cone was grown on CNT film by a previously reported electrochemical deposition method in a mixed aqueous solution of 0.84 M $NiCl_2{\cdot}6H_2O$, 0.75 M NH_4Cl, and 1 M H_3BO_3 with a current density of 15 mA cm^{-2}, which was allowed to obtain Ni cone on CNT films by 1000 s and the deposition temperature was kept at 60 °C [32]. In a three-electrode configuration, the pristine CNT film, platinum wire and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. After Ni cone was deposited on CNT film, as-prepared samples were washed by deionized water to remove residual solution and then dried in vaccum. MnO_2 NBs on the Ni cone/CNT film were fabricated using a electrochemical deposition process similar to the one previously reported [33]. In order to deposit MnO_2 NBs onto the Ni cone/CNT film, the mixed aqueous solution (0.1 M$Mn(Ac)_2$, 0.2 M NH_4Ac, and dimethyl sulfoxide (DMSO, 20 vol%)) served as electrolyte and Ni cone@CNT film, platinum plate and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. And the electrochemical deposition process was carried out at a current density of 2 mA cm^{-2} for different times (200–700 s) and the electrodeposition temperature was kept at 70 °C. Thereafter, the as-prepared MnO_2 NBs@Ni cone/CNT film (MnO_2 NBs@Ni/CNT film) was cleaned by deionized water, and then vaccum dried at room temperature.

2.2. The fabrication of MoS_2 nanosheet arrays (NSAs)/carbon nanotube fibers (CNTFs) (MoS_2 NSAs/CNTFs)

First, before use, CNTFs were treated in O_2 plasma for 5 min at 150 W. And then, the MoS_2 nanosheet arrays (NSAs) were grown on CNTFs by a hydrothermal method in accordance with our previously reported method [31]. In a typical procedure, 0.519 g of ammonium molybdate tetrahydrate and 0.4565 g of thiourea were added into 50 mL deionized water. After stirring for several hours, the mixed solution was then transferred into a 50 mL Teflon-lined autoclave with the CNTFs immersed in the solution. Later, the autoclave was sealed and maintained at 200 °C for 9 h. After the autoclave was cooled down to room temperature, the as-obtained MoS_2NSAs/CNTFs was taken out for water washing and then vacuum dried at 60 °C for 8 h.

2.3. Assembly of ACFFSCs devices

The PVA/LiCl solid gel electrolyte was prepared by slowly adding 10 g of PVA into 100 mL of deionized water, followed by heating at 95 °C by vigorous magnetic stirring, until the mixture solution became clear. Then 20 g of LiCl was added into PVA aqueous solution with strong magnetic stirring. Thus, PVA/LiCl gel electrolyte was obtained. The MoS_2NSAs/CNTFs electrode was then coated with PVA/LiCl gel electrolyte and kept at 60 °C for 2 h to evaporate the excess water. After drying, a MnO_2 NBs@Ni/CNT film was wrapped around a MoS_2 NSAs@/CNTFs. A second layer PVA/LiCl gel electrolyte was then coated onto the constructed ACFFSCs, which embraces two effect, first, the second layer of PVA/LiCl gel electrolyte insulates the electrodes, avoiding the short circuit of the device; second, the active substances avoid being suffered from fall off from the current collectors due to the existing of second layer of PVA/LiCl gel electrolyte.

2.4. Fabrication and Characterization of the wearable humidity sensor

2.4.1. Fabrication of CNT composite wet sensitive materials

First, multi-walled carbon nanotube (MWCNT) of 20 mg was added into 200 mL deionized water by ultrasonic dispersion. The acquisition was defined as A. Second, MEBA-co-KH570 binary copolymer was prepared introducing in SI as a previously reported method [9]. And then 0.5 g MEBA-co-KH570 binary copolymer was dispersed in 24.5 mL deionized water, which was defined as B. Last, the A and B were mixed and stirred for 3 h and ultrasonic dispersion 2 h, and then the humidity sensitive material was fabricated successfully.

2.4.2. Fabrication and characterization of integrated device

First, the as-fabricated ACFFSCs device was coated by polydimethylsiloxane (PDMS), and was then surface-treated by ultraviolet (UV) for 10 min. Second, the MEBA-co-KH570/MWCNT composite was spray-coated and attached on the surface of ACFFSCs device/PDMS fiber at slow speed and drew the external electrode in its edges using carbon nanotube film. Finally, the fiber-shaped supercapacitor-humidity sensor integrated configuration was obtained.

2.5. Materials characterization

X-ray diffraction (XRD) measurements were conducted on a X-ray diffractometer using Cu Kα radiation (XRD, D8 Advance Panalytical X' Pert Pro) from 10° to 90°. The morphology and microstructures of the samples were observed by the field emission scanning electron