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Cotton fabric and zeolitic imidazolate framework (ZIF-8) derived hierarchical nitrogen-doped porous carbon nanotubes/carbon fabric electrodes for all-solid-state supercapacitors

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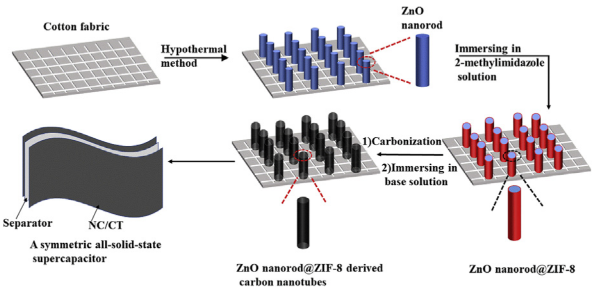
HIGHLIGHTS

- A 3D porous nitrogen-doped carbon cloth composite electrode was prepared.
- Porous nitrogen-doped carbon skeleton promotes the electrochemical properties.
- The composite electrode shows a specific capacitance of 390 F/g at 2 mV/s.
- The flexible all-solid-state supercapacitor delivers high energy density.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a facile self-sacrifice template approach is developed to fabricate a nitrogen-doped carbon nanotubes/carbon fabric electrode with a hierarchically porous structure from core-shell ZnO@ZIF-8 nanorod array layers on the cotton fiber surface inside cotton fabrics. Numerous pores are also generated on the carbon nanotube walls. The nitrogen-doped porous carbon nanotube array layer provides large surface area, proper porosity and heteroatom-doped carbon skeleton, leading to an enhanced electrochemical performance. This flexible electrode exhibits a high specific capacitance of 390 F/g at a scan rate of 2 mV/s. This electrode also shows good long-term cycling stability and stable electrochemical performance under mechanical deformations. The assembled all-solid-state symmetric supercapacitor exhibits a high energy density of 23.4 Wh/kg at a power density of 91.4 W/kg.

1. Introduction

Flexible supercapacitors are regarded as one of the most promising energy storage devices for powering wearable electronics due to their light weight, flexibility, high power density, long cycling life, rapid charge/discharge rate, safety, easy maintenance and environmental friendliness [1–6]. However, the low capacitance and energy density are the main issues blocking their practical application. Therefore, developing high-performance flexible supercapacitor electrode materials is the key to achieve the satisfied electrochemical performance [6–9].

Among various active materials (i.e., carbon materials, metal oxides and conducting polymers), 2D thin-film carbon materials, especially the carbon fabric, can storage energy through the electric double-layer capacitance (EDLC) mechanism, which have aroused the general attention due to their high conductivity, good chemical stability, and

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excellent flexibility [10–13]. Several reported literatures reveal that the cotton fabric weaved by cellulose fibers is an inexpensive natural product, which has great potential in the fabrication of flexible carbon electrode materials through thermally treatment in inert atmosphere [14–17]. The resulting carbon fabrics possess high electrical conductivity and good mechanical properties. Meanwhile, this strategy can be easily scaled up due to the commercially available cotton fabric. According to the energy storage mechanism of EDLC, carbon supercapacitor electrodes storage energy through the physical adsorption of electrolyte ions on the interface between the electrode material and electrolyte [18–20]. The electrochemical capacitance is proportional to the accessible surface area of the carbon electrode [21]. Hence enlarging the surface area of carbon fabric is an effective approach to enhance its electrochemical performance. Apart from that, to further increase electrochemical capacitance, proper doping heteroatoms into carbon framework is desirable for enhancing the conductivity, surface wettability as well as capacitance by inducing additional pesudocapacitance. To date, several strategies have been adopted to prepare high-performance cotton fabric derived carbon fabric electrodes. Xue et al. prepared a flexible carbonized cotton fabric supercapacitor electrode, which exhibited stable electrochemical performance under the mechanical folding condition [22]. However, its specific capacitance was only ~14 F/g at a current density of 0.22 A/g using 1 mol/L Na_2SO_4 as the electrolyte. Li et al. also observed the similar low electrochemical performance of 1.5 F/g at 1.0 A/g for a pure cotton derived carbon fabric electrode using 1 mol/L H_2SO_4 as the electrolyte [23]. The unsatisfied energy storage capacity of cotton derived electrodes severely limits their practical application. Although using the activating agent (KOH and NH_3) during the thermal treatment of cotton fabric could effectively increase surface area and form N-doping skeleton of the carbon fabric to increase the electrochemical performance, however, these approaches significantly degraded the mechanical strength and flexibility of the carbon fabric electrodes, and arose safety concerns [23,24]. Therefore, designing and tuning the electrode structure of cotton fabric derived carbon fabric electrodes with the key characteristics including large surface area, accessible porosity, proper heteroatom doping and robust electrode structure is still a great challenge in flexible supercapacitors.

In this work, a facile self-sacrifice template approach is developed to construct a nitrogen-doped porous carbon nanotube array layer on the carbon fiber surface inside cotton derived carbon fabrics through carbonizing the core-shell ZnO@ZIF-8 nanorod array layers. The nitrogen-doped carbon nanotubes with microporous walls provide large surface area, proper porosity and heteroatom-doped carbon skeleton, leading to the significant enhancement of electrochemical performance. The strong interaction between carbon nanotube array layers and fiber surfaces, and robust electrode structure guarantee a good electrochemical and mechanical stability when it was tested in a long-term cycling process and under the mechanical deformation condition. The assembled all-solid-state systematical supercapacitor provides an efficient, flexible energy storage device which shows high energy density and good flexibility.

2. Experimental

2.1. Materials

Cotton fabric is a commercial product purchased from a local market. Zinc acetate dihydrate, triethylamine, sodium hydroxide, zinc nitrate hexahydrate, 2-methylimidazole, and hexamethylenetetramine were obtained from Sinopharm Chemical Reagent Co., Ltd. Isopropyl alcohol, ammonium chloride, N,*N*-Dimethylformamide, and ammonium chloride were purchased from Shanghai Lingfeng Chemical reagent Co., Ltd. All chemicals were analytical grade and used without further purification.

2.2. Synthesis

2.2.1. Synthesis of ZnO seed solution

ZnO seed solution was prepared as follows. 5.0×10^{-3} mol of zinc acetate dihydrate was added in 50.0 mL of isopropyl alcohol under stirring at 85 °C for 15 min. 700 μL of triethylamine was added dropwise to the above solution. The resulting solution was stirred for 10 min. Then the ZnO seed solution was cooled to room temperature for 3 h.

2.2.2. Synthesis of ZnO growth solution

0.15 mol of hexamethylenetetramine and 0.15 mol of zinc nitrate hexahydrate were dissolved sequentially in 250 mL of H_2O. This resulting solution was stirred for 24 h at room temperature.

2.2.3. Growth of ZnO nanorods on cotton fabrics

A piece of cotton fabric (20 cm × 30 cm) was cleaned by immersing it in 1.0 mol/L NaOH aqueous solution at 100 °C for 1 h. The cotton fabrics were collected, rinsed thoroughly with H_2O and dried in air.

The ZnO nanorod/cotton composite fabric was prepared according to a reported method with a little modification [25]. The clean cotton fabric (4 cm × 3 cm) were first dipped in the ZnO seed solution for 5 min and then rinsed with ethanol. The dip-coated cotton fabric was dried at 120 °C for 1 h in an oven, and then further dried at room temperature for 12 h. The seed-treated cotton was fixed on a PTFE frame and then suspended vertically in 80 mL of the ZnO nanorod growth solution and incubated at 95 °C for 8 h in an oven. The container was taken out from the oven, cooled to room temperature, and then further incubated at room temperature for 12 h. Finally, the cotton fabric was collected from the growth solution, thoroughly rinsed with H_2O and dried naturally in air at room temperature.

2.3. Synthesis of ZnO nanorod@ZIF-8/cotton composite fabrics

The ZnO nanorods on the cotton fiber surface were coated with ZIF-8 shells according to a reported method with a little modification [26]. 2 g of 2-methylimidazole was first dissolved in a mixture of 45 mL of DMF and 15 mL of H_2O. Then the ZnO nanorod/cotton composite fabric was immersed in the above solution at 70 °C for 5 h. Finally, the ZnO nanorod@ZIF-8/cotton fabric was collected, washed by H_2O and dried at 60 °C for 3 h.

2.3.1. Synthesis of N-doped CNT/carbon fabric electrodes

The ZnO nanorod@ZIF-8/cotton fabric was immersed in 1.0 mol/L NH_4Cl aqueous solution for 1 h and then dried at 120 °C for 1 h in an oven. Finally, the NH_4Cl-treated ZnO nanorod@ZIF-8/cotton fabric was calcined at 800 °C for 300 min with a heating rate of 5 °C/min in nitrogen gas flow. The carbonized fabric was dipped into 3% of ammonium hydroxide to remove ZnO. The resulting carbon fabric was denoted as NC/CT.

In a control experiment, the pure cotton fabric was also calcined at 800 °C for 300 min with a heating rate of 5 °C/min in nitrogen gas flow. The obtained carbon fabric was named as P/CT.

2.3.2. Fabrication of all-solid-state supercapacitor devices

The gel electrolyte was prepared using a reported method [27]. Briefly, 1 g of polyvinyl alcohol (PVA) was added in 10 mL of 1 mol/L H_2SO_4 at 85 °C under string. When the mixture solution became clear, it was cooled to room temperature.

Two identical NC/CT fabrics (1 cm × 1 cm) were first immersed into the PVA/H_2SO_4 gel electrolyte for 5 min. After that, they were sandwiched by a filter paper which was used as the separator and then pressed together. The supercapacitor device was encapsulated by polyethylene terephthalate (PET) film and dried at room temperature overnight until the PVA-H_2SO_4 electrolyte was solidified.