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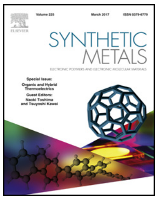

Flexible N-doped active carbon/bacterial cellulose paper for supercapacitor electrode with high areal performance

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ABSTRACT

A flexible N-doped activated shaddock peel carbon (N-ASPC)/graphene (GN)/bacterial cellulose (BC) hybrid paper electrode with remarkable mechanical properties and large mass loading (8 mg cm^{-2}) is fabricated. This flexible electrode integrates extraordinary special capacitance N-ASPC from resource-rich fruit waste (shaddock peel), highly conductive GN and ultrafine three-dimensional (3D) fibrous network structure BC, which exhibits remarkable areal capacitance of 2004 mF cm^{-2} (250.5 F g^{-1}), excellent rate performance with 82.3% retention from 2 to 40 mA cm^{-2}, good cyclic stability with 97% retention over 10,000 cycles, ultrahigh tensile strength (32 MPa) and good conductivity (1550 S m^{-1}). The symmetric supercapacitor based on two identical N-ASPC/GN/BC film electrodes with an operation voltage of 1.4 V in Na_2SO_4 electrolyte can deliver a maximum energy density of 0.158 mW h cm^{-2} and a maximum power density of 28 mW cm^{-2}. Therefore, the binder-free N-ASPC/GN/BC electrodes hold great promise for flexible energy-storage devices.

1. Introduction

Flexible energy storage devices have gained considerable attention owing to the ever-growing demand for wearable electronics with multiple functionalities, and the lightweight, flexibility and sufficient compactness are critical feature [1–5]. Among them, supercapacitors (SCs) bridge the dielectric capacitors and batteries, which show attractive characteristics including fast recharge capability, high-power density, long-time lifespan and operational safety [6–9]. Therefore, they can serve as state-of-the-art energy storage and provide stable output for various portable electronics. There is no doubt that a flectional or stretchable electrode is one of the critical components for the flexible supercapacitors [13,14]. However, a facile method for mass production of free-standing carbon films with ultrahigh mechanical capacity, and satisfactory electrochemical properties is still a challenge but highly desired. It is well known that carbon materials remain the primary candidate used as electrode materials in supercapacitors on account of stably physicochemical and thermodynamic property, large specific surface area (SSA), and abundant pore structures [10–12]. At present, free-standing electrodes have been widely prepared by carbon materials such as graphene [13–16], carbon nanotube [17,18], carbon nanosheets [11,12] and carbon cloth [9,19] etc. Nevertheless, the areal capacitance of graphene papers and carbon nanotube films is limited, usually under 100 mF cm^{-2}, because of the low mass loading and the plenty of aggregation caused by strong π-π interactions during the preparation process [15,16]. Carbon cloth, a conductive textile, is usually used as current collectors or scaffolds in flexible electrodes [19]. However, its small SSA and poor porosity make a slight mass loading of active materials, and the binding force of the two is vulnerable. Additionally, relatively high prices, insufficient supply and complex process have hindered large-scale application of these materials.

Porous carbon materials from renewable carbon sources have long been studied as supercapacitor electrode materials and have been commercial applications due to their abundance, low-cost, simple preparation process and environmentally benign. They can provide plenty of adsorbing sites and fast transport channel for electrolyte ions, and thus boost the discharge capacitance on the basis of electrical double-layer mechanism [10–12]. In addition, to further improve their capacitive performance, suitable carbon resource is essential. Shaddock peel, naturally abundant and available fruit waste, is usually burnt or discarded. Actually, its outstanding water holding capacity and the numerous cellulose fibers existing in its white sponge-like layer will provide a shortcut to prepare 3D porous carbon materials with high electrochemical performance [20]. Recently, researches for porous carbon

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materials are mainly based on traditional rigid electrodes instead of flexible electrodes. As industrially produced cheap biomass materials [21], BC has a 3D interconnected nanofibrous network structure consisting of a randomly assemble nanofibers with widths of 20–100 nm and plentiful surface hydroxyl groups, and thus provides sufficient SSA, extensive porosity and high tensile strength [22–24]. Given these merits, BC endows the flexible electrode with great hydrophilicity and high mass loading when used as supported substrate. To deal with the poor conductivity caused by insulated BC, highly conductive graphene nanosheets are introduced into the hybrid electrode. The GN acts as expressway accelerating the transport of electron in the film and improves the electrochemical utilization of porous carbon materials.

In this paper, we adopt BC as flexible and lightweight scaffold to support N-doped activated shaddock peel carbon/graphene (N-ASPC/GN) as active materials for supercapacitor electrode. By means of intrinsic nature of shaddock peel, the N-ASPC with well-developed porosity and large specific surface area is easily obtained. In contrast to rigid electrodes combining metal current collector and active materials via binder, the hybrid film forms a continuous compact network with N-ASPC/GN penetrated into the voids of BC to provide fast ions diffusion and electron transfer. The N-ASPC/GN/BC electrode combine the advantages of nanofiber network for BC, high capacitance for N-ASPC and high conduction for GN, thus, excellent mechanical property, large loading mass, improved specific capacitance and good cycle performance can be obtained. In addition, the symmetrical SCs coupled with two N-ASPC/GN/BC films show good capacitive characteristics and high energy density. Hence, the as-prepared paper should be the promising flexible electrode for high-performance bendable SCs.

2. Experimental section

2.1. Synthesis of N doped porous carbon materials

All of the chemicals were of analytical grade and used without further purification. Shaddock peels, gathered by daily fruit market with removal of the outside yellow skin, were cut into white pieces, washed by deionized water (DI water) to remove impurities and then freeze-dried to preserve the sponge-like structure. Typically, obtained shaddock peels (1.5 g) were soaked in the 30 mL solution of 1 M $CO(NH_2)_2$ before magnetic stirring for 6 h and freeze-dried. Subsequently, the resultant mixture was carbonized in N_2 flow at 800 °C for 1 h to form the N-doped shaddock peel carbon (N-SPC). The N-SPC was then mixed with KOH at a KOH/C ratio of 2:1. After heated up to 800 °C and held for 1 h at a ramp rate of 5 °C min^{-1}, the product was washed repeatedly with 1 M HCl and deionized water for several times. Finally, the sample was dried at 80 °C for 6 h, and named as N-ASPC. For comparison, pure shaddock peels without being mixed with $CO(NH_2)_2$ solution and activation, were pyrolysed directly under the same carbonization procedure to obtain the SPC.

2.2. Fabrication of N-ASPC/GN/BC paper electrodes

Typically, 5 g BC membrane (3% wt, Hainan Yida Food Industry Co.,Ltd) was pulped with a mechanical homogenizer to obtain a suspension of BC nanofibers. The mixture then undergone vacuum filtration to get a BC paper. GN was prepared by graphite sheet using the modified Hummer's method [25,26]. 20 mg of GN and 60 mg of modified SPC were dispersed in 80 mL DI water with vigorous stirring for 1 h to get a homogeneous dispersion. Afterward, the modified-SPC/GN composite solution was poured onto the obtained BC paper to form a hybrid film. After washing several times with DI water and drying at 60 °C for 6 h, we obtained the free-standing N-ASPC/GN/BC and N-SPC/GN/BC paper. The loading of the active materials is 8 mg cm^{-2} (the total mass of modified SPC and GN). The control sample was designed as SPC/GN/BC.

2.3. Characterizations

The morphology and the microstructure of all samples were characterized by scanning electron microscope (SEM, Hitachi S-4800). The surface functional group and elemental analysis were observed by X-ray photoelectron spectroscopy (XPS, VG ESCA-LABMK II). The electronic conductivity of the paper electrodes was recorded with the four-point probe method (RST-9, 4 Probes Tech Co.). The specific surface area, total pore volume and pore diameter distribution were obtained by nitrogen adsorption/desorption measurements (ASAP 2020 at 77 K). Mechanical properties were characterized using a universal a tension tester (CMT 8102). Contact angle measurements were performed on an OCA20 (Dataphysics) using a 6 M KOH droplet as indicator.

2.4. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system and a two-electrode configuration. In the three-electrode system, the N-ASPC/GN/BC paper was cut into a piece ($1 \times 1\ cm^2$) as the working electrode, a platinum sheet was used as the counter electrode, and the Hg/HgO electrode was the reference electrode in a 6 M KOH. Symmetric supercapacitor was assembled by two identical N-ASPC/GN/BC films with 6 M KOH and 1 M Na_2SO_4 as electrolyte, respectively. The cyclic voltammetry (CV) test, the galvanostatic charge-discharge (GCD) measurements and the electrochemical impedance spectroscopy (EIS) were carried out with a CHI660E electrochemical workstation (Chenhua, Shanghai).

The specific capacitance was calculated from the GCD curves using the following equations:

$$C_a = \frac{I \times \Delta t}{S \times \Delta V} \quad (1)$$

$$C_g = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

where C_a and C_g are the areal and gravimetric capacitance, I is the discharge current (A), Δt represents the discharge time (s), ΔV refers to the voltage window (V), S corresponds to the surface area (cm^2) and m is the mass of active materials (g). The areal energy density (E, W h cm^{-2}) and areal power density (P, W cm^{-2}) of the symmetric device were evaluated according to the following equations:

$$E = \frac{C \times \Delta V^2}{2} \times \frac{1}{3600} \quad (3)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (4)$$

where C is the areal capacitance. ΔV and Δt have the same notations as above.

3. Result and discussion

3.1. Preparation and characterization of samples

The schematic representation for the fabrication of N-ASPC/GN/BC paper is illustrated in Fig. 1. Initially, the N-ASPC was