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Novel freestanding N-doped carbon coated Fe_3O_4 nanocomposites with 3D carbon fibers network derived from bacterial cellulose for supercapacitor application

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ABSTRACT

Freestanding N-doped carbon coated Fe_3O_4 particles nanocomposites with three dimensional (3D) carbon fibers network (NC@Fe_3O_4/CF) derived from bacterial cellulose (BC) was fabricated by simple hydrothermal and carbonization. This self-supporting structure, as promising electrode without current collector or conductive additive, showed high area capacitance and volume capacitance (1.36 F·cm^{-2}, 2300 F·cm^{-3} at 3 mA·cm^{-2}). Simultaneous, the electrode showed good cycle life (88.5% capacitance retention over 4000 cycles) and wide potential window (− 1.2 to 0 V), possessed the property of pseudo and carbon materials. This low-cost, non-toxic and high capacity freestanding electrode is a potential candidate for supercapacitor applications.

1. Introduction

Compared to the traditional batteries, supercapacitors as one of environmental-friendly energy storage devices with various advantages, such as long charge-discharge cycle life, high charging capacity and power density [1]. All-solid-state supercapacitors have become a new research area, considering the tendency of wearable device, which is safer, thinner and lighter [1–3]. Based on the charge store mechanism, one is electric double layer capacitor (EDLC), which includes most of carbon materials with long cycle life, like active carbon, porous carbon, carbon nanotubes (CNTs), grapheme, etc. [4]. However most have low capacitance, only 15–40 μF·cm^{-2} [5]. Another is faradaic redox capacitor, which contains conductive polymer (PPy, PANI and PEDOT), transition metal oxide (TMOs) such as RuO_2, WO_3, MnO_2, and Fe_3O_4 [6,7]. It has high energy density, but poor structure stability due to the pseudo-capacitive behavior [8].

In order to improve the stability of TMOs and capacitance of carbon materials, carbon-based metal oxide composites have been developed in recent years. WO_3/carbon aerogel composites showed high capacity and 95% capacitance retention over 4000 cycles [9]. 3D rGO/CNTs/MnO_2 exhibited 319 F·g^{-1} capacitance and 85.4% capacitance retention over 3000 cycles [10]. Among them, Fe_3O_4 with 346.5 mAh·g^{-1} theoretical capacity at $Fe^{3+} \rightleftarrows Fe^0$ possible states transfer, low cost, nontoxic and large resources on the earth [11], and has received widely attention. In order to avoid the volume change and agglomeration of Fe_3O_4, conductive shell is always needed. As reported, the promising carbon shellcould greatly enhance the cycle stability by forming strong covalent bond with Fe_3O_4. However most Fe_3O_4 composite materials are powders or need metal current collectors are poor flexibility, weaken electrical conductivity, high cost and weight (even to 40 wt%) and difficult to assembly, [12]. It is urgent to design multidimensional carbon materials, like 2D grapheme, 3D mesoporous carbon, as the flexibility conductive self-supporting template or shell.

With respect to bacterial cellulose (BC), a kind of biocellulose hydrogels, with high Young's modulus, carbon content and special 3D nano network, produced by *Gluconacetobacter xylinus* under suitable culture condition [13,14]. Compared to plant cellulose, BC has higher crystalline, purity and fine fiber diameter of about 50 nm. Tong et al. carbonized BC-supported Ru particles for Li-O_2 batteries [15], Hu et al. made N,P-co-doped carbon nanowires from BC [16], and Huang et al. carbonized BC as flexible cathodes for lithium–sulfur batteries [17]. BC has become an attractive base material to fabricate low cost, high performance and freestanding carbon electrode.

In this research, a simple method was used to prepare N-doped carbon coated Fe_3O_4 particles on freestanding 3D BC carbon fiber network (NC@Fe_3O_4/CF). N-doped carbon shell could be used as a buffer against volume change of Fe_3O_4, during charge-discharge process. Furthermore, Fe_3O_4 added electrode showed increased potential voltage ranges and areal capacitance (C_a) without any conductive additive or adhesion agent.

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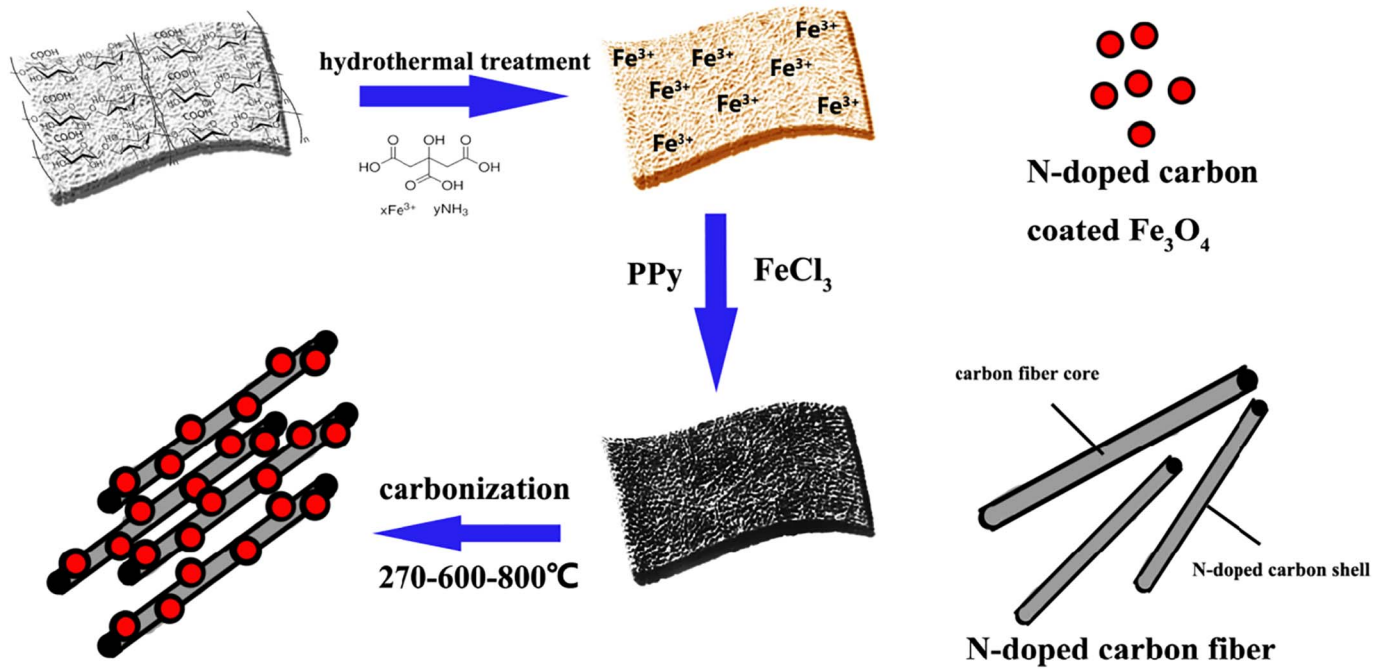

Scheme 1. Graphic illustration of freestanding NC@Fe_3O_4/CF electrode synthesis process.

2. Experimental

2.1. Materials

Ammonium ferric citrate (AFC), absolute ethyl alcohol, $FeCl_3$, hydrochloric acid (HCl), ammonium persulfate (APS), sodium dodecyl benzene sulfonate (SDBS) and pyrrole monomer are analytical reagents without further purification. The BC was cultured by our group [18].

2.2. Preparation of ferric hydroxide/BC (Fe-BC) precursor film

At first, the obtained BC films were boiled in the 1 mol/L NaOH solution [19]. Then, they were treated by the 1 mol/L APS solution under ultrasonic agitation and named as A-BC. Later, they were washed by deionized (DI) water and removed excess water. After, they were put into 50 mL 0.1 mol/L ammonium ferric citrate solution and removed into Teflon autoclave at 180 °C for 12 h. Finally, the obtained Fe-BC films were washed several times by DI water and absolute ethyl alcohol.

2.3. Preparation of N-doped carbon coated Fe_3O_4/c-BC freestanding electrode

The Fe-BC films were put into mixed solution with 1 g SDBS, 100 mL DI water and 2 mL pyrrole monomer and ultrasonic agitation for 1 h. Then 10 mL 1 mol/L $FeCl_3$ solution was drop into mixed solution at 4 °C ice bath for 5 h. The obtained PPy@Fe-BC films were freeze drying for 12 h. Finally, the dried films were carbonized at 270, 600 and 800 °C for 1 h each, under nitrogen atmosphere, and the obtained freestanding film was named as NC@Fe_3O_4/CF. For comparison, the Fe-BC and PPy@BC were also carbonized under same condition, and named as Fe_3O_4/CF, NC@CF, respectively.

2.4. Characterization

The Nitrogen adsorption-desorption isotherms were obtained by the Micromeritics (TriStar II 3020 3.02) and N_2 adsorption isotherms at 77 K. Pore diameter distribution was calculated by nitrogen adsorption isotherms. The different samples were analyzed by Fourier transforms infrared spectroscopy (FTIR Thermal Fisher Nicolet is10) and X-ray diffraction (XRD BRUKER AXS GMBH D8) was measured with Cu Kα radiation at a scanning speed of 5° min^{-1}. The scanning electron microscope (SEM Hitachi SU-1510), High Resolution Transmission Electron Microscopy (HRTEM) and transmission electron microscope (TEM Jem 2100) were also employed to observe the micro-morphology of the films. The X-ray photoelectron spectroscopy (XPS Thermo Fisher-250xi) with monochromatic Al Kα was used for chemical analysis. Thermo gravimetric analysis (TGA) and derivative thermo gravimetric analysis (DTG) were measured at 20 °C min^{-1} from 30 °C to 800 °C in air (TA Q500). The Raman spectra of samples were obtained by Raman spectroscopy Renishaw 2000.

2.5. Electrochemical measurements

For the electrochemical measurement, freestanding films were cut into 0.8 cm × 0.8 cm (the mass is 3.5 mg) and tested in 1 mol/L KOH solution by three-electrode systems, in which Ag/AgCl was used as reference electrode, platinized platinum was used as the counter electrode. The capacitance of film electrodes were calculated by following equation:

$$C_a = I\Delta t/(S\Delta V),\ C_V = I\Delta t/(V\Delta V)$$
$$V = S \times D. \quad (1)$$

where C_a (Fcm^{-2}) is the area capacitance, C_V (Fcm^{-3}) is the volume capacitance, I (A) is the measure current, $\triangle t$ (s) is the time of discharge process, S (cm^2) and V (cm^3) are the area and volume of sample respectively, D (cm) is the average thickness of cross section of the film (in Fig. S2), $\triangle V$ (V) is the potential of discharge process.

3. Result and discussion

3.1. Formation of NC@Fe_3O_4/CF composite fibers

The NC@Fe_3O_4/CF composite fibers were fabricated by hydrothermal and carbonization in Scheme 1. At first, the treated A-BC with carboxyl and hydroxyl groups absorbed large amount of ammonium ferric citrate (AFC) solution. During hydrothermal process, the citric acid radical of the double salt AFC worked as adjuvant, first. With the reaction proceeded, it decomposed into CO_2 and H_2O, formed abundant