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Novel collagen waste derived Mn-doped nitrogen-containing carbon for supercapacitors

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ABSTRACT

Heteroatom doped carbon originated from natural and renewable biomass has recently attracted tremendous attention related to electrode material of supercapacitors. Herein, we reported a practical and facile strategy to synthesize Mn-doped N-containing carbon materials based on collagen waste obtained from leather processing for supercapacitors, and this method was applicable to most metals. Mn-doped N-containing carbon was fabricated primarily by chelating metal ions with bayberry tannin immobilized collagen fiber, followed by a carbonization treatment. The as-prepared Mn-doped N-containing carbon material exhibited a high specific capacitance (272.62 F g^{-1} at the current density of 1.0 A g^{-1}), high rate capability (72.21% capacitance retention with increasing current density from 1 to 20 A g^{-1}), and after 6000 cycles remained 81.4%. Especially, it showed favorable thermal stability under extreme conditions (264.9 F g^{-1} and 262.65 F g^{-1} at 60 °C and 0 °C water bath under the current density of 1 A g^{-1}, respectively). The results indicated that Mn-doped N-containing carbon was a practically potential electrode material for supercapacitors.

1. Introduction

Supercapacitor is an important bridge between traditional dielectric capacitor and battery [1–3]. The reserves of solar energy, wind energy, the braking in electric vehicles and other renewable energy sources are the typical large-scale applications [4,5]. The capacitance of the supercapacitor mainly comes from the surface charge separation at the electrode-electrolyte interfaces, and the Faraday oxidation-reduction reaction [6–9]. Among the various electrode materials, carbon materials are the most widely used and account for more than 80% in commercial supercapacitors [10,11]. In the carbon materials, the number of pores, the discontinuities of the conductive channels, and the influence of the oxygen-containing functional groups have limited the power density. In order to further enhance the performance of carbon-based supercapacitors [12,13], the introduction of heteroatoms into carbon materials has been developed [14,15], which is considered as a strategy to improve the energy density and power density.

Over the past few decades, heteroatoms, such as nitrogen (N), phosphorus (P), sulfur (S), and so on [16–21], have been doped into the carbon framework to tailor the physical properties, enhance the surface Faraday reaction rate and maintain the high rate capacity and long cycle life of carbon materials. However, manganese (Mn), as one of the first row transition metal element, has similar capacitance enhancement properties with iron (Fe), cobalt (Co) and nickel (Ni), and it has been widely used to prepare doped carbon electrode materials [22–24]. Meanwhile, many kinds of precursors have been explored to prepare heteroatoms doped carbon materials, such as polymers, organic salts, plant precursors and animal precursors, etc. Among them, biomass has drawn more attention due to its low cost, large quantity, renewable and good environmental compatibility [25–28]. Collagen waste is obtained from the

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leather industry, and its main component is collagen fibers (CF). CF, one of the abundant natural biomass, has traditionally been used in tanning to form fiber bundles, interwoven and interlace in the dermis, giving the leather a high mechanical strength [29]. CF is composed of collagen, where three polypeptide chains are rigidly bonded together by α-helix, and a large number of active groups such as -NH_2, -COOH and -OH exist in the peptide chain [30,31]. At the same time, collagen as biological materials is widely applied in medicine, food and beverage, cosmetics and other fields [32], which guarantees the rich source as a raw material for carbon materials.

Moreover, through the crosslinking of aldehyde, collagen fiber can react with tannin to prepare collagen fiber immobilized tannin materials. The material has a strong adsorption capacity for metal ions and has been widely used in environmental protection, metallurgy, medicine and chemical engineering [33–35]. The doping method that carbonization after the material chelated with metal ions provides a new idea for the preparation of doped carbon material. At the same time, the preparation of doped carbon materials by chelation of collagen fiber immobilized tannin has not been reported. Accordingly, it is highly desirable to exploit a general strategy to synthesize heteroatom-doped carbon materials based on collagen fiber.

Herein, with collagen waste as carbon and N source, we demonstrated a novel metal ion chelation strategy to fabricate Mn-doped N-containing carbon materials. This is the first report of synthesizing Mn-doped N-containing carbon by metal ion chelation method with collagen fibers that were extracted from collagen waste. In this strategy, bayberry tannin immobilized collagen fiber (CF-BT) was used to chelate metal manganese ions. And followed by carbonization, the Mn-doped N-containing carbon materials were successfully fabricated and applied for supercapacitors. The results demonstrated that the prepared Mn-doped N-containing carbon exhibited a high specific capacitance, a long cycle life, and a favorable tolerance to extreme conditions, suggesting it a promising candidate for an efficient electrode material for supercapacitors.

2. Experimental

2.1. Materials

All reagents and materials used in the experiment were of analytical purity and used without further purification. A scrap of the collagen fibers and bayberry tannin were provided by the Key Laboratory of Leather Chemistry and Engineering of Ministry of education of Sichuan University, and collagen fibers were extracted from collagen waste. Glutaraldehyde ($C_5H_8O_2$) was purchased from the Nanjing Chemical Reagent Co., Ltd. Sodium bicarbonate ($NaHCO_3$) was purchased from the Chengdu Kelong Chemical Reagent Factory. Manganese sulfate ($MnSO_4$) was purchased from the Sinopharm Chemical Reagent Factory.

2.2. Preparation of CF-BT

15 g of collagen fiber as N and carbon source and 9 g of bayberry tannin were added to 400 mL of distilled water and reacted at 25 °C for 24 h. After filtration and washing, the precipitant was put into 300 mL of distilled water containing 20 g/L of $C_5H_8O_2$ and pH was adjusted to 6.4–6.6, reacting at 25 °C for 1 h and then 50 °C for 4 h. The product was washed with distilled water and dried at 60 °C in vacuum for 12 h to obtain CF-BT.

2.3. Preparation of the Mn/N-C-x

The CF-BT was immersed in 0.10 M $MnSO_4$ solution and 0.10 M $NaHCO_3$ was slowly dropped to adjust pH to 4.5. The precipitant was separated after mechanical agitation for 48 h, washed with water and alcohol, and then lyophilized using a freeze dryer at a sublimation temperature of −78 °C and a pressure of 0.04 mbar. The dried CF-BT@$MnSO_4$ was calcined under N_2 atmosphere at 600–1000 °C at a heating rate of 5 °C min^{-1}, and held at the corresponding temperature for 2 h to obtain the final Mn-doped N-containing carbon samples (Mn/N-C-x samples). The synthetic materials were denoted as Mn/N-C-x, where x was the carbonization temperature.

2.4. Materials characterization

Scanning electron microscopy (SEM; JSM-6390/LV, Japan) was utilized to characterize the morphology of the materials. Transmission electron microscopy (TEM) and energy filter TEM (EFTEM) images were collected on a JEM-ARM 200F (JEOL, Japan) atomic resolution analytical microscope with an acceleration voltage of 200 kV. N_2 adsorption analysis was performed by an ASAP 2020 (Micrometrics, USA) accelerated surface area and a micrometrics pore instrument equipped with an automatic surface area analysis tool, and the specific surface area was calculated using Barrett-Emmett-Teller (BET) at 77 K. X-ray diffraction (XRD; X Pert pro, Netherlands) patterns of the materials were carried out with Cu K_α radiations ($\lambda = 0.15406$ nm) performed from 3° to 80° at a speed of 2° min^{-1} at a voltage of 60 kV and a current of 50 mA. X-ray photoelectron spectroscopy (XPS) analyses were carried out using a Kratos Axis Ultra (Kratos Analytical, UK) photoelectron spectrometer with a monochromatic Al K_α X-ray source. Fourier transform infrared spectroscopy (FT-IR) spectra were taken by a Nicolet Avatar 370 FT-IR spectrometer (Thermo Nicolet, USA) in the wavenumber range of 4000–400 cm^{-1}. Differential scanning calorimetry analyses (DSC; Q600, TA, USA) were carried out using a thermal gravimetric analysis instrument under nitrogen at a heating rate of 2 °C min^{-1}. The Raman pattern was characterized by using a 514.5 nm Ar^+ line as an excitation source on a Renishaw System 2000 spectrometer (Horiba Jobin Yvon, Japan).

2.5. Electrochemical measurements

All electrochemical tests were performed on a CHI 760D electrochemical workstation using a three-electrode test system using platinum sheet electrode as counter electrode, the electrode of the active material was applied as the working electrode, the Hg/HgO electrode as the reference electrode, and the 1.0 M KOH aqueous solution as the electrolyte. The cyclic voltammetry (CV) curve was obtained at a scanning speed of 5–50 mV s^{-1} at an operating potential range of −1.0-0 V relative to Hg/HgO electrode. The galvanostatic charge-discharge (GCD) test was carried out at a current density of 1–20.0 A g^{-1} and a potential range of −1.0-0 V relative to the Hg/HgO electrode. In addition, electrochemical impedance spectroscopy (EIS) was measured at an amplitude of 5 mV and an open circuit potential in the frequency range from 100 kHz to 10 mHz.

The working electrode was prepared as follows: First, 80 wt% of the active material, 10 wt% of carbon black and 10 wt% of polytetrafluoroethylene (dispersed in N-methylpyrrolidone) were mixed together and ground to a slurry. The slurry was then supported on nickel foam with an area of 1.0 cm^2 and dried under vacuum at 80 °C for 1.5 h. Next, the electrode was pressed at a pressure of 10 MPa and then dried in a vacuum oven at 100 °C for 12 h. The mass loading of active material on each collector was 5.0–6.0 mg.