Sustainable nitrogen-rich hierarchical porous carbon nest for supercapacitor application

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ABSTRACT

Chitosan has high synthetic flexibility, making it a promising nitrogenous bioresource for industrial applications. Nitrogen-rich hierarchically porous carbon (NHPC) was successfully synthesized by hydrothermal carbonization and self-activation of a chitosan-transition metal ion (Zn^{2+}) complex. The N_2 adsorption-desorption isotherm revealed that the as-made NHPC had large specific surface area ($1067\,m^2\,g^{-1}$) and a unique hierarchical pore structure (0.6–6.4 nm). Scanning electron microscopy (SEM) indicated a 3D finely interconnected nest architecture for NHPC. X-ray photoelectron spectroscopy (XPS) analysis demonstrated that the nitrogen atoms in the chitosan were protected by coordination with zinc ions, and most of them were still retained in the carbon matrix (6.36 at%) after high temperature activation. Electrochemical measurements exhibited that NHPC delivers a high specific capacitance ($228.7\,Fg^{-1}$ at $1\,A\,g^{-1}$), impressive rate capability (the specific capacitance at $20\,A\,g^{-1}$ was $174\,Fg^{-1}$, maintaining 74.6% of the initial capacitance at $0.5\,A\,g^{-1}$), and outstanding long-term cycling stability (98.3% retention after 5000 cycles), together with excellent energy density of $25.7\,Wh\,kg^{-1}$ at the power density of $500\,W\,kg^{-1}$. This study offers a novel strategy for synthesizing NHPC as one of the desirable electrode material candidates for energy storage.

1. Introduction

Supercapacitor, as one of the most promising and eco-friendly energy storage devices, has attracted increasing interests due to its high power density, fast charge/discharge rates, and long cycle life (Chen et al., 2017; Jing & Yamauchi, 2016; Salunkhe et al., 2015; Salunkhe et al., 2016). Supercapacitors can be divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors based on distinct charge storage mechanisms. EDLCs generally store energy by accumulating charges at the electrolyte/electrode double layer interfaces through electrostatic attraction, while pseudocapacitors offer electrical energy by Faradaic redox reaction of the particular electrochemical active species. Electrode material plays a dominant role in determining the performance of supercapacitor. Among diverse candidate electrode materials for supercapacitors, porous carbons are comprehensively studied because of their low cost, tunable pore size, large surface area, high conductivity, and outstanding chemical stability. Activated carbon is the most commonly used porous carbon electrode material in EDLC devices (Bhattacharjya & Yu, 2014). Although micropores within active carbons can effectively enlarge the specific surface area and thus enhance the capacitance, activated carbons still suffer from the low energy density and poor rate capability at high current density because

insufficient hydrophilicity and high degree of tortuous microporosity of the activated carbon electrodes hindered electrolyte ions diffusion.

Heteroatom incorporation into carbon framework has been proven to be an efficient methodology to improve surface hydrophilicity, and offer pseudocapacitance for carbon host. Among various heteroatoms (such as boron (Yu et al., 2015), sulfur (Deng et al., 2015), nitrogen (Chen et al., 2012), phosphorus (Bairi et al., 2015), et al.), nitrogen is the extensively investigated dopant element and can even endow an electron donor character to carbon. Furthermore, the well-developed hierarchical pore channels combining micropores with mesopores and/or macropores together can decrease diffusion distance and facilitate the ion migration. Therefore, nitrogen-doped hierarchical porous carbon (NHPC) is considered as an alternative promising electrode candidate for supercapacitors (Zhang et al., 2014).

Currently, NHPCs are usually synthesized by template approaches. For example, Zhou et al. prepared NHPC by a hard template/KOH activation combination strategy using nano-SiO_2 as a sacrificed hard template and amino-phenolic resin as a precursor (Zhou et al., 2015). The prepared NHPC-800 carbon exhibited a high capacitance of $114.0\,F\,g^{-1}$ at the current density of $40\,A\,g^{-1}$. Yan et al. synthesized a well-defined soft template using polyacrylonitrile (PAN) as nitrogen-enriched carbon source and polymethylmethacrylate (PMMA) as

sacrificial block in advance and obtained NHPC through carbonization of the PAN-b-PMMA diblock copolymer (Yan et al., 2016). The as-made NHPC showed excellent rate capability of 67.8% capacitance retention as the current density elevated from 0.5 to 20 A g^{-1}. Considering the huge number of potential applications, chitosan, a member of the nitrogen-containing biomass family, is supposed to be a sustainable alternative precursor as a starting material for NHPC. Chitosan is obtained by N-deacetylation of chitin, which consists of the N-acetyl-glucosamine monomer. Chitin mainly exists in the exoskeletons of insects and crustaceans, and the annual production amount has been estimated to be almost as high as that of cellulose (Kumar, 2000). Unlike chitin, chitosan is water-soluble and thus has high synthetic flexibility, making it a promising nitrogenous bioresource for industrial applications. Chitosan is therefore under intensive investigation at present (Ahmad & Mirza, 2018). Great efforts have been made to develop chitosan-derived electrode materials and chitosan-based gel electrolyte for supercapcitors (Hao et al., 2015; Ling et al., 2015; Sun et al., 2015; Yamagata et al., 2013).

Chitosan has a regular distribution of amino and hydroxyl groups on its chain and hence possesses strong affinity for transition metal ions. Therefore, chitosan is generally used to remove toxic heavy metals from wastewater by forming complexes (Beheshti et al., 2016; Chen et al., 2009). In addition, chitosan-metal complexes can be applied in antibacterial (Higazy, 2010) and heterogeneous catalysis (Yue et al., 2010) such as hydrogenation (Han et al., 2015) and oxidation (Kramareva et al., 2004). However, to the best of our knowledge, chitosan–metal complexes have so far seldom been utilized as precursors for novel NHPC as electrode material for energy storage (Sun et al., 2014). Inspired by the complexation behavior of chitosan for metal ions, in this work, we report a facile template-free approach to prepare NHPC as electrode material for supercapacitors through hydrothermal treatment and self-activation. Because chitosan possesses plentiful complexation possibilities of metal ions with numerous amino or hydroxyl groups, a chitosan-metal complex can establish a stable carbon matrix via hydrothermal carbonization reaction. Moreover, hydrothermal carbonization of biomass can offer oxygen functional groups to resultant hydrochar and reduce the degree of aromatization (Hu et al., 2010). $ZnCl_2$ has been employed as a chemical activation agent for pore generation in carbon-based materials (He et al., 2013; Lua & Yang, 2005). And just as a Zn ion can coordinate with chitosan, $ZnCl_2$ can efficiently boost pore development in the carbon frameworks by chemical activation during high-temperature pyrolysis. The resulting NHPC with a unique hierarchical pore structure and nitrogen species exhibits superior electrochemical performance when employed as an electrode for supercapacitors.

2. Experimental section

2.1. Materials

Chitosan was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China), with a viscosity of 100~200 mPa·s and a deacetylation degree ≥ 95%. Zinc chloride was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Acetic acid, hydrochloric acid, acetone, ethanol, and potassium hydroxide were supplied by Sinopharm Chemical Regent Co. Ltd., China. All the reagents were used as received without further purification. Millipore water was used in all experiments.

Polytetrafluoroethylene (PTFE, a binder) was provided by Mitsui Dupont Fluorochemicals Inc. Nickel foam (current collector, 99.9%, 1.5 cm in thickness), acetylene black (conductive additive), and hydrophilic polypropylene membrane (diaphragm) were supplied by Hunan Corun New Energy Co., Ltd. The nickel foam slices were purified before testing. First they were immersed in 0.1 M HCl for 24 h, and were subsequently rinsed several times with acetone and ethanol. Finally, the nickel foam slices were vacuum-dried at 50 °C for 8 h and stored in a resealable bag until needed.

2.2. Preparation of the chitosan-zinc complex derived hierarchical porous carbon

NHPC was synthesized as follows: 1 g of chitosan was dissolved in 30 ml distilled water in a beaker assisted with 1 ml 1 M acetic acid solution under ultrasonic conditions. Zinc chloride solution, which was prepared beforehand by dissolving 3 g of zinc chloride in 10 ml distilled water in a vial, was added quickly into the chitosan solution with vigorous stirring, at room temperature, to obtain a gelatinous chitosan-zinc complex in a very short period of time. Subsequently, the mixture was transferred into an 80-ml Teflon-lined autoclave and heated in an oven at 160 °C for 8 h. The hydrothermal product was then placed into an air-circulating oven at 105 °C overnight to remove the water, after being cooled to room temperature. The resulting black hydrochar was put into a quartz boat and placed at the center of a tube furnace, which was heated with a ramp rate of 10 °C min^{-1} under nitrogen atmosphere and kept at 800 °C for 1 h. The as-made carbon was ground and stirred with 50 ml 0.1 M HCl solution to remove the remaining zinc ions. The precipitate was filtrated and washed intensively with distilled water until the filtrate reached a neutral state. Finally, the obtained material was dried in a vacuum oven at 50 °C for 8 h and denoted as NHPC800-3. The synthetic procedure of producing NHPC derived from chitosan-zinc complex is illustrated in Fig. 1. Bodek (Bodek & Kufelnicki, 2010) proposed that only amino groups in microcrystalline chitosan are involved in Zn^{2+} complexation, whereas for Co^{2+}, complexes are formed *via* both the amino and the hydroxyl groups. For comparison, nitrogen-doped carbon (denoted as NC) was also prepared, without the zinc chloride solution.

2.3. Characterization

N_2 adsorption/desorption isotherms of the carbon samples were performed on an autosorbiQ instrument (Quantachrome U.S.) with carbons degassed at 250 °C for a minimum of 3 h prior to measurements. The specific surface area was calculated using the multi-point Brunauer-Emmett-Teller (BET) method. The total pore volume was derived from the adsorbed N_2 amount at a relative pressure P/P_0 of 0.995. The micropore volume was obtained via the *t*-plot method. The pore size distribution was calculated using the Non-local Density Functional Theory (NLDFT) equilibrium model. The morphology of the carbons was observed by scanning electron microscopy (SEM, HitachiSU-70, Hitachi Corp.,Tokyo, Japan) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, U.S.). X-ray diffraction (XRD) patterns were recorded on a powder diffractometer (Rigaku, MiniFlex600, Japan) with Ni-filtered Cu-K radiation (λ = 0.154 nm) at a scanning rate of 0.050° s^{-1} in a 2θ = 10-80°. Raman spectroscopy was recorded using a laser Raman spectrometer (Renishaw inVia RM10000 spectrograph, England) with an excitation wavelength of 532 nm. Elemental analysis of C, N, and H was performed using a Flash EA 1112 Elemental Analyzer (Thermo Fisher Scientific, U.S.). X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo Scientific Escalab 250Xi (U.S.) equipped with a monochromatic Al-Kα X-ray source. XPSPEAK4.1 was applied to fit the XPS results.

2.4. Electrochemical tests

Three-electrode and symmetrical two-electrode systems were used to investigate the electrochemical performance of the as-made carbons. All the measurements were conducted on a CHI660E electrochemical workstation (Chenghua, Shanghai, China) in 6 M KOH aqueous electrolytes. The working electrode was prepared by rolling a homogeneous paste consisting of 80 wt% active material, 10 wt% of acetylene black, and 10 wt% PTFE onto a slice of nickel foam (1 cm^2). The working electrode was subsequently dried in a vacuum oven at 120 °C overnight before pressing under a pressure of 10 MPa for 30 s. The mass of active material loading on a working electrode (~240 μm in thickness) is