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Sustainable nitrogen-containing hierarchical porous carbon spheres derived from sodium lignosulfonate for high-performance supercapacitors

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ABSTRACT

Nitrogen-containing carbon sphere with hierarchical porous structure is obtained through a facile thermostabilization and carbonization method of biomass-derivative sodium lignosulfonate. The synthesis route we proposed is cost-effective and environment-friendly without additional nitrogen precursor, activation or templating agent. The as-prepared carbon spheres exhibit high specific surface area of 1255–1939 $m^2 g^{-1}$ and moderate surface nitrogen content of 1.14–1.66 at.%. When assembling into supercapacitors with 7 M KOH aqueous solution as electrolyte, the carbon sphere shows superior gravimetric specific capacitance up to 276 $F g^{-1}$ at 0.1 $A g^{-1}$, high gravimetric energy density of 7.8 Wh kg^{-1} and power density of 6.2 kW kg^{-1}, together with unprecedented cycling stability (99.5% capacitance retention after 10000 cycles). Notably, in 1 M $SBPBF_4$/PC organic electrolyte, the carbon sphere based supercapacitor presents impressive gravimetric energy density of 34.3 Wh kg^{-1} and power density of 9.4 kW kg^{-1}. These outstanding electrochemical performances suggest that the as-prepared porous carbon spheres should be a promising candidate for the field of energy storage.

1. Introduction

Supercapacitors have attracted increasingly growing interest as novel energy storage devices in scientific researches, owing to their unique characteristics like high power density, fast charge-discharge rate and excellent cycling stability [1,2]. Generally, the electrochemical performance of supercapacitors is basically depended on the electrode materials, and the most challenged issue supercapacitors faced is the relative low energy density. Thus, tremendous effort has been devoted to develop advanced materials as potential supercapacitor electrodes [3]. Nanoporous carbons, the most commonly used supercapacitor electrode materials, have attracted extensive attentions because of their large surface area, high electron conductivity, adjustable pore size, extraordinary chemical stability and relative low cost [4,5]. Recently, researchers are concentrated to develop new nanoporous carbons in different forms for high-performance supercapacitors, such as hierarchical porous carbons [6], templated carbons [7], carbon spheres [8], carbide-derived carbons [9], carbon nanotubes [10], and graphene [11].

Among them, carbon spheres as a promising zero-dimensional (0D) material have gained considerable interests for potential applications in electrochemical energy storage including supercapacitors [12] and Li-ion batteries [13], catalysis [14], heavy metal adsorption [15], CO_2 capture [16], and biomedicine [17]. In particular, renewed and intensive efforts with remarkable advances in supercapacitor has been achieved [18,19], due to extra features of carbon spheres such as high surface-to-volume ratios, high packing density, uniform shape and size, and high fluidity. Traditionally, carbon spheres are fabricated by directly pyrolysis of a spherical carbon precursor, such as glucose [20,21], resol [16,22] and lignin [15,23]. While the synthesis of spherical carbon precursors has been achieved by mainly three methods: microemulsion polymerization [13,17,23], hydrothermal reaction [8,16,20,24,25] and

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coating polymerization on spherical templates [14,22,26]. However, the expensive and corrosive agents, the high-pressure apparatus used, and the time consuming synthesis process post a great challenge for large-scale production of carbon spheres commercially. Furthermore, in order to enlarge specific surface area (SSA) and develop micro-/meso-porosity, chemical activation strategy has been commonly adopted to modulate the physical/chemical property of carbon spheres [8]. Nevertheless, because of the strong surface etching by chemical activation agents, it is hard to fully preserve the well-defined spherical morphology. Therefore, a novel and cheap strategy to fabricate porous carbon spheres rationally is highly desirable.

Most of carbon materials are prepared from fossil raw materials which are unsustainable. Thus, as alternative carbon precursors, biomass and their derivatives with advantages of abundance, reproducibility, readily availability and environmental friendliness are achieving significant research interests [27]. As the second most abundant renewable biopolymer on earth, lignin is accounting for approximately 30% of organic carbon in the biosphere and generated from plant about 0.5–3.6 billion tons annually [28]. Till now, lignin has been largely discarded or used as low grade burning fuel [29], causing secondary environmental pollution and a waste of biomass resource. As a heterogeneous and amorphous phenolic macromolecule, lignin is composed of three primary phenyl propane type units, i.e. p-coumaryl, coniferyl alcohol and sinapyl alcohol, resulting in high carbon content [28]. Lignin, including lignosulfonate, is also the by-product in a chemical pulping process, with total amount estimated to be ca. 70 million tons per year [30]. Therefore, lignin may be the most promising candidate precursor for carbon materials. However, due to its complex 3-dimensional structure, lignin has rarely been employed to synthesise carbon spheres. To date and to the best of our knowledge, there are few articles reported for the fabrication of carbon spheres from lignin [13,15,17,23], where all the carbon spheres are prepared by using polymer-lignin composite precursors, and simultaneously none of them is applied as supercapacitor electrode materials. So, in order to convert lignin to high-valued materials, further efforts are still needed to design and synthesis of lignin-based carbon spheres, especially carbon spheres for supercapacitor application with large surface area and hierarchical porous structure.

In this work, a facile method for fabrication of nitrogen-containing hierarchical porous carbon spheres (HPCSs) has been proposed by using biomass-derivative sodium lignosulfonate (SLS) as carbon and nitrogen precursor. A thermostabilization treatment prior to carbonization was introduced to prevent fusing of the spherical precursor, and self-activation/templating strategy was adopted to gain hierarchical porosity. Morphology, structure and surface chemistry of the carbon spheres prepared from different carbonization conditions was investigated extensively. Then, electrochemical performance of the obtained carbon samples as supercapacitor electrode materials was evaluated systematically in both aqueous and organic electrolyte. Furthermore, key factors dominating capacitive performance of the carbon materials were explored and discussed carefully. Finally, a comprehensive supercapacitive performance comparison was made between our materials and other recently reported or commercial available advanced carbons.

2. Experimental

2.1. Chemicals

The commercial sodium lignosulfonate with spherical structure used in this work was obtained from Shandong province of China. The organic electrolyte of spiro-(1, 1′)-bipyrrolidinium tetrafluoroborate in propylene carbonate (1 M $SBPBF_4$/PC) was purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. Hydrochloric acid, potassium hydroxide, and all the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd, and were used as received without further purification.

2.2. Preparation of hierarchical porous carbon spheres

At first, thermostabilization of SLS was conducted in a rotated horizontal tube furnace to keep the spherical structure with the following heating procedure: (1) temperature was increased from room temperature to 120 °C at 5 °C min^{-1}, and was held at 120 °C for 2 h; (2) temperature was increased from 120 °C to 200 °C at 0.5 °C min^{-1}, and was kept at 200 °C for 4 h; (3) the sample was cooled down to room temperature. A constant air flow was maintained during the thermostabilization process. The stabilized precursor was heated up to 700–900 °C at 5 °C min^{-1} and kept for 1 h under a nitrogen flow of 200 mL min^{-1}. The resulting product was subsequently washed by 1 mol L^{-1} hydrochloric acid solution to remove the residual inorganic impurities and then with sufficient deionized water, followed by drying at 120 °C for 12 h. The as-prepared hierarchical porous carbon sphere was named as HPCS-X, where X represents the heat treatment temperature (700–900 °C).

2.3. Material characterization

Thermogravimetric analysis (TGA) was performed on a STA449F3 (NETZSCH) under N_2 flow with a ramping rate of 10 °C min^{-1}. X-ray diffraction (XRD) data was collected using a Bruker D8 Advance with Cu Kα_1 radiation. Morphology of the samples was obtained by scanning electron microscopy (SEM, Hitachi S4800), and elemental analysis was conducted using energy dispersive spectroscopy (EDS, EMAX 350). Nitrogen adsorption-desorption was utilized to characterize porous structure at 77 K on a Micromeritics ASAP 2020. SSA was calculated by Brunauer-Emmett-Teller (BET) method, and pore size distribution (PSD) was obtained by the Density Functional Theory (DFT) method. Raman spectroscopy was recorded using a Horiba LabRAM HR800 with excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALAB 250 Xi) was conducted to identify surface elemental composition.

2.4. Electrochemical measurements

Electrochemical performance of the HPCS-based supercapacitors was evaluated in 7 M KOH aqueous electrolyte and 1 M $SBPBF_4$/PC organic electrolyte. The working electrode was prepared by a mixture of 80 wt% of carbon sample, 10 wt% of acetylene black and 10 wt% of polytetrafluoroethylene (PTFE) binder, and then pressing onto a nickel foam or onto an aluminum mesh (mass loading of the electrode: 5.9–10.2 mg cm^{-2}). The electrode was subsequently vacuum-dried at 120 °C for 4 h. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were performed using a Solartron SI 1280B electrochemical workstation and an Arbin BT2000 battery test equipment respectively. Electrochemical impedance spectroscopy (EIS) was recorded by a CHI660E electrochemical workstation with a potential amplitude of 5 mV in a frequency range from 0.01 Hz to 100 kHz. For a three-electrode electrochemical setup in aqueous electrolyte, the carbon sample was served as working electrode, and a Hg/HgO electrode and a platinum sheet were used as reference electrode and counter electrode with a potential range from −1.0 to 0 V. In a two-electrode symmetric cell, two electrodes with same weight and size