Nano-micro carbon spheres anchored on porous carbon derived from dual-biomass as high rate performance supercapacitor electrodes

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HIGHLIGHTS

- The optimal NMCSs@RSPC-1 carbon composite materials are controllably constructed.
- Continuous hierarchical pore structures with tunable multi-level size distribution.
- Enriched-heteroatoms tune the electrical and chemical properties of carbon surface.
- High specific capacitance coupled with superior rate performance is obtained.
- The electrochemical performances of different samples are compared in detail.

ARTICLE INFO

ABSTRACT

Hierarchical nano-micro carbon spheres@rice straw-derived porous carbon composites are successfully synthesized by the in situ decoration of the porous carbon with carbon spheres from glucose under the assistance of cetyltrimethyl ammonium bromide micelles and further activated by KOH. The scanning electron microscope images clearly show the carbon spheres disperse homogeneously and orderly onto the surface and in the inner macropores of the porous carbon. The diameter of the carbon spheres varies from 475 nm to 1.6 μm, which can be easily controlled by introducing extra inducing agent. The optimal composites exhibit a large specific surface area ($1122 \, m^2 \, g^{-1}$), rich content of oxygen (14.2 wt %), and tunable hierarchical porous structure. When used as supercapacitor electrodes, the novel composites with abundant fruits present a high specific capacitance of $337 \, F \, g^{-1}$ at $1 \, A \, g^{-1}$, excellent rate retention of 83% from 1 to $20 \, A \, g^{-1}$ and a good cycling stability with 96% capacitance retention after 10000 cycles. In this strategy, the thought of shared ion-buffering reservoirs is proposed and the mutual promotion effects between the carbon spheres and porous carbon in the composites are also practically demonstrated to contribute the enhanced electrochemical performances.

1. Introduction

Supercapacitors, as a sort of advanced power-type energy storage devices, have been intensively applied to consumer electronics, memory back-up systems and industrial power, and there will be provided with more opportunities in the near future for its good durability and high safety performances [1,2]. The energy of supercapacitors originates from the surface reactions of their electrode materials, including electric double layer capacitance and pseudocapacitance, which are respectively caused by electrochemical adsorption-desorption of electrolytic ions at the electrode-electrolyte interface (represented by carbon materials) and fast surface redox reactions (typical of metal oxides and electronically conducting polymers) [3–7]. Among

the enormous researches, various porous carbons, such as activated carbons [8], carbon spheres [9], carbon nanotubes [10], and graphene [11], have attracted immense interest as supercapacitor electrodes due to their highly-pure capacitive behavior, great structural stability and advantage for large-scale manufacture. Based on the charge storage mechanism of electric double-layers of carbon based electrode materials, the specific surface areas provide the electroactive sites to form electrical double-layers for the accumulation of ions at the electrode-electrolyte interface. Usually, the specific surface area of porous materials is directly proportional to the content of micropores [12]. However, the capacitance increase is limited even for the most microporous sample because many micropores are inaccessible, especially under high current density owing to the lack of the handy diffusion

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pathway of electrolytic ion [3]. Under the charge storage process, on the other hand, the hierarchical pore structures with interconnected macro-, meso- and micro-pores can significantly improve the electrode kinetics by providing continuous ion diffusion pathways, making the electroactive sites effective for electrostatically storing energy and contributing the enhanced rate performance [13,14]. By all appearances, it is a valuable research to develop a material with well-balanced pore size distribution.

Plant biomass is mainly composed of cellulose, hemicellulose, lignin and plant protein [15]. All these components occupy stable molecular microstructures which are in favor of creating porous structures when we employ biomass as supercapacitor precursor materials. In addition, besides the principal carbon, the other parts of elements of oxygen, nitrogen and boron in biomass play a significant role in the capacitive properties by additional pseudo-capacitance, shown by relevant researchers [16–19]. Therefore, considerable efforts to develop carbon materials from renewable biomass precursors, such as bacterial cellulose [20], poplar catkins [21], eulaliopsis binata [22], waste tea-leaves [23] and hemp [24], have been devoted by electrode material researchers. The resultant results indicated that these being-prepared carbon materials from various biomasses showed great potential application in energy storage devices. General speaking, Carbon materials from self-template carbonized biomass precursors exhibit different fine microstructures because different organisms and even different parts of the same biomass are exploited. Therefore, the ingenious morphologies and porous structures are difficult to control during the preparation process of biomass-based carbon materials. These inevitably lead to inhomogeneous performances of the carbon materials from the same biomass. Artificial synthetic templates with replicable porous structure are usually used to design advanced carbon materials, which boost the controllability of material preparation to some extent [25,26]. However, these technologies are not only time-consuming, but also involve costly complex preparation process and hazardous chemicals, which hinder their scalable and wide practice application. Therefore, introduction of controllable structures into ingenious biomass-based carbon materials to build tunable high-performance carbon materials with hierarchical porosity may establish a versatile and effective route to handle the above-mentioned problems.

Rice straw (RS) is one of the most abundant agricultural crop wastes with annual outputs being about 180–270 million tons in China [27]. More importantly, large amounts of macropores of RS carbon inherited from the inherent vascular bundles and cellular structures of RS can be available for ion-buffering reservoirs, which can be applied as shared ion-buffering reservoirs to serve for other micro-mesoporous materials. Moreover, unique meso- and micro-pores introduced by chemical activation of Si with alkali can provide electrolytic ion-transport channel and contribute to the active sites [28]. Therefore, the natural porous structures of RS carbon make it much promising for use as hard-template for further production artificial controlled morphology. Hydrothermal glucose carbon spheres owing to their easily-tunable size distribution and homogeneous morphology have attracted much attention in material science [29–31]. Moreover, these carbon spheres can inherit the hydrophilicity and lipophilicity of the hydrothermal precursor, which is desired for electrode materials for supercapacitors [32,33]. However, strong agglomeration and low yield of such carbon spheres restrict its application.

In this work, we firstly employ RS and glucose as dual-biomass carbon sources to develop the nano-micro carbon spheres@rice straw-derived porous carbon composite materials (NMCSs@RSPC) via the hydrothermal treatment with the help of cetyltrimethyl ammonium bromide micelles (CTAB). CTAB, a cationic surfactant, can ionize a large amount of CTA^+ which adsorbed on the surface of pyrolytic carbon (PC) in the modified process. During subsequent hydrothermal carbonization and KOH activation, the positively charged amine groups of CTAB not only induced the formation and attachment of the carbon spheres on the modified PC (MPC) due to the electrostatic attractions,

but also built a bridge between the two carbons to prevent the carbon spheres from falling off and reuniting. Depending on the synergistic effects of the carbon spheres and porous carbon as well as the defects introduced by KOH activation, the novel NMCSs@RSPC-1 exhibits multi-level size pore structures with interconnected macro-, meso- and micro-pores distribution. The as-fabricated porous structures use the specific surface to full advantage such that the final composites exhibit remarkable excellent electrochemical performances with a high specific capacitance and rate capability. Moreover, the highly-reversible faradic redox reactions of heteroatoms-doping in the composites can significantly provide extra pseudocapacitance and enhance the cycling stability. The enlarged carbon spheres obtained by inducing the hydrothermal carbonization between glucose molecules can effectively remedy the blemish of the low yield of glucose-derived hydrothermal carbon materials.

2. Experimental

2.1. Synthesis of NMCSs@RSPC-1

RS was collected from Dazhushan farm of the Hunan province, China. Prior to use, RS was cut into small pieces and then washed with deionized water and dried at 80 °C. All other chemicals were analytical grade and purchased from Kermel Reagent (Tianjin) Co., Ltd. without further treatment before use.

PC was firstly obtained by dealing with the dried RS at 400 °C for 2 h. After cooling to room temperature, the intermediate product was ground to fine powder with a mortar and then washed with deionized water and dried at 80 °C. To obtain the MPC, 0.2 g cleaned PC was dispersed in 40 mL CTAB aqueous solution (0.25 g CTAB per 10 mL water) and the mixed solution was then stirred for 5 h after sonication for 1 h. In turn, the MPC was obtained by filtration and then immersed in 70 mL glucose solution with a certain glucose content of 5.2 g. After stirring for 0.5 h, hydrothermal treatment of the resulting solution was carried out at 180 °C for 5 h in a sealed 100 mL Teflon-lined stainless steel autoclave. The black-brown precipitates were collected by rinsing with deionized water and anhydrous ethanol for several times and then aged at 120 °C for 10 h. Finally, the hydrothermal samples were mixed with equal mass with KOH and then carbonized at 750 °C for 2 h under Ar flowing. We obtained the resulting products called for NMCSs@RSPC-1 after washing with 1 M HCl and drying at 80 °C overnight.

For comparison, two control samples were also fabricated by a similar approach to that of NMCSs@RSPC-1 but without additional CTAB or both CTAB and glucose, denoted as NMCSs@RSPC-0 and RSPC, respectively. The number labels 0 and 1 mean whether the composites added CTAB.

2.2. Characterization

Scanning electron microscopy (SEM) was carried out with a MIRA3 TESCAN (Fig. 1a, c and d) and a HELIOS NANOLAB 600i (Fig. 1b) instrument. Transmission electron microscopy (TEM) was investigated with a Tecnai G2 F20 S-TWIX instrument. XRD spectrum was collected with a SIEMENS D500 diffractometer with Cu Kα radiation (λ = 0.15056 nm). Raman spectroscopy was performed at ambient temperature using a LabRAMHR-800 system with an excitation wavelength of 488 nm. X-ray photo-electron spectroscopy measurements (XPS) were conducted on an ESCALAB 250 instrument with Al Kα radiation. N_2 adsorption-desorption isotherms were obtained by an ASAP 2020 instrument at 77 K. The BET and QSDFT methods were respectively used to determine the specific surface areas and the pore size distributions of the materials.

2.3. Electrochemical measurement

A three-electrode configuration which respectively used platinum