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Preparation of Nitrogen and Sulfur dual-doped Mesoporous Carbon for Supercapacitor Electrodes with Long Cycle Stability

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ABSTRACT

Nitrogen and sulfur dual-doped mesoporous carbons (NSMCs) have been fabricated through a facile template-mediated pyrolyzing method using poly(ethyleneimine) (PEI) as sources of nitrogen (N) and carbon (C), ferrous sulfate($FeSO_4\,7H_2O$) as both precursor of sulfur (S) and activation reagent along with nanoscaled silica as sacrificial supports. The composition, morphology, and microstructure of the products are characterized using X-ray diffraction, scanning electron microscopy, nitrogen sorption analysis and X-ray photoelectron spectroscopy. It reveals that these NSMCs possess a BET surface area over 1064 $m^2\,g^{-1}$and abundant mesoporous structure with pore size ranged from 4 to 20 nm. The atomic percentages of N and S functionalities are found to be 4.00 at.% N and 0.83 at.% S, indication of successful incorporation of both nitrogenand sulfur into carbon network. Benefiting from the aforementioned characteristics, these NSMCs show perfect supercapacitive performances, which have been demonstrated by cyclic voltammetry and constant-current charge/discharge cycling techniques. In 0.5 M H_2SO_4 electrolyte, the specific capacitance (SC) of the as-prepared NSMCs electrode can reach 280 F/g at a current density of 1 A/g. Even at a high rate capability of 100 A/g, the NSMCs electrode still shows the SC value as high as 232 F/g, retaining 83% of that at 1 A/g. Also, the electrode exhibits excellent charge/discharge cycling stability, and no measurable capacitance losses is observed even after 5000 cycles, making them potentially promising for high-performance energy storage devices.

1. Introduction

Supercapacitors (SCs) are of particular interest in recent years owing to their ability to supply high power in short-term pulse and long cycling durability, which make them very efficient energy storage devices for applications such as hybrid power sources for electrical vehicles, digital telecommunication systems and other energy fields [1,2]. Due to the electrochemical charge accommodation at the electric double layer and the occurrence of Faradic reactions, SCs shows higher power density than batteries and higher energy density than conventional dielectric capacitors [3,4]. Porous carbon materials, especially the activated carbons remain the most common and important electrode candidates for SCs due to their high surface area, stable physicochemical properties, low-cost, and availability [5,6]. However, the pores are mainly contributed by micropores (<2 nm), which are not suitable for quick electrolyte ion diffusion. As a result, the activated carbon-based SCs usually suffer from electrode kinetic problems and insufficient conductivity, which results in a dramatic decrease in capacitance with increasing current density [7].

It has been demonstratedthat the pore size distribution of porous carbon plays an important role in electrochemical performances [8–10]. The carbon material becomes hardly accessible if its pores are smaller than the solvated ions [11]. Since the pores cannot be wetted by the electrolyte, the capacitance value is limited. For obtaining the high electrochemical performance, mesoporous carbon has been strongly recommended for SCs as electrode materials [10,12,13]. The mesoporous carbon, especially with 3D configurations, can buffer electrolytes to reduce ion transport resistance and ion diffusion distance for high-rate SCs applications, and the large accessible specific surface

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area of mesoporous can also enhance the charge storage [14,15]. Benefiting from the aforementioned characteristics, the specific capacitance of mesoporous carbon could reach 100–290 F/g even in aqueous electrolytes [16–18].

More recently, incorporation of doping heteroatoms into mesoporous carbon has attracted considerable attention for energy storage devices [19,20]. The incorporation of nitrogen, for example, was found to considerably improve the specific capacitance, because the nitrogen-containing functional groups can induce pseudocapacitive effects and improve the wettability of carbon materials to electrolyte solution [21]. Besides, nitrogen doping also can increase the electronic conductivity of carbon materials [22]. In fact, extensive research efforts have been made to explore heteroatoms such as nitrogen(N), boron(B) and sulfur(S) for application in oxygen reduction reactions (ORRs) [23,24] and lithium-ion batteries(LIBs) [25,26]. However, few studies have looked at the effect of sulfur modification on porous carbon, especially N- and S-dual doped porous carbon for supercapacitors.

In this paper, we report the design and synthesis of newly N- and S-dual doped mesoporous carbons (NSMCs) based on the combination of hard-templating synthesis with nitrogen-enriched poly(ethyleneimine) (PEI) as sources of N and C, and ferrous sulfate ($FeSO_4$ $7H_2O$) activation, targeting simultaneous optimization of both porous structures and surface functionalities of the carbon materials in one-step procedure without adding any extra N and S precursors. The capacitive performances of NSMCs as electrode material of SCs were studied in 0.5 M H_2SO_4 electrolyte, and their relationships with morphology, high specific surface area, nitrogen/sulfur species and electrochemical characteristics of the samples are discussed in detail. We will demonstrate that the as-prepared NSMCs possess a high specific surface area of 1064 g cm^{-2} and an optimized surface functionality with the desired N and S doping, which leads to an excellent capacitive performance with these NSMCs as the active materials and, greatly enhanced property for aqueous supercapacitors.

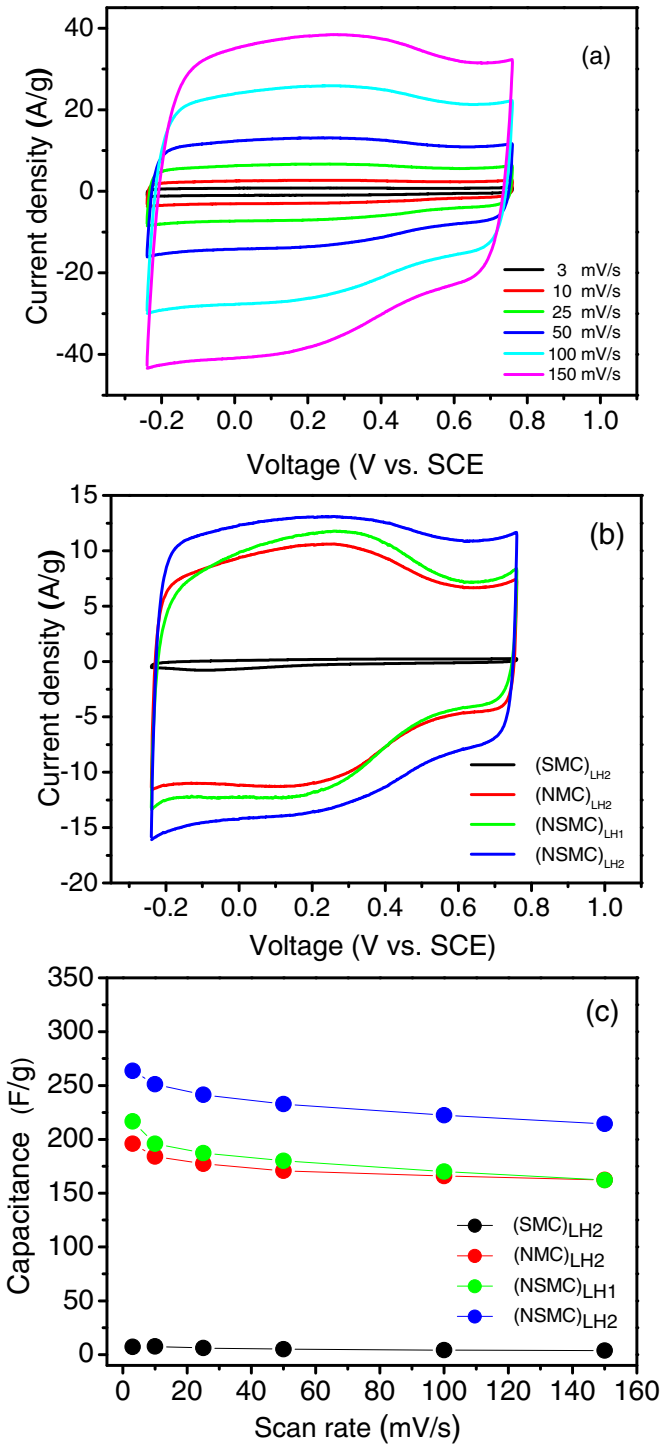

Fig. 1. CV curves of (a) $(NSMC)_{LH2}$ at different scan rates varying from 5 mV/s to 150 mV/s, (b) $(NSMC)_{LH1}$, $(NMC)_{LH2}$ and $(SMC)_{LH2}$ at a scan rate of 50 mV/s between -0.24 V and 0.76 V(vs. SCE) in 0.5 M H_2SO_4 and (c) Variation of capacitance of $(NSMC)_{LH1}$, $(NSMC)_{LH2}$, $(NMC)_{LH2}$ and $(SMC)_{LH2}$ plotted as a function of scan rate in 0.5 M H_2SO_4 electrolyte.

2. Methods

2.1. Preparation ofNSMCs

The procedure for the preparation of NSMCs was analogous to what reported by our group [27]. The NSMCs were synthesized by dispersing $FeSO_4$ $7H_2O$ and PEI onto the surface of SiO_2 (HangzhouWanjing New Material Co., Ltd 10–15 nm indiameter). Typically, 4.5 g PEI was added to a calculated silica solution (the PEI content with respect to the silica was 45 wt.%) under magnetic stirring and sonicated condition. Then an aqueous solution of $FeSO_4$ $7H_2O$ (Sinopharm Chemical Reagent Co., Ltd Fe:PEI = 1:3) as activation reagent was added into the SiO_2-PEI solution under magnetic stirring to form a reddish-brown nitrogen-iron chelate, and further sonicated for 8 h in the sonobath. After that, a uniform and viscous solution of PEI-silica-Fe was placed in a drying oven overnight at 85 °C, and heated at 800 °C for 1 h in a tubular furnace under N_2 atmosphere with a heating rate of 20 °C min^{-1} to accomplish the activation, pyrolysis and carbonization process. The SiO_2 was then leached out using excess amount of 40 wt% hydrofluoric acid (HF) for 24 hours, and the resulting powder was washed with D.I. water until neutral, and dried overnight. In order to further improve the electrochemical performance, the resulting powder was again refluxed in 0.5 M H_2SO_4 at 80 °C for 8 h. The final NSMCs were obtained after re-pyrolyzing at 800 °C for 1 h under a N_2 atmosphere.

2.2. Measurement Techniques for Structural Characterization

The morphology of the mesoporous carbon was characterized by scanning electron microscopy (HITACHI/S-4800). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2550 V diffractometer with Cu Kα radiation operating at 30 kV and 40 mA. Nitrogen adsorption-desorption isotherms were measured at low-temperature with the help of Micromeritics ASAP 2020 gas adsorption apparatus (USA). The Brunauer-Emmett-Teller (BET) surface area of the samples was measured using nitrogen