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Nitrogen-doped hollow carbon spheres with enhanced electrochemical capacitive properties

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ABSTRACT

Nitrogen-doped hollow carbon spheres (N-HCS) with uniform size have been synthesized via the hydrothermal method using pyrrole as the precursor. After carbonization at 850 °C, the average diameter of N-HCS is ca. 370 nm with shell thickness of ~15 nm. The electrochemical capacitive behavior of N-HCS was investigated by cyclic voltammetry and galvanostatic charge–discharge method in 1.0 M H_2SO_4 aqueous solution. Results show that N-HCS have high specific capacitance (345.2 F g^{-1} at 0.2 A g^{-1}) and high-rate capability with the increase of the scan rate from 10 to 1000 mV s^{-1} due to the synergetic effects of the unique hollow nanostructure and the N-doped thin carbon shell. In addition, the capacitance retains 98.1% after 1500 cycles even at a high loading current density of 10 A g^{-1}.

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1. Introduction

Electrochemical capacitors (EC), which are also known as supercapacitors, have attracted worldwide research interest due to their higher specific power and longer cyclic life as compared to secondary batteries [1]. To enhance EC performance, various materials, such as activated carbons, transition-metal oxides and conducting polymers, have been prepared as the candidates for electrochemical capacitors [2,3]. Among them, carbon-based materials have been widely investigated because of their large surface areas, high chemical stability, non-toxicity, good corrosion resistance, excellent electric conductivity and relatively low cost [4].

In general, the capacitive behavior of carbon-based electrode materials can be improved by accelerating the capacitive or nonfaradaic process based on charge separation at the electrode/solution interface or/and the pseudocapacitive process involving faradaic redox reactions that occur within active electrode materials through three ways: (1) increasing the surface area with tailored structures [5], (2) compositing with transition metal oxides [6,7] or conducting polymers [8], and (3) introducing heteroatoms into the porous carbon materials [9]. The carbon materials with large surface area are usually obtained through increasing the micropores of the material, but it leads to the problem of ionic transportation. Transition metal oxides/carbon nanocomposites or conducting polymers/carbon nanocomposites may block the accessible pore structure and inevitably leads to a decrease in the specific surface area of the resultant composites [10]. Compared with the two kinds of materials mentioned above, heteroatoms modified carbon materials seem to be the most promising supercapacitor materials with the combined effects of the capacitive charging of the double-layer and the Faradaic redox (pseudocapacitive) reaction of the active groups resulting from the introduction of heteroatoms to the carbon materials.

Recently, nitrogen-containing groups doped in a carbon matrix have been proved helpful for the enhancement of the specific capacitance [11–14]. Due to the carefully designed structure and the additional Faradaic redox reactions of nitrogen-containing groups, various nitrogen-doped carbon-based materials including activated carbon [15–17], carbon nanospheres [18,19], nanopipes [20,21], nanowires [22] and ordered mesoporous carbon [23] have been fabricated for supercapacitor application. On the other hand, due to the remarkable features including well-defined interior voids, low density, high surface-to-volume ratio and surface permeability, the outstanding properties of hollow micro-/nano-materials have been attracting great interest in many technical areas such as drug delivery, lithium-ion batteries, catalyst supports, sensing, biomedical applications, and so on [24]. These imply that nitrogen-doped hollow carbon materials can be used as the desirable electrode materials for supercapacitors.

Herein, we fabricated nitrogen-doped hollow carbon spheres (N-HCS) via the hydrothermal method using pyrrole as the precursor and investigated their electrochemical capacitive behavior. The as-prepared N-HCS exhibit high specific capacitance and excellent high-rate capability because of their hollow interior and N-doped thin shell.

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2. Experimental

2.1. Reagents

SiO_2 particles (diameter, ~360 nm) were purchased from Alfa Aesar (USA) and used as received. All other chemicals used in this work, such as pyrrole monomers, $(NH_4)_2S_2O_8$ (APS), and tris(hydroxymethyl)aminomethane (TRIS), were of analytical grade and used without further purification.

2.2. Preparation of N-HCS

Different from the chemical vapor deposition (CVD) method reported by Deshmukh and Su et al. [25,26], a more convenient and simple method was applied to prepare N-doped hollow spheres as the following three steps. Firstly, the polypyrrole (PPy)/SiO_2 core–shell particles were synthesized via the hydrothermal method reported by Liu [27] with modification. Typically, 400 mg silica spheres were washed thoroughly with 50 mM TRIS buffer (pH = 8.5) and centrifugated for three times. The deposit was re-suspended in 80 mL 50 mM TRIS buffer (pH = 8.5). Then, 1.2 mL of pyrrole monomer was dropped into the mixture under stirring at room temperature. After further stirring for 1 h, 40 mL of 10 g/L APS aqueous solution was added slowly. The mixture was then transferred to a 200 mL Teflon autoclave and maintained at 140 °C for 8 h. The autoclave was allowed to cool down to room temperature naturally after heat treatment. The resulting dark-gray precipitates were washed with distilled water and ethanol, and centrifugated (5000 rpm, 5 min) for several times to remove the tan colored solution, and then dried at 60 °C for 8 h under vacuum. Secondly, the obtained PPy/SiO_2 particles were pyrolyzed in a nitrogen atmosphere at 850 °C for 1 h to prepare the N-doped carbon/SiO_2 spheres. Finally, the product, denoted as N-HCS, was obtained via removing the silica core of the N-doped carbon/SiO_2 spheres in 2 M HF + 8 M NH_4F aqueous solution at 20 °C for 2 h, followed by successive centrifugation (13000 rpm, 10 min) and washing several times, and drying at 110 °C for 12 h. The yield of N-HCS, calculated via dividing the mass of N-HCS by the amount of polypyrrole, was about 6%.

2.3. Characterization

Transmission electron microscopic (TEM) and scanning electron microscopic (SEM) analyses were conducted on JEM-3010 and JSM-6490 instruments, respectively. Nitrogen sorption isotherms and Brunauer–Emmett–Teller (BET) surface areas of the materials were determined by an ASAP 2020 automatic micropore and chemisorption analyzer (USA). Nitrogen content in N-HCS was determined by elemental analyzer (TCH-600, USA). The structure of N-HCS was examined by X-ray diffraction (XRD) (D/MAX-RA).

2.4. Electrochemical measurements

The electrochemical performance of the as-prepared N-HCS was evaluated on a CHI 660C electrochemical workstation (Chenhua Instrument Company of Shanghai, China) at room temperature. A conventional three-electrode cell was used with a Pt foil and a saturated calomel electrode as the counter and the reference electrodes, respectively. For the preparation of the working electrode, 4 mg of N-HCS was dispersed in 2 mL of deionized water with ultrasonication for 15 min to form well-dispersed ink, and then 20 μL of the ink was transferred to the surface of a pre-polished glassy carbon electrode (diameter, 5 mm). The electrode was then dried in an oven at 60 °C and finally coated with 5 μL of Nafion solution (0.5 wt% in ethanol). 1 M H_2SO_4 aqueous solution was used as the electrolyte and deaerated with high pure N_2 (99.99%) for 30 min before the electrochemical measurement.

3. Results and discussion

3.1. Structural characterization

The TEM images of N-HCS are presented in Fig. 1. The morphology of N-HCS was also investigated by SEM (Fig. 1e). From Fig. 1a, b and e, uniform carbon spheres with hollow structure and rough surface can be clearly observed, and the size distribution was evaluated statistically through measuring the diameter of 200 carbon spheres in the selected SEM image (Fig. 1f). The average diameter of carbon spheres is ca. 370 nm. The related high-magnification image (Fig. 1c) reveals more detailed structural information of N-HCS. The shell thickness of N-HCS is ca.15 nm, and the structure of the as-prepared hollow carbon sphere is amorphous, which can also be confirmed by XRD result (Fig. 1d). From Fig. 1d, two broad and weak diffraction peaks can be observed at 2θ values of around 25° and 43°, corresponding to (0 0 2) and (1 0 1) lattice planes of hexagonal graphitic carbon, respectively, indicating a poor graphitic crystallinity of N-HCS [28–30].

For further understanding the porous texture, N_2 adsorption–desorption isotherms of N-HCS were measured. The BET specific surface area of N-HCS is 759.1 $m^2\,g^{-1}$, and the corresponding N_2 adsorption–desorption isotherms are shown in Fig. 2a. From Fig. 2a, a pseudo-type I mixed with type IV isotherms and an H_1-type hysteresis loop can be observed [28]. A gradual step of the N_2 isotherm at low relative pressure ($p/p_0 < 0.3$) is due to the N_2 adsorption in micropores. While, at a higher relative pressure (p/p_0 = 0.80–0.99), a hysteresis loop is obtained, resulting from the adsorption among the interspace of the N-HCS [19]. In order to obtain more information on the porosity, the pore size distribution (PSD) was calculated via the Density Functional Theory (DFT) method from the N_2 adsorption isotherms assuming slit-shape geometry of the pores. The PSD of N-HCS is mainly below 2 nm and the highest PSD peak centers at 0.6 nm (Fig. 2b), revealing the micropore construct of the carbon shell.

It has been known that carbon materials containing moderate content of nitrogen lead to improved wettability of carbon surface, and enhance its capacitance behavior [14,31].

The nitrogen content of N-HCS was measured by elemental analysis and is 8.66 wt%. It can be expected that the N-HCS would have good capacitive properties.

Based on the above characteristics of N-HCS, such as high specific surface area, moderate content of nitrogen and the existence of the hollow interior which can serve as an ion-buffering reservoir to minimize the diffusion distance to the interior surface of the thin carbon shell [32], it is reasonable to believe that N-HCS could be extremely attractive materials for supercapacitors.

3.2. Electrochemical properties

The capacitive behavior of N-HCS has been investigated by cyclic voltammetry (CV) in 1.0 M H_2SO_4 aqueous solution at different scan rates and the corresponding results are presented in Fig. 3. It can be observed from Fig. 3 that all the curves exhibit quasi-rectangular shape with a couple of wide and reversible peaks which should derive from the Faradic redox reactions involving the oxygenated and nitrogenated functionalities on the carbon surface. With the increase of the scan rate from 10 mV s^{-1} to 1000 mV s^{-1}, the quasi-rectangular shape of the curves keeps almost the same without obvious distortion, indicating a small equivalent series resistance (ESR) and a quick electrolyte ion transport in the pores of the N-HCS materials, which is very important for providing the supercapacitors with high power density [33].

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