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Short communication

Mesoporous nitrogen-doped carbon hollow spheres as high-performance anodes for lithium-ion batteries

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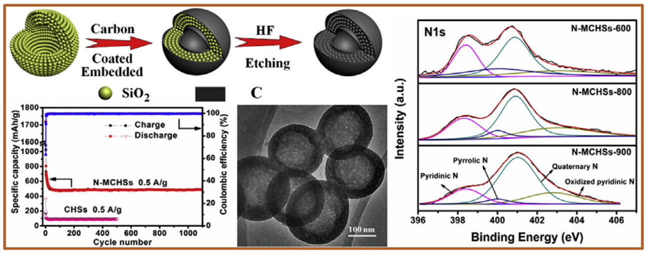
HIGHLIGHTS

- Mesoporous carbon hollow spheres with "carbon bridges" shell were prepared.
- N-doped carbon hollow sphere show high capacity and cycle stability.
- Carbonization temperature could largely affect graphitization degree and N contents.
- Pyridinic N has a highly influence on the Li storage properties for N-doped C.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen-doped mesoporous carbon hollow spheres (N-MCHSs) were prepared using mesoporous silica hollow spheres as template and dopamine as carbon precursor. The N-MCHSs demonstrate high specific surface area and vegetable sponge-like mesoporous shell with interconnected "carbon bridges", facilitating continuous electron transport and Li ion diffusion, and making the whole structure more stable. The influence of N contents and N-bonding configuration on the Li storage of N-MCHSs is discussed. The N-MCHSs carbonized at 800 °C demonstrate high reversible capacity and excellent rate performance, delivering a capacity of 485 mAh g^{-1} at a current of 0.5 A g^{-1} after 1,100 cycles. Even up to 4.0 A g^{-1}, a high capacity of 214 mAh g^{-1} can be remained. The high electrochemical performance of N-MCHSs can be ascribed to mesoporous carbon hollow spheres structure and high level pyridinic nitrogen doping.

1. Introduction

Lithium ion batteries (LIBs) are promising power sources in portable electric devices and hybrid vehicles due to high energy density and high working voltage. Graphitic carbon is a widely used anode material in commercial LIBs because of its low cost, good conductivity and excellent chemical stability. However, the low

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specific capacity (theoretical capacity of 372 mAh g^{-1}) and slow lithium ion diffusion rate of graphite anodes cannot meet the increasing demands of rapidly developing LIBs markets. Many strategies have been recently developed to improve lithium (Li) storage properties of carbonaceous anodes. One strategy is to fabricate nanostructured morphologies to shorten diffusion length of Li ion transport, including carbon nanotubes [1], nanofibers [2], hollow nanospheres [3], graphene [4], porous carbon [5], and their hybrids [6]. In particular, the hollow carbon nanospheres are promising anode materials for high rate LIBs [3,7,8] because they offer a large electrode/electrolyte reaction interfaces and enhanced charge-transfer reactions. Another route to improve the specific capacity of carbonaceous anodes is to prepare heteroatom-doped carbon nanomaterials, including phosphorus [9], boron [10], sulfur [11] and nitrogen [12] doped carbon nanotubes and nanospheres. The electronegativity (3.5) of N is higher than that of carbon (3.0), thus nitrogen doped (N-doped) carbon materials are favorable for Li insertion due to the stronger interactions between the N-doped carbon and the Li ions. Therefore, N-doped carbon could deliver substantially greater specific capacities in comparison with non-doped carbon materials. For instance, N-doped carbon fiber has been reported to deliver a reversible capacity of 943 mAh g^{-1} at a rate of 2 A g^{-1} after 600 cycles [13], which is much higher than theoretical capacity of 372 mAh g^{-1} for graphite carbon anodes.

In this work, we report N-doped mesoporous carbon hollow spheres (N-MCHSs) as high-performance LIBs anodes. The N-MCHSs could be simply fabricated using mesoporous hollow silica spheres ($MHSiO_2$) as the template and dopamine as carbon and nitrogen precursor. The dopamine (DA) could be self-polymerized on the inner and outer shell and impregnated into mesopores within the shell of $MHSiO_2$ to produce polydopamine (PDA) coating on $MHSiO_2$ ($MHSiO_2$@PDA). The N-MCHSs were obtained by thermal carbonization of PDA under Ar and subsequent removing $MHSiO_2$ template *via* HF etching. Remarkably, the resulting N-MCHSs demonstrated a high specific surface area and vegetable sponge-like mesoporous shells with interconnected “carbon bridges”. Such unique features of N-MCHSs are favorable for electrolyte and Li ion diffusion and can facilitate the rapid electron transport during charging and discharging of LIBs. The N-MCHSs pyrolyzed at 800 °C exhibited a high reversible capacity of 485.7 mAh g^{-1} after 1,100 cycles at a current density of 0.5 A g^{-1} and also exhibited an excellent rate performance with 50% capacity retention when current density increased 8 folds from 0.5 to 4 A g^{-1}. In order to reveal the role of N atoms in N-MCHSs, nitrogen-free carbon hollow spheres (CHSs) with similar structure, shell thickness and surface area were also prepared using $MHSiO_2$ as the template and glucose as carbon precursor. Compared with nitrogen-free CHSs, the N-MCHSs exhibit better electrochemical performance. Moreover, the Li storage properties of N-MCHSs are found to be associated with N content and N-bonding configuration in N-MCHSs. The high electrochemical performance of N-MCHSs can be ascribed to hollow vegetable sponge-like mesoporous carbon nanospheres and pyridinic nitrogen doping.

2. Experimental details

2.1. Preparation of mesoporous hollow silica spheres ($MHSiO_2$)

The $MHSiO_2$ were prepared according to the previously reported method [14]. Typically, 0.6 g of cetyltrimethylammonium bromide (CTAB) was dissolved in ethanol/H_2O solution (100 mL C_2H_5OH in 240 mL H_2O) containing 4 mL of concentrated ammonia aqueous solution (25 wt %). Subsequently, 4 mL of tetraethoxysilane (TEOS) was added drop-wise under vigorous stirring. The white precipitation was collected by centrifugation and then incubated in pure water at 85 °C for 48 h to form $MHSiO_2$ *via* the spontaneous self-transformation approach.

2.2. Preparation of the N-MCHSs

The N-MCHSs were fabricated using $MHSiO_2$ as the template and dopamine as C and N precursor. The tri-block copolymer PEO-PPO-PEO (P123) was used as a structure-directing agent. Typically, 2-amino -2-hydroxy-methyl-propane-1,3-diol (Tris) (0.48 g) was dispersed in 400 mL of deionized water to form Tris buffer solution with pH = 8.5, and then $MHSiO_2$ (0.40 g), P123 (1.6 g), and 1.6 g DA were added. After 6 h vigorous stirring, the precipitates were collected by filtration and washing. The obtained samples were further carbonized under Ar. After removing $MHSiO_2$ by diluted HF etching, the N-MCHSs were produced. The samples thermally treated at 600, 800 and 900 °C for 3 h are denoted as N-MCHSs-600, N-MCHSs-800 and N-MCHSs-900, respectively. The nitrogen-free CHSs were prepared by hydrothermal treatment of glucose at 180 °C for 6 h using mesoporous SiO_2 hollow nanospheres as templates, followed by thermal treatment under Ar at 800 °C and chemical etching mesoporous SiO_2 in HF solution.

2.3. Material characterization

The $MHSiO_2$, CHSs and N-MCHSs were characterized by field-emission scanning electron microscopy (FE-SEM, FEI nanoSEM 450), transmission electron microscopy (TEM, FEI Titan 60–300 Cs), X-ray diffraction (GAXRD, Philips X'Pert Pro), X-ray photoelectron spectroscopy (XPS, ESCALB MK-II, VG Instruments, UK), Energy-dispersive X-ray spectroscopy (EDX, Oxford INCA 200) and Raman spectroscopy (HR RamLab). The nitrogen adsorption and desorption isotherms were obtained using the Brunauer-Emmett-Teller (BET) (Micrometrics; ASAP2010) method after degassing the samples at 573 K for 6 h.

2.4. Electrochemical measurements

Typically, N-MCHSs or CHSs (70 wt %), 10 wt % Super-P carbon black (Sinopharm Chemical Reagent Co., Ltd), and 20 wt % sodium alginate (99%, Sigma Aldrich) were mixed in water solution to form slurry. The slurry was spread onto a Cu foil, followed by vacuum drying at 80 °C for 12 h. The active mass loading is 0.53–0.61 mg/cm^2 measured by analytical balance (BT25S, Sartorius). The electrolyte was a 1 M solution of $LiPF_6$ in a 1:1 vol/vol mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). A celgard 2400 film (Celgard, LLC Corp., USA) was used as the separator and pure Li foil as the counter electrode. The 2016 coin-like cells were assembled in a glove box filled with ultra-high purity argon. The galvanostatic charge and discharge experiment was performed with a battery tester LANDCT2001A (Wuhan LAND electronics Co., Ltd., China) at the potential range of 0.01–3.0 V (vs Li/Li^+). Cyclic voltammetry (CV) was conducted on a CHI750E electrochemical workstation (Shanghai CH Instrument Company, China) at a scanning rate of 0.1 mV s^{-1} in a potential range of 0.01–3.0 V (vs Li/Li^+). Electrochemical Impedance Spectroscopy (EIS) measurements were also performed over a frequency range of 0.01 Hz–100 kHz by applying an AC perturbation of 5 mV on a CHI 750e electrochemical workstation.

3. Results and discussion

As illustrated in Scheme 1, the $MHSiO_2$ were firstly fabricated and then coated by PDA by a simple dopamine self-polymerization method [15]. The PDA could be coated on the inner and outer shell