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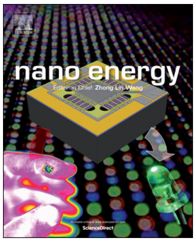

RAPID COMMUNICATION

Enhanced storage capability and kinetic processes by pores- and hetero-atoms- riched carbon nanobubbles for lithium-ion and sodium-ion batteries anodes

Huawei Song[a], **Na Li**[a], **Hao Cui**[a,b], **Chengxin Wang**[a,b,*]

[a]*State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics Science and Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, People's Republic of China*
[b]*The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-sen, (Zhongshan) University, Guangzhou 510275, People's Republic of China*

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Abstract
Efficient electrodes with impressive storage capability and fast kinetic processes are urgently needed in meeting the demand for high energy and large rate powering devices. Through a simple silica templated ionic liquids (ILs) impregnating method and an annealing process, nitrogen and oxygen co-doped carbon nanobubbles are synthesized. The fabricated carbon nanobubbles feature multiscale nanopores and abundant few-layer graphitic zones in the thin shells of several nanometers. When used as anodes for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), the nanobubbles not only exhibit excellent storage capability and rate performance, but also achieve enhancing cyclibility in the long-term cycles. Further analysis on the charging curves and the electrochemical impedance spectroscopy (EIS) reveal the enhancing cyclibility and storage capability might depend on the interfacial capacitance derived from quasi-connection between Li^+ or Na^+ and the hetero-atom evolving dissociative groups, while the superior rate performance might be attributed to the low interfacial charge-transfer resistance in the carbon nanobubbles electrode.

Introduction

Ever since Ikeda of Sanyo filed his first patent on graphite as intercalation anodes, graphite had been intensively explored for good electron and ion conductivity, stable structure, lightness, and easy availability in rechargeable

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[*] Corresponding author at: State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics Science and Engineering, Sun Yat-sen (Zhongshan) University, Guangzhou 510275, People's Republic of China. Tel./fax: +86 20 84113901.
E-mail address: wchengx@mail.sysu.edu.cn (C. Wang).

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batteries and other energy devices [1-4]. Traditional graphite electrodes, though with excellent cyclibility, are largely compromised when being directed to some energy- or power-intensive fields as electric vehicles and smart grids [5-9]. Therefore, it is an urgent task to develop substitutes with high energy storage capability. In this aspect, one way is to design their derivatives by morphological modification. Specifically, Yoshio et al. obtained high lithium storage by using foliated natural graphite [10]; Ruoff et al. fabricated conductive ultrathin graphite foam exhibiting excellent electrochemical stability superior to common substrates as Al and Cu foils [11]. Another is to focus on some emerging carbon materials such as graphene, carbon nanotubes, partially graphitic carbon with high specific surface area and their heteroatom doped derivatives [12-18].

Recently, ionic liquids (ILs) have been extensively utilized as precursors to fabricate mesoporous carbon and their heteroatom doped derivatives for low vaporized pressure, homogenous heteroatom source [19-23]. Compared with traditional graphite materials, these ILs derived carbon not only provide more abundant active sites benefiting from large specific surface area available for loading guest species, but also facilitate the processes for doped atoms′ inclusion [24-26]. Besides heteroatoms′ uniform distribution, the in-situ evolving process also avoids structure collapse accompanying the doping [19,23].

Based on the mentioned virtues, herein, nitrogen and oxygen co-doped carbon nanobubbles are fabricated by using a silica templated ILs impregnation method. The synthesized bubbles wholly inherit the superior conductivity of traditional graphite and the large specific surface area of some emerging carbon directives; In addition, multiscale pores and uniform hetero-doping C-N and C-O groups significantly improve the ions transporting and charge-transfer processes. Benefiting from those factors, the nanobubbles exhibit superior storage capability and enhancing cyclibility as being expected for LIBs and SIBs anodes.

Material and method

Synthesis of N-CNBs

N-CNBs were prepared by an ionic liquid impregnation silica templated method followed by an annealing process. The silica nanospheres were firstly synthesized by a modified Stöber approach [27]. 4 mL tetraethoxysilane (TEOS) and 1 mL ammonia (w%=26%) were dispersed in a mixture solvent of ethanol and de-ionized water (v/v=1:1). To obtain monodisperse SiO_2 nanospheres, the mixture was stirred for 6 h, and then rinsed with de-ionized water for twice. After dried for 6 h at 80 °C, SiO_2 nanospheres would be obtained by grinding the transparent white gel.

To synthesis the N-CNBs, 2 g SiO_2 nanospheres were dispersed in an ionic liquid (1-alkyl-3-methylimidazolium bromide, purchased from Chinese Academy of Science) solution (W%=2%). After impregnation for 24 h, the slurry was centrifugated and dried for 12 h at 80 °C, and then annealed at 750 °C for 3 h. Monodisperse N-CNBs would be obtained by washing away the template by hydrofluoric acid. Scheme 1 also illustrates the synthesis process in detail.

Physiochemical characterization

Morphologies of the samples were characterized by thermal field emmission SEM (Quanta 400F) under 20 kV, STEM and TEM (FEI Tecnai G2 F30) under 300 kV. Structures, composition and elemental analysis were performed by XRD (D/MAX 2200 VPC) with Cu Kα radiation scaning at 5°/min from 10° to 80°, Raman, and XPS (ESCA Lab250). Pores were characterized by BET.

Electrochemical characterization

For electrochemical characterization, electrodes were fabricated by pasting a slurry mixture of N-CNBs, polyvinylidene fluoride, and acetylene black with a weight ratio of 8:1:1 on copper foil by an automatic thick film coater (AFA-I). Then the coating film was desiccated in an vacuum chamber at 120 °C for 12 h. After that the foil is pressed by an electromotive roller (MR-100A) and tailored to appropriate size by a coin-type cell microtome (T-06) (Every piece with a loadage of active materials ca. 500 μg). Standard cells (CR2032) with the above tailored foils as working electrode and lithium foils (or sodium plates for sodium ion batteries (SIBs)) as the reference and counter electrode, polypropylene micromembrane as the separator, 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) with a weight ratio of 1:1 (or $NaClO_4$ in ethylene carbonate (EC) and diethyl carbonate (DEC) with a weight ratio of 1:1 for the SIBs) as the electrolyte, were assembled in an Ar-filled universal glove box with an oxygen and water vapor pressure less than 0.3 ppm. Cyclic voltammograms scanning at 0.2 mV s^{-1} in a voltage window of 0-3 V and electrochemical impedance spectroscopy (EIS) scanning from 1 MHz to 0.01 Hz with an ac signal amplitude of 10 mV were both carried out on an Ivium electrochemical workstation. For cycling and rate performance, the electrodes were

Scheme 1 Illustration for synthesis of silica nanospheres template and the carbon nanobubbles.