



# Nitrogen-doped porous interconnected double-shelled hollow carbon spheres with high capacity for lithium ion batteries and sodium ion batteries



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## ABSTRACT

Nitrogen-doped porous interconnected double-shelled hollow carbon spheres (N-DHCSs) have been synthesized by chemical treatment of Fe<sub>3</sub>O<sub>4</sub>@C precursors using HNO<sub>3</sub> at low temperature. When the precursors are disposed with HCl or H<sub>2</sub>SO<sub>4</sub>, uniform porous interconnected double-shelled hollow carbon spheres (DHCs) are prepared. Comparing with DHCs, the as-prepared N-DHCSs show higher Li-storage capacity and both show good cycling stability as anode materials in lithium ion batteries. The N-DHCSs offer a capacity of 512 mA h g<sup>-1</sup> at 1.5 C after 500 cycles and their porous interconnected double-shelled hollow structure could be well kept. The N-DHCSs also show high reversible capacity of 598 mA h g<sup>-1</sup> at 1 C after cycled at different current densities. In addition, the N-DHCSs as anode materials in sodium half-cell exhibit high reversible capacity of 120 mA h g<sup>-1</sup> at a current rate of 0.2 A g<sup>-1</sup> after 100 cycles.

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## 1. Introduction

Carbon based materials like graphite have already been commercially used as anodes for lithium ion batteries (LIBs) due to their numerous advantages, such as low cost resource, high coulombic efficiency and good cycle stability [1]. However, the reversely low specific capacity (theoretical capacity 372 mA h g<sup>-1</sup>) and poor rate performance limit its broader applications. Therefore, lots of work has been investigated to explore more alternative carbon-based anode materials to obtain a good cycle performance and great specific capacity [2,3].

Recently, it is a very active area of research on the development of carbon-based materials with well-defined characteristics on nanostructure [4,5]. Nanoscale carbon spheres and other ordered porous monoliths have shown good prospect not only as alternative anodes for LIBs application, but also for supercapacitor electrodes, catalyst supports, H<sub>2</sub> storage, water-purification and separation materials [4–6]. Nanographene-constructed hollow

carbon spheres calcinated at 700 °C with the shell thickness of ~70 nm showed the reversible capacity of 600 mA h g<sup>-1</sup> at rate of C/5 after 30 cycles in lithium ion batteries. Upon increasing the charge/discharge rates to 1 C and 5 C, its reversible capacities can be maintained at 390 mA h g<sup>-1</sup> and 275 mA h g<sup>-1</sup>, respectively [7]. Hollow carbon nanospheres with the shell thickness of ~12 nm showed a high capacity of 310 mA h g<sup>-1</sup> after 200 cycles at a rate of 1 C in lithium ion batteries (LIBs) [8] and a reversible capacity of 160 after 100 cycles at a current density of 50 mA g<sup>-1</sup> for the first ten cycles and then 100 mA g<sup>-1</sup> for latter cycles in sodium ion batteries (NIBs) [9]. Hollow nanostructure anode materials provide high capacity and high rate capability, which can be attributed to the high surface area, much freedom for volume change, and short path length for Li<sup>+</sup> transport, which can decrease the overpotential times and permit better reaction kinetics at the electrode surface [10]. As a result, hollow nanoscale carbon sphere is a promising material for rechargeable batteries.

According to previous work, introduce N heteroatoms which can modify the surface with functional groups in carbon materials, which can further increase the electrochemical performance. Multifarious ways [11–14] have been proposed to get nitrogen-doped carbon materials. For instance, the nitrogen-doped porous

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carbon nanofiber webs prepared under a nitrogen atmosphere at 650 °C delivering a reversible capacity of 943 mA h g<sup>-1</sup> at a current density of 2 A g<sup>-1</sup> after 600 cycles [11].

Nitrogen-doped graphene nanosheets prepared by annealing graphite oxide in ammonia atmosphere at 800 °C exhibited high reversible capacity of around 900 mA h g<sup>-1</sup> at a current density of 42 mA g<sup>-1</sup> after a few cycles [12]. These traditional nitrogen doping processes are always included the precursor mixing with nitric gas under high temperature calcinations. While, previous reports have demonstrated that the collapse of the one shell hollow sphere usually happened under heat treatment [15,16].

Our previous work has shown that nitrogen-doped carbon materials could be obtained at low temperature (~60–70 °C) using HNO<sub>3</sub> as N provider [13]. In addition, Lou et al. presented that double-shell structure does not collapse comparing with one shell hollow spheres [17]. Inspired by these two threads, here we synthesize nitrogen-doped porous interconnected double-shelled hollow carbon spheres by the HNO<sub>3</sub> treatment of Fe<sub>3</sub>O<sub>4</sub>@C precursors. With mass percentage 2.17% nitrogen the N-DHCSs possess mesoporous and macropores, and the Brunauer-Emmett-Teller (BET) of the N-DHCSs is about 300 m<sup>2</sup> g<sup>-1</sup>. Based on the unique and uniform porous interconnected double-shelled hollow nanostructure with appropriate nitrogen doping, the electrochemical performance with both lithium and sodium are evaluated. The N-DHCSs deliver a reversible capacity of 512 mA h g<sup>-1</sup> at a current density of 1.5 C after 500 cycles in lithium ion batteries. The uniform porous interconnected double-shelled hollow carbon structure could be well kept even after 500 cycles in LIBs. After cycled at different current densities, a high reversible capacity of 598 mA h g<sup>-1</sup> can still be obtained at 1 C. Moreover, the N-DHCSs as anode materials in sodium ion batteries also show high reversible capacity of 120 mA h g<sup>-1</sup> at a current rate of 0.2 A g<sup>-1</sup> after 100 cycles and exhibit significant performance at different current densities.

## 2. Experimental

### 2.1. Synthesis

All chemicals were of analytical grade and purchased from Shanghai Chemical Industrial Corp. and used as received without further purification.

#### 2.1.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> porous hollow nanosphere Precursor

Typically [18], 0.59 g FeCl<sub>3</sub>·6H<sub>2</sub>O, 1.275 g sodium citrate (C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·Na<sub>3</sub>·2H<sub>2</sub>O) and 0.36 g urea were dissolved in 40 ml distilled water. Polyacrylamide (PAM, 0.3 g) was added under continuous stirring for 1 h. Then the solution was turned into a 55 ml Teflon-lined autoclave and maintained at 200 °C for 12 h. The black precipitation (Fe<sub>3</sub>O<sub>4</sub>) was washed with distilled water and ethanol several times under magnetic condition.

#### 2.1.2. Synthesis of DHCSs and N-DHCSs

As-prepared black precipitation (0.18 g) was dispersed in 20 mL aqueous glucose (0.5 M). The suspension was placed in a 55 mL Teflon-lined autoclave and maintained at 180 °C for 6 h. The precipitation was still centrifuged and washed with distilled water and ethanol many times under magnetic condition. After stoving at 60 °C under vacuum condition, the brown powder was calcinated at 550 °C for 5 h in Ar flow. Then the black product was treated with 2 M HCl to remove the core. The non-magnetic black precipitation was washed with distilled water until the pH was about 7. The final product was dried overnight at 70 °C in an oven. By contrast, nitrogen-doped porous interconnected double-shelled hollow carbon spheres were also got under the same condition, except 10 wt% HNO<sub>3</sub> was instead of HCl at temperature ~60–70 °C.

### 2.2. Characterization

The product was characterized by X-ray powder diffraction (XRD) through a Philips X'pert X-ray diffractometer anode with Cu-Kα radiation (λ = 1.54182 Å). Use a transmission electron microscope (TEM, H7650) and a high resolution transmission electron microscope (HRTEM, JEOL-2010) to observe the microstructure. The scanning electron microscopy (SEM) pictures were taken on a field emission scanning electron microscope (FESEM, JEOL-JSM-6700F 20 KV). X-Ray photoelectron spectroscopy (XPS) measurements were recorded on a GESCALAB KII -ray photoelectron spectrometer. Raman spectra were recorded with an excitation laser wavelength of 514.5 nm at room temperature. The Brunauer-Emmett-Teller (BET) tests were measured on a Micromeritics ASAP 2020 porosimetry system and accelerated surface area. The pore size distribution (PSD) was estimated by means of Barret-Joyner-Halenda (BJH) model and analyzing nitrogen adsorption data. IFS-85 (Bruker) spectrometer was used to test FTIR spectra. The element contents were determined by an elemental analyzer (Vario ELIII) under different pure gases atmosphere.

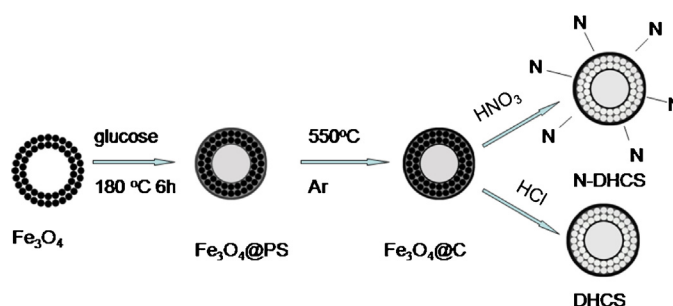
### 2.3. Electrochemical measurements

The electrochemical measurements were measured using coin-type (CR 2016) half cell. The working electrode was prepared by coating 80 wt% active materials (DHCSs or N-DHCSs), 5 wt% super P, and 15 wt% polyvinylidene fluoride (PVDF) on a copper foil collector. The copper foil was dried in a vacuum oven at 110 °C for 12 h. The nonaqueous electrolyte for lithium ion batteries was 1 M LiPF<sub>6</sub> with a mixed solution of dimethyl carbonate (DMC), ethylene carbonate (EC) and diethyl carbonate (DEC) (1: 1: 1, in wt.%) and for sodium ion batteries, an electrolyte composition of 1 M NaClO<sub>4</sub> in PC (Propylene carbonate). The coin-cell was tested with galvanostatic cycling on a battery test system (LAND CT2001) in the voltage window of 0.01–3.00 V versus Li<sup>+</sup>/Li in lithium ion batteries and in the voltage window of 0.01–2.00 V versus Na<sup>+</sup>/Na in sodium ion batteries. Cyclic voltammetry (CV, CHI660e) was carried out at a scanning rate of 0.1 mV s<sup>-1</sup> starts from 0.01 to 3.00 V (vs. Li<sup>+</sup>/Li) at room temperature.

## 3. Results and discussion

### 3.1. Synthesis of the DHCSs and N-DHCSs

The DHCSs and N-DHCSs morphology were experimentally realized as shown schematically in Scheme 1. The double-shelled hollow carbon spheres are prepared using Fe<sub>3</sub>O<sub>4</sub> porous hollow nanospheres as the template. First, monodisperse Fe<sub>3</sub>O<sub>4</sub> porous hollow nanospheres were received by hydrothermal method [18]. The Fe<sub>3</sub>O<sub>4</sub> porous hollow nanospheres were consist of Fe<sub>3</sub>O<sub>4</sub> particles. The Fe<sub>3</sub>O<sub>4</sub> porous hollow spheres were then uniformly



**Scheme 1.** Schematic of the synthesis steps for DHCSs and N-DHCSs.

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