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Short communication

Macro-mesoporous hollow carbon spheres as anodes for lithium-ion batteries with high rate capability and excellent cycling performance

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HIGHLIGHTS

- MMHCSs with a particular nanostructure was synthesized by a facile template method.
- Dual scale pores (macro- and meso-pores) co-existed in MMHCSs.
- MMHCSs exhibit a high capacity of 530 mAh g^{-1} at 2.5 A g^{-1} over 1000 cycles.
- An excellent rate capability of 180 mAh g^{-1} still can be attained at 60 A g^{-1}.

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ABSTRACT

In this work, nanostructured macro-mesoporous hollow carbon spheres (MMHCSs) with high surface areas (396 m^2 g^{-1}) were synthesized as anode materials via a facile template-based method. A macroporous structure was created on the surfaces of the mesoporous hollow carbon spheres without destroying their spherical structure by etching in 20% HF. The unique nanostructure (imperfect hollow spheres) and the beneficial characteristics of amorphous carbon gave the MMHCSs a high reversible capacity of 530 mAh g^{-1} at 2.5 A g^{-1} over 1000 cycles. Remarkably, the MMHCSs retained an excellent rate capability of 180 mAh g^{-1} at 60 A g^{-1}, which was superior to that of perfectly structured mesoporous hollow carbon spheres (without macropore (MHCSs)).

1. Introduction

Lithium-ion batteries (LIBs) occupy the majority of the battery market for portable electronic devices. Compared to other batteries (e.g., lead acid batteries, nickel cadmium batteries, nickel zinc batteries, etc.), LIBs have distinct advantages because of their highly reversible specific capacity, long cycling life, excellent rate performance, and high safety [1–7]. Recently, the increasing popularity and incorporation of LIBs into portable electronic equipment and the ever-increasing demand for higher power devices, including electric vehicles, have resulted in stricter requirements for battery safety, capacity, and cycling and rate performance. These factors have accelerated the development of next-generation LIBs. Graphite-based materials are the most common anode materials for commercial LIBs because of their stable performance, low cost, and natural abundance. Nevertheless, graphite-based materials cannot meet current demands because of two main disadvantages: the low theoretical specific capacity (372 mAh g^{-1}) and the poor rate performance. In order to overcome these limitations, research has focused on the development of a series of materials with high capacity and good cycling performance [8–10]. Silicon-based materials have recently been

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considered to be the most likely candidates as effective anode materials due to their ultra-high theoretical capacity (4200 mAh g^{-1}). Unfortunately, the large volume changes of silicon-based materials during Li^+ insertion and extraction processes have limited their development [11–14]. Therefore, research on advanced carbon-based materials is ongoing.

Many carbonaceous anode materials have been investigated in recent years, and these materials generally have high theoretical capacity and contain unique nanostructure. Such as carbon nanotubes [15], carbon nanofibers [16], carbon nanobeads [17], orderly mesoporous carbon [18], hierarchical mesoporous carbon [19], N-doped carbon materials [20], graphene [21], porous carbon [22], hollow carbon spheres [23], and hybrids of these structures [24]. Among these carbon materials, mesoporous hollow carbon spheres obtained from the pyrolysis of organic materials have higher specific capacity and superior cycling performance compared to the others [23]. Amorphous carbon has a low degree of graphitization and possesses many lattice defects, which can provide sufficient sites for Li^+ insertion [9,20,23,25]. In addition, their mesoporosity also increases the specific surface area of active materials, which not only enhances the electrode/electrolyte interface for charge/discharge reactions but also shortens the Li^+ diffusion distance and improves electrochemical reaction activity [18,23,26]. Furthermore, the hollow structure of carbon spheres can ease the volume expansion effects of Li^+ insertion during discharge process [23].

In this work, we introduce a facile method to synthesize macro-mesoporous hollow carbon spheres (MMHCSs) by using silica spheres as a template, dopamine as a carbon source, and triblock copolymer PEO-PPO-PEO (P123) as a pore-forming agent [26,27]. We create an imperfect hollow carbon sphere structure of the MMHCSs, which have a macroporous structure that can be formed on the surfaces of the MMHCSs by an etching process without destroying their basic spherical structure. Although hollow carbon spheres (prefect structure) have been used as anode materials [23,26,28–31], but this imperfect hollow carbon sphere structure has not been reported previously. More importantly, the MMHCSs anode has an excellent rate performance and good cycling capability because of this imperfect (macropore) structure.

2. Experimental

2.1. Preparation of monodisperse silica spheres

Typically, 370 nm monodisperse silica spheres were synthesized by a modified stober method [32]. Generally, tetraethoxysilane (TEOS, GC grade, > 99%, Aladdin) was vacuum distilled before the experiment for the following spheres synthesis. 4.8 ml of TEOS was mixed with 50 ml of absolute ethanol (EtOH) and stirred for 20 min at 30 °C to prepare solution A. 8.4 ml of ammonia aqueous solution (NH_4OH, 25 wt%) was mixed with 18 ml absolute ethanol (EtOH) and 25 ml of deionized water (H_2O) to prepare solution B. After stirring for 20 min at 30 °C, solution B was rapidly added to solution A under vigorous stirring for 4 h at 30 °C. The precursors were collected by centrifugation (washing by deionized water for 3 times and absolute ethanol for 2 times, respectively) and then air-dried at 60 °C for 24 h.

2.2. Preparation of macro-mesoporous hollow carbon spheres

Firstly, 100 mg of 2-amino-2-hydroxymethyl-propane-1, 3-diol (Tris), 180 mg of triblock copolymer PEO-PPO-PEO (P123) and 350 mg of 370 nm monodispersed silica spheres were dissolved in 100 ml of deionized water under vigorous stirring for 5 h at room temperature. Then, 400 mg of dopamine hydrochloride was dispersed in this mixed solution and stirred for 36 h at room temperature. The particles were collected by centrifugation (3 times by deionized water and 2 times by absolute ethanol) followed by vacuum drying at 60 °C for 24 h. After that, the dried products were heated at 400 °C under an Ar atmosphere for 3 h with the heating rate of 1 °C min^{-1}, which was followed by further calcining at 800 °C for 3 h (5 °C min^{-1}). Finally, the powders were immersed in 20% HF (Aladdin CP, 40.0%) solution and etched for 1 h at room temperature (immersed in 10% HF for 1 h with 3 times to prepared Mesoporous hollow spheres (MHCSs)). The final products of MMHCSs were collected by centrifugation (washed for 3 times by deionized water and 2 times by absolute ethanol), and then vacuum dried at 60 °C for 24 h.

2.3. Characterization

The fundamental characterizations of the MMHCS were investigated by X-ray diffraction (XRD) (Rigaku Ultima IV, Cu Kα radiation, 40 kV, 40 mA). Scanning electron microscope and TEM observation was carried out on a Quanta FEG 250 (FEI) and a JEOL 2100 F microscope. Raman spectra was performed on a Renishaw Micro-Raman Spectroscopy System. Brunauer-Emmett-Teller (BET) surface area and pore size distributions were received from nitrogen physisorption at 77 K on an autosorb-iQASIQ analyzer (Quantachrome).

The electrochemical performance of the MMHCS was measured with 2025 coin-type cells and lithium metal foil as the reference electrode. The working electrodes were prepared by coating the

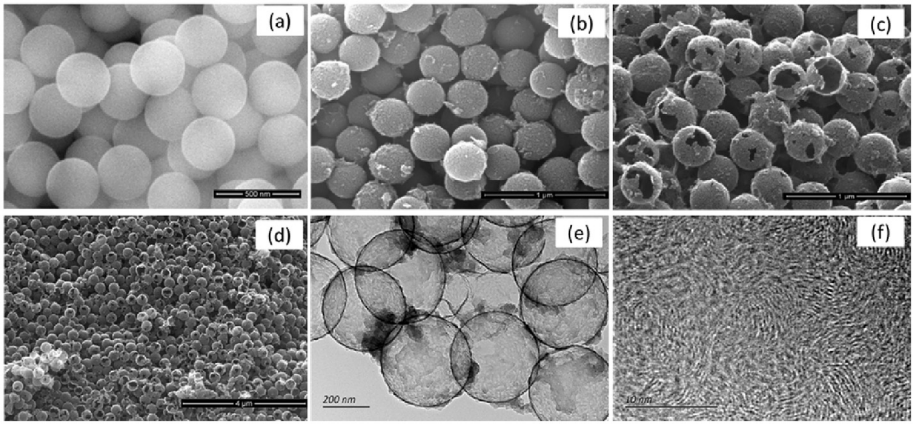

Fig. 1. SEM image of the (a) monodispersed silica spheres, (b) MMHCSs without etching, (c–d) MMHCSs. (e) TEM image of the MMHCSs. (f) HRTEM image of MMHCSs.