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Porous silicon in carbon cages as high-performance lithium-ion battery anode Materials

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ABSTRACT

We demonstrate the synthesis of porous Si in carbon cages (PoSi@CC) via the oxidation of magnesium silicide, coating of carbon layer and subsequent acid washing. Different from the traditional porous Si@C core-shell(PoSi@CS) structure, new structure and morphology of PoSi@CC are obtained, and better electrochemistry performance is expressed. As the anode materials of lithium-ion batteries, the PoSi@CC particles show a capacity of 864 $mAhg^{-1}$ with 91.7% capacity retention after 100 cycles at the current density of 0.4 Ag^{-1}. When the current density increases to 1.6 and 3.2 Ag^{-1}, the capacity can be maintained at 590, 475 $mAhg^{-1}$, respectively. The good cycling and rate performance can be attributed to the unique structures of the porous Si in carbon cages. The outer carbon layer can alleviate the pulverization and stabilize solid electrolyte interphase (SEI) film, while the enough space in the PoSi@CC particles can buffer the volume change during the charge/discharge process, which may be responsible for the enhanced electrochemical performance.

1. Introduction

Energy storage has the great opportunity as well as the challenge for the development of human beings [1–4]. With the high-speed growth of the market in consumer electronics, renewable energy storage and electric vehicles, superior-performance lithium-ion batteries are unprecedentedly anticipated, which should combine high specific energy density with long cycle life [5–8]. Si has been the most promising candidate for the next-generation anode materials, expressing a theoretical specific capacity of 4200 $mAhg^{-1}$, which is much higher than the commercial graphite (372 $mAhg^{-1}$) [9]. Unfortunately, Si anodes suffer tremendous volume change as high as 300% when the lithium ions are inserted and extracted, resulting in the pulverization and capacity degeneration [10–13]. Moreover, the solid electrolyte interphase (SEI) film is unstable and grows thick during the charge/discharge process, leading to low Columbic efficiency and poor cycling performance of Si anodes [14–17].

To overcome the above-mentioned disadvantages, Si@C core-shell structures have been designed, because the carbon shell can improve the conductivity and buffer the volume change somehow [18]. However, suffering constant outside expansion from the inner core, the carbon shell may crack and even expedites the fracture of the whole particle [19]. To address this problem, tremendous efforts have been devoted to create voids in Si particles. For example, voids have been introduced in the double-walled Si nanotubes [20,21], yolk-shell structures [22,23], pomegranate [24], the three-dimensional (3D) flexible Si in C nanofibers [25] as well as conformal graphene cages growing on Si particles [26], which leads to the enhanced cycling stability. The traditional synthesis of porous Si@C structures includes the first synthesis of bare porous Si structures and then the coating of carbon layer [27–30]. However, the carbon layer is cling to the Si particles and will also fill some pores, which may lead to the poor effect of buffering volume expansion [31].

More recently, Cui and his group demonstrate the nonfilling carbon coating of porous silicon micrometer-sized particles for high-performance lithium battery anodes [32]. In that case, the carbon layer is not cling to the porous Si particles, which is considered to better volume buffering effect and results in better

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long-cycle performance. Motivated by this idea, we prepare the porous Si in carbon cages with an optimized structure via the modification of our previous synthetic process of porous Si@C structures [31]. We first oxidized the magnesium silicide (Mg_2Si) particles through the annealing process in air, then deposited the carbon layer on the intermediate products, and finally removed the template by acid washing, to leave the pores inside Si and the free room between Si and carbon cages. Such a design has obtained multiple benefits: (1) the well-defined pores inside would greatly relieve the swelling stress to outer carbon layer and keeping the layer intact; (2) benefiting from intact carbon layer, the SEI could keep stable and thin, which is helpful to improve the Columbic efficiency and is significant to full-cell with limited lithium ions [33]; (3) the static carbon cages also stabilize the overall electrode by alleviating the electrode thickness aviation, which is referred to as the breathing effect [34]; (4) the carbon cages protect Si from contacting with electrolyte directly, minimizing side reaction and irreversible lithium consumption; (5) the inside porous Si is touched with the carbon cages at many sites, which gives many conductive routes to lithium-ion transportation, compared with the one-point contact between core and shell like the yolk-shell. These benefits are believed to result in good electrochemical performance.

2. Experiment

2.1. Synthesis of PoSi@CC particles

The carbon cages should be completely encapsulated to prevent Si from penetration by electrolyte, while the internal free space is also necessary for Si expansion. Therefore, we have adjusted and optimized the synthetic conditions as follows. Firstly, Mg_2Si powder (purity > 99%), purchased from Aldrich, were smashed in an agate mortar and then ground in a planetary ball mill (QM-3SP2, Nanjing University Instrument Company of China) at 300 rpm for 10 h to obtain uniform microparticles. Then, the Mg_2Si microparticles were heated in a tube furnace at 650 °C for 20 h with mixed gases ($Ar:O_2 = 99:1$). After that, the products were coated with the carbon layer via chemical vapor decomposition (CVD) process of acetylene gas at 650 °C for 3 h. Finally PoSi@CC particles were obtained by removing the residual MgO using 1 M HCl solution. For comparison, the porous Si particles were firstly synthesized, followed by the coating of carbon layer to form porous Si@C core-shell particles.

2.2. Morphology and Structure characterization

The morphology of the samples was characterized by a field emission scanning microscope (FESEM, HITACHI S4800) and a transmission microscope (TEM, HITACHI HI-7700). Energy dispersive spectroscopy (EDS) was recorded by a Tecnai G2 F20 ChemiSTEM attached with a Oxford X-Max 80T EDX detector system. Raman spectroscopy was conducted using a HR800 Raman Spectrometer with an Ar ion laser at 514 nm. X-ray photoelectron spectroscopy (XPS) was measured by employing a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al Kα line (1486.6 eV). Brunauer-Emmett-Teller (BET) specific surface area and pore diameter distribution were determined from the results of N_2 adsorption/desorption measurements using a Beckman Coulter Omnisorp 100cx. X-ray diffraction (XRD) was performed on

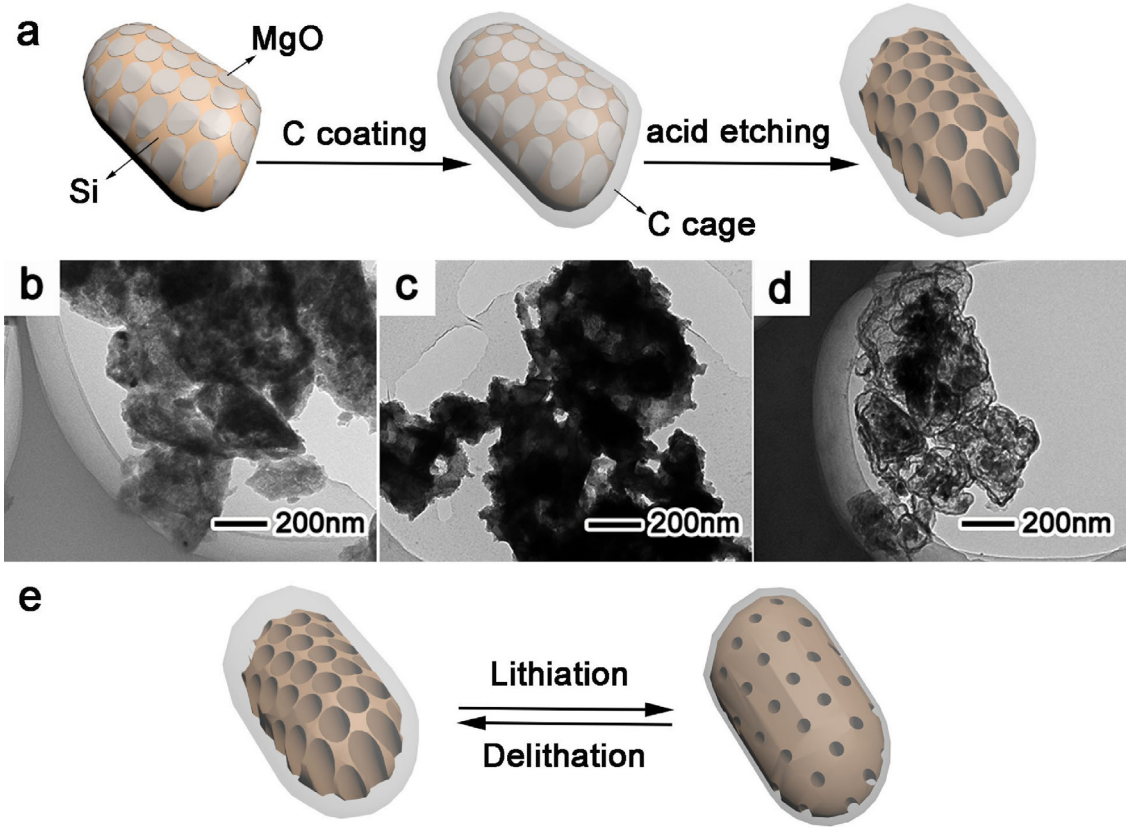

Fig. 1. (a) Schematic illustration for the synthesis of PoSi@CC; (b-d) TEM images of the products after thermal oxidation of Mg_2Si (b), after carbon coating (c) and after acid etching (d); (e) A schematic illustration of an individual PoSi@CC particle during lithiation/delithiation process showing that no pulverization happen.