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Core-shell yolk-shell Si@C@Void@C nanohybrids as advanced lithium ion battery anodes with good electronic conductivity and corrosion resistance

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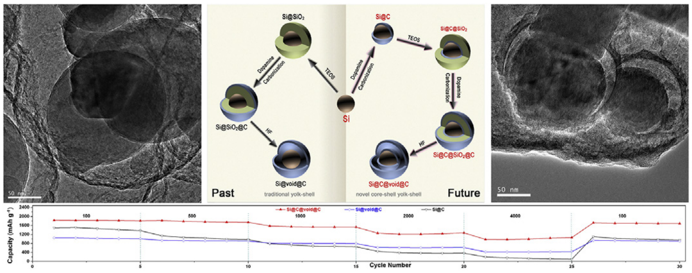
HIGHLIGHTS

- A core-shell yolk-shell Si@C@void@C nanohybrid is proposed for the first time.
- The Si@C@void@C provides better conductivity and corrosion resistance.
- The Si@C@void@C exhibits high reversible capacity and good rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

Yolk-shell Si@void@C nanostructure has greatly improved the low Li^+/electron conductivity and buffered the huge volume variation of Si, whereas the surface corrosion and passivation of the Si yolks in electrolytes still limit the lithium storage capability. Herein, core-shell yolk-shell Si@C@void@C nanohybrids were proposed and successfully prepared for the first time. Compared with Si@void@C, the newly-proposed structure introduced core-shell Si@C nanoparticles as the yolks instead. Such extra carbon shell can not only decrease the electrical resistance between Si yolks and hollow carbon shells but also effectively protect Si yolks from electrolyte corrosion, *i.e.*, the formation of Li_2SiF_6 layers on Si surface confirmed by X-ray diffraction and transmission electron microscopy. As a result, the Si@C@void@C electrodes exhibited remarkably enhanced reversible capacity, cycling stability (~1366 mA h g^{-1} after 50 cycles at 500 mA g^{-1}, with a capacity retention of ~71% with respect to the initial reversible capacity of 1910 mAh g^{-1} at 100 mA g^{-1}), and rate performance (with a capacity retention of ~60% at 4000 mA g^{-1}). This work shows the paramount role of the inner carbon shell of Si@C@void@C in limiting the electrolyte corrosion and probably improving the electronic conductivity.

1. Introduction

Nowadays commercialized Li-ion batteries (LIBs) are mostly based on graphite anodes (with a theoretical capacity of 372 mAh g^{-1}, for LiC_6) and cannot meet the ever-increasing demands for high energy/power densities for electric vehicles (EVs) [1]. Among

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dozens of potential substitutions, Si is projected as the most promising one due to its abundance in the earth's crust, environmental friendliness, low operation potential (<0.5 V vs. Li/Li^+) and in particular, ultrahigh theoretical capacity (3579 mAh g^{-1}, for $Li_{3.75}Si$ at room temperature) [2,3]. However, the commercial applications of Si are hindered by troublesome disadvantages, e.g., insufficient Li^+/electron transport and huge volume variations (~180%, Si↔$Li_{3.75}Si$) causing structural collapse, electrical isolation, and substantial formation of solid electrolyte interphase (SEI) films during (de)alloying with lithium ions [4,5]. Some inspiring achievements have been obtained and mainly focused on preparing Si nanomaterials such as nanoparticles [6], nanowires [7], nanotubes [8], and hierarchical nanospheres [9] and constructing composites involving Si/carbon [10,11], Si/metal [12–14], and porous/hollow materials [15,16].

As comprehensive modifications, core-shell Si@C and yolk-shell Si@void@C nanostructures are the most effective [5,17–19]. As for the core-shell Si@C structure, the compact carbon shell can not only effectively improve the conductivity but also inhibit the electrolyte corrosion on the Si surface to a large extent. For example, Du et al. obtained core-shell Si@C nanohybrids by grafting aniline monomers to the Si surface and subsequent carbonization [20]. The conductivity increased to ~5.4 × 10^{-2} S cm^{-1} and the electrodes exhibited a reversible capacity of ~750 mAh g^{-1} after 100 cycles. Nevertheless, the core-shell structure does not have enough space to buffer the vast volume expansions of alloying Si and as a result the integrity of the structure would be difficult to keep and the compact carbon shell would be broken [21,22]. In contrast, yolk-shell Si@void@C structures have been attracting much more attention since the void space provided can better manage the volume expansions of Si-Li alloying and maintain the structure integrity [15,22–35]. For instance, Li et al. synthesized yolk-shell Si@void@C composites by HF etching of SiO_2 layer in the core double-shell Si@SiO_2@C intermediates and showed a capacity of 654 mAh g^{-1} after 100 cycles even at 1000 mA g^{-1} [24].

Note that, the yolk-shell structure has two non-ignorable problems: (i) insufficient electronic contact between Si yolks and hollow carbon shells and (ii) the corrosion of Si yolks from outside electrolytes. For the contact disadvantage (i), Park et al. proposed a Si-encapsulating hollow carbon, in which Si yolks had more contact with carbon shell, by electroless etching of Fe and partial Si atoms in Si@Fe_3C/C intermediates [25]. They identified that the electrochemical performance of this structure was much better than that of the Si@void@C counterpart due to improved electrical contact between the Si yolks and the hollow carbon shell. As the other obstacle, the corrosion disadvantage (ii) of Si yolks has not received enough attentions. We found that the lithium storage performance of Si seriously depended on immersing durations in the $LiPF_6$-based electrolyte due to different corrosion extents. Veith et al. also observed the phenomenon of corrosion and passivation on Si surface and confirmed its insulator character through neutron reflectometry measurements [36].

Besides, the yolk-shell Si@void@C nanostructures are generally prepared by etching the SiO_2 intermediate layer of core double-shell Si@SiO_2@C with HF [15,22–24] or directly etching core-shell Si@C precursors with HF [25,28] or NaOH [26,27]. The empty space between the Si yolks and the carbon shell is a paramount factor and should be controllable to adequately accommodate the huge volumetric variation of Si. In fact, however, it is hard to completely avoid the erosion of Si yolks by HF or NaOH and to accurately control the space in these methods. In our previous study [34], we developed a facile method to obtain yolk-shell Si@void@C nanocomposites using resorcinol-formaldehyde coating and direct LiOH etching, without SiO_2 pre-modification on Si particles. After numerous experiments, however, we found that etching the Si@SiO_2@C or Si@C precursors trended to form the mixture of core-shell Si@C, Si/pore@C, yolk-shell Si@void@C, and even hollow carbon, as shown in Fig. S1, rather than the uniform yolk-shell structured products. The different degree of chemical corrosion might originate from the difference in the particle size, surface components, and also crystal directions of Si cores [37].

Herein, we reported the observation of enhanced conductivity and suppressed surface corrosion and passivation of Si cores by adopting core-shell Si@C nanoparticles as the yolks instead, *i.e.*, preparing core-shell yolk-shell Si@C@void@C nanostructure. Besides, the introduction of the inner carbon shell provided an effective protection of the Si cores from extra corrosion when etching the SiO_2 intermediate layer to obtain the anticipated thicknesses of void space. The obtained Si@C@void@C demonstrated a remarkably improved cycling stability and rate performance (with a reversible capacity of 1366 mAh g^{-1} at 500 mA g^{-1} and a capacity retention of ~60% at 4000 mA g^{-1}). This work provides a novel clue to develop advanced Si- or Sn-based anode materials for energy storage.

2. Experimental

2.1. Chemicals

Silicon nanoparticles (50–100 nm in diameter) were bought from Shanghai Chaowei Nano Technology Co. Ltd., China. Battery-grade electrolytes, *i.e.*, 1 M $LiPF_6$ dissolved ethylene carbonate (EC), dimethyl carbonate (DMC), ethylene methyl carbonate (EMC) in a 1:1:1 vol ratio, with 5 wt% fluoroethylene carbonate (FEC) as the additive were purchased from Yichun Jinhui New Energy Materials Co., Ltd., China. Dopamine hydrochloride, tetraethoxysilane (TEOS), and hydrofluoric acid (40 wt%) were purchased from Aladdin Industrial Corporation (Shanghai, China).

2.2. Materials synthesis

2.2.1. Synthesis of core-shell Si@C nanohybrids

Commercial nano-Si particles (0.36 g) were dispersed in the mixture solution of Tris-buffer (200 mL, 10 mM, pH ≈ 8.5) and ethanol (20 mL). After the ultrasonic treatment for 20 min, dopamine (0.36 g) was added to the above mixture and kept continual stirring for 24 h. Hereafter, the products were centrifuged, washed with deionized water for three times, and then dried at 60 °C for 12 h. Finally, under the protection of Ar, the dried products were carbonized at two steps of high temperatures: 400 °C (at a heating rate of 1 °C min^{-1}) for 2 h and subsequent 800 °C (5 °C min^{-1}) for 3 h.

2.2.2. Synthesis of core double-shell Si@C@SiO_2 nanohybrids

In a typical synthesis, the obtained Si@C nanoparticles (0.3 g) and cetyltrimethylammonium bromide (CTAB, 0.14 g) were firstly dispersed in the ethanol (120 mL) and H_2O (60 mL) mixture solution. After the ultrasonic treatment for 0.5 h, ammonia (28%, 3.0 mL) was added to the solution and kept vigorously stirring. Subsequently, tetraethoxysilane (TEOS, 3.0 mL, pre-dispersed in 30 mL ethanol) was dropwise added and kept stirring for 4 h. Hereafter, the product was collected by centrifugation, washed with ethanol for three times, and dried at 80 °C to obtain the core double-shell Si@C@SiO_2 nanohybrids.

2.2.3. Synthesis of core-shell yolk-shell Si@C@void@C nanohybrids

Typically, the Si@C@SiO_2 nanohybrids (0.7 g) were dispersed in the Tris-buffer (100 mL, 10 mM, pH ≈ 8.5) solution. After the ultrasonic treatment for 20 min, dopamine (0.15 g) was added, and kept stirring for 24 h. The products were centrifuged, washed with