



## Short communication

## Rational design of three-dimensional macroporous silicon as high performance Li-ion battery anodes with long cycle life

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## HIGHLIGHTS

- 3D porous and 0D hollow silicon are both synthesized by magnesiothermic reduction.
- 3D Si@C electrode exhibits stable cycling performance and high coulombic efficiency.
- This work provides a better understanding of controllable magnesiothermic reduction.

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## ABSTRACT

Three-dimensional (3D) macroporous silicon with stable interconnected structure is prepared by magnesiothermic reduction based on deliberate design, while flexible morphological control of zero-dimensional (0D) hollow nanospheres is realized via simply altering the conditions of the same reaction. When used as anode materials in lithium-ion batteries, the empty space in both structures allows for effective accommodation of large volume changes during lithium insertion and extraction. Due to the robustness of the interconnected porous structure, the 3D Si@C electrode exhibits better electrochemical properties with a reversible capacity of 1058 mAh g<sup>-1</sup> after 800 cycles and 91% capacity retention (only 0.012% capacity degradation per cycle). The coulombic efficiency of the 3D porous electrode stabilizes at 99.4% in later cycles. The results demonstrated herein provide a better understanding of the controllable magnesiothermic reduction reaction, which is potentially an efficient method for large scale synthesis of high-performance Si anodes.

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## 1. Introduction

Silicon has recently attracted considerable attention as a promising lithium-ion battery (LIB) anode primarily due to its high theoretical gravimetric capacity of ~4200 mAh g<sup>-1</sup> and its relatively low discharge potential [1,2]. The development of silicon-based anodes with high-capacity and long cycle life is expected to accelerate the emergence of next generation LIBs for electric vehicles and portable electronic devices [3–5]. However, large volume expansion of Si-based materials occurs during charging and discharging processes, resulting in structural failure and pulverization [6,7]. Switching from bulk materials to nanostructured electrodes, including 0D, 1D, 2D and 3D structures, is an effective

strategy to alleviate the problem [8–13].

In particular, porous Si enables us to take advantages of its unique structures and to make up for the shortcomings, since the free space in the pores can partially accommodate the large volume expansion and thereby enhance the cycling stability [14–16]. Moreover, the porous structure of electrode materials is of critical importance in determining the transport behavior of Li ions, in which their diffusion in electrodes, electrolyte and at the electrode/electrolyte interface directly affects the electrochemical performance [17–19]. Approaches for preparing such porous Si-based materials include coating templates or infiltration of a silica template within the void space of opals and removing templates by etching or thermal annealing. Macroporous inverse-opal Si-based materials and 3D porous silicon were synthesized using this method, which presented excellent cycling stability [20,21]. However, the complicated and high-cost synthesis process may hinder its large-scale production. Another approach to fabricate porous Si

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involves morphological transformation of pristine solid bulk particles [22–24]. For instance, Cho and co-workers reported a metal-assisted chemical etching process to produce 3D porous silicon, which exhibited a high reversible storage capacity of ~2050 mAh g<sup>-1</sup> [25]. More recently, several groups fabricated porous Si by using Si-based alloys or SiO as sources via de-alloying or disproportionation of SiO and subsequent chemical etching [26–28].

Since Sandhage et al. employed hot magnesium vapor to reduce diatom frustules in 2007, various silicon nanostructures have been synthesized by the same magnesiothermic reduction reaction [29–32]. In these literature, the reduced silicon replicas preserve the structures of different silica templates. To date, there have been no reports on the synthesis of 3D porous and 0D silicon fabricated from the same precursor by altering the reaction conditions of magnesiothermic reduction. Herein, a rational design and a controllable route have been developed to synthesize Si-based materials with distinguishing morphologies. We employed SiO<sub>2</sub> spheres to produce 3D macroporous Si and 0D hollow nanospheres via magnesiothermic reduction and acid etching process. By controlling the state of magnesium during the reaction, either 3D macroporous Si or 0D hollow nanospheres could be obtained. The 3D porous Si retained over 90% of its initial capacity after 800 cycles at a rate of 1 C (= 2 A g<sup>-1</sup>) with remarkable coulombic efficiency.

## 2. Material and methods

### 2.1. Preparation of 3D porous Si

Templating silica spheres with a diameter of about 200 nm were synthesized by a modified Stöber method [33]. For the reduction, 2 g of the as-synthesized SiO<sub>2</sub> spheres and 1.5 g of magnesium powder were well mixed and introduced into a corundum boat, which was heated in a tube furnace at 700 °C for 5 h under Ar gas flow with a ramp rate of 5 °C min<sup>-1</sup>. The obtained powder was first stirred in 1 M HCl solution for 6 h to remove MgO and then immersed in 10% HF for 12 h to remove unreacted SiO<sub>2</sub>.

### 2.2. Preparation of 0D hollow Si nanospheres

2 g silica precursors were ground in a agate mortar with 2 g magnesium powder. Then, the mixture was heated in a tube furnace under vacuum at 700 °C for 2 h with a ramp rate of 5 °C min<sup>-1</sup>. The obtained powder was first stirred in 1 M HCl solution for 6 h to remove MgO and then immersed in 10% HF for 12 h to remove unreacted SiO<sub>2</sub> in the inner core of the spheres.

### 2.3. Preparation of 3D/0D Si@C composites

The 3D/0D Si powder was coated with carbon via a chemical vapor deposition (CVD) method using acetylene as carbon source. Thermal decomposition was carried out at 650 °C for 3 h in a quartz furnace under a nitrogen (90%) and acetylene (10%) mixed gas.

### 2.4. Structural characterizations

The morphology of the samples were characterized by a field emission scanning electron microscope (FESEM, HITACH S4800) with an energy-dispersive X-ray spectroscopy (EDS) attachment. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded by an FEI F20 TEM. X-ray diffraction (XRD) patterns were collected using a Rigaku D/max-ga X-ray diffractometer with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Raman spectra were carried out on an HR800 Raman Spectrometer using an Ar ion

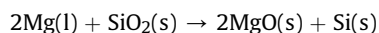
laser at 514 nm. Thermogravimetric analysis (TGA) measurements were obtained using a SDT Q600 V8.2 Build 100.

### 2.5. Electrochemical measurements

The electrode for the battery test was made of 3D or 0D Si@C active material (70 wt%), Super P carbon black (15 wt%) and sodium carboxymethyl cellulose binder (15 wt%). The loading of the active materials is typically 0.5–0.6 mg cm<sup>-2</sup>. For the electrochemical properties, CR2025 type coin cells were assembled in an argon-filled glove box (Mbraun, Labstar) with the Si powder as the working electrode and a lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF<sub>6</sub> in the mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 in volume ratio) with 3 vol % vinylene carbonate (VC). The cells were electrochemically cycled at a rate of 1 C (= 2 A g<sup>-1</sup>) between 0.01 and 1.0 V vs Li<sup>+</sup>/Li. Cyclic voltammetry (CV) measurements over the same potential range were recorded on an Arbin BT 2000 system at a scan rate of 0.1 mV s<sup>-1</sup>.

## 3. Results and discussion

The synthesis process of 3D porous and 0D hollow Si is schematically summarized in Fig. 1. In this work, the magnesiothermic reaction was carried out under argon atmosphere, molten magnesium flowed into the interstices between the SiO<sub>2</sub> spheres upon reaching its melting point of 650 °C. The silica precursors were partially in direct contact with liquid magnesium and reduced to form Si/MgO/SiO<sub>2</sub> composite, which was further treated by acid etching. The reaction occurred as below:



Due to the exothermic nature of the magnesiothermic reduction, a large amount of heat was released during the reaction [34,35]. The high temperature caused fusion and agglomeration of the as-synthesized silicon domain into larger crystals. As a result, the pristine spherical structure of silica was changed to an interconnected 3D porous network. On the other hand, prior researches on the magnesiothermic reduction have demonstrated that the reaction between gaseous magnesium and silica at a relatively low temperature (650°~700 °C) is thermodynamically favored under a low pressure [29,36]. In our experiment, magnesium evaporated upon heating to 700 °C under vacuum, while SiO<sub>2</sub> spheres were surrounded by Mg gas and reduced inwards. The obtained SiO<sub>2</sub>-Si/MgO core-shell spheres were converted into 0D hollow Si spheres after selective removal of MgO and unreacted SiO<sub>2</sub> in the inner core.

Fig. 2a–c shows SEM images of the 3D porous Si. Though transferred from monodispersed silica spheres (Fig. S2a in the Supporting Information), the resulting Si replicas preserved no typical morphological features of the starting material. A significant population of macropores can be identified from these images and silicon has been transformed into the framework of the highly porous particles. This unique 3D structure is further confirmed by the TEM image shown in Fig. 2d, which exhibits a coherent porous network with interconnected tunnels. The HRTEM image (Fig. 2d, inset) also shows lattice fringes corresponding to Si (111) lattice, indicating the crystalline character of the 3D porous Si. In contrast, the resulting 0D hollow Si nanospheres retained the spherical morphology with a similar diameter of the silica precursors as observed in Fig. S1a–c. The TEM and HRTEM images (Fig. S1d and inset) reveal the hollow structure of the crystalline spheres. The thickness of the spherical shell is estimated as 5–10 nm and the area outlined by white dotted lines suggests a shared shell between two interconnected spheres.

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