



RAPID COMMUNICATION

# Scalable synthesis of Si nanostructures by low-temperature magnesiothermic reduction of silica for application in lithium ion batteries



Xinling Liu<sup>a,b</sup>, Yanfeng Gao<sup>a,b,\*</sup>, Renhua Jin<sup>c</sup>, Hongjie Luo<sup>a,b</sup>,  
Peng Peng<sup>b</sup>, Yu Liu<sup>b</sup>

<sup>a</sup>School of Materials Science and Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, China

<sup>b</sup>Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China

<sup>c</sup>Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-2-7 Rokkakubashi, Yokohama 221-8686, Japan

Received 31 August 2013; received in revised form 10 November 2013; accepted 7 December 2013

Available online 17 December 2013

## KEYWORDS

Silica;  
Nano-silicon anode;  
Magnesiothermic  
reduction;  
Polyethyleneimine;  
Biomimetic

## Abstract

Nanostructured silicon (Si) is a promising candidate for use in lithium ion batteries. In this work, one-dimensional SiO<sub>2</sub> was obtained using linear polyethyleneimine (LPEI) as a biomimetic template/scaffold/catalyst, which was subsequently employed to fabricate nanostructured Si with a size of less than 10 nm in a SiO<sub>2</sub> matrix using a solid-solid magnesiothermic reaction at a relatively low temperature of 500 °C. This procedure proved to be cost-effective and high-yielding and generated a product that could withstand a significant Si volume change during lithium insertion/extraction by combining the advantages of Si nanostructures with the buffer effect of the SiO<sub>2</sub> matrix. In this manner, excellent cycling stability and a discharge capacity of more than 900 mAh/g were observed after 50 cycles. This work expands the structure-derived applications of bioinspired/biomimetic silica.

© 2013 Elsevier Ltd. All rights reserved.

## Introduction

Silicon is an appealing candidate for use as anode material in lithium ion batteries because of its high capacity (approximately 4200 mAh/g for a fully lithiated Li<sub>4.4</sub>Si state) and low discharge potential. Unfortunately, the poor cycling stability of silicon anodes caused by the severe volume change during lithium insertion/extraction processes

\*Corresponding author at: School of Materials Science and Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, China. Tel./fax: +86 21 6990 6213.

E-mail address: [yfgao@shu.edu.cn](mailto:yfgao@shu.edu.cn) (Y. Gao).

significantly limits the practical applications of this material [1,2]. Two main strategies have been employed to overcome this problem. The first strategy involves designing and fabricating various silicon nanostructures, including nanowires, nanotubes, and nanoparticles. Because stress caused by a volume change can be relaxed much more quickly at the nanoscale, nanostructured Si is more resistant to large volumetric strains and mechanical fracture than the bulk or micro-sized particles. The second strategy is the compositional regulation that can be achieved by constructing Si-based composites in which the active Si component is dispersed in or coated by other active/inactive materials that do not undergo a large volume expansion during the lithiation process, which consequently offsets the significant expansion of silicon and maintains the structural integrity of the electrode [3-5]. Thus, Si-based materials with improved electrochemical performance can be achieved by rational structural and compositional design.

Si nanostructures can be directly obtained via the transformation of biological or bioinspired  $\text{SiO}_2$  using a reduction reaction that preserves the initial structure [6]. Living creatures, such as diatoms and sponges, are experts at fabricating biogenic and species-specific silica nanostructures using a variety of cellular and biochemical processes, which employ biopolymers at ambient conditions [7]. As a result, this system not only provides useful silica materials but can also serve as valuable inspiration for materials design and synthesis, as demonstrated by the success of tailoring silica nanostructures using various bioinspired/biomimetic protocols [8-13]. However, comparatively speaking, the development of bioinspired/biomimetic silica applications has been rather slow, and many novel materials based on these unique structures and applications remain to be discovered.

Inspired by biopolymers, such as polyamines and polypeptides, that function as templates/scaffolds/catalysts for the formation of biosilica in diatoms, we used a linear polyamine, polyethyleneimine (LPEI), to direct the silica formation process [14-16]. In this system, LPEI molecules in solution self-assembled into one-dimensional (1D) crystalline fibrils-based aggregates that served as templates. When the aggregates are mixed with silica precursors, the amine groups on the fibrils' surface of LPEI act as catalysts promoting the hydrolysis and condensation of the silica precursors site-selectively on the aggregates to give LPEI@ $\text{SiO}_2$  hybrids while retaining the initial LPEI morphology. The morphology is preserved after the removal of LPEI using a calcination treatment. Generally, the primary 1D nanostructures of LPEI@ $\text{SiO}_2$  or  $\text{SiO}_2$  are observed as fibrils or tubes with diameters ranging from several nanometers to ca. 30 nm and lengths ranging from 10 s nm to several  $\mu\text{m}$ , depending on the experimental conditions. These structural characteristics make LPEI@ $\text{SiO}_2$  or  $\text{SiO}_2$  an attractive raw material for obtaining nanostructured Si materials.

Herein, we demonstrated the synthesis of biomimetic/bioinspired one-dimensional nanostructured silica, its subsequent magnesiothermic reduction to nanostructured Si and final application in lithium-ion batteries. In this study, using solid-solid magnesiothermic reduction occurring at as low as 500 °C,  $\text{SiO}_2$  can be transformed into Si without significantly changing its morphological framework. Although this method does not afford the complete reduction of  $\text{SiO}_2$

(i.e., the products appear as a mixture of  $\text{SiO}_2$  and Si), crystalline Si nanoparticles with a size of less than 10 nm can be obtained. At the same time, the unreduced or partially reduced  $\text{SiO}_2$  matrix can act as a buffer that resists volume expansion, which is favorable for application as a Si anode through the aforementioned compositional regulation. Indeed, a steady capacity of more than 900 mAh/g over the course of 50 cycles is achieved using this electrode material.

## Experimental section

### Synthesis of LPEI@ $\text{SiO}_2$

The preparation of LPEI (linear polymer with a  $M_w \sim 20,000$ ) was performed according to a previously described procedure [16]. LPEI@ $\text{SiO}_2$  was synthesized by dissolving 0.53 g of LPEI in 10 mL of  $\text{H}_2\text{O}$  at 85 °C, and then allowing the hot solution to cool to room temperature to produce white gel-like aggregates. Next, 20 ml of a silica source solution containing methyl silicate, ethanol and  $\text{H}_2\text{O}$  (at a volume ratio of 3:7:10) was added to the LPEI aggregates. After stirring for 1 h at room temperature, the suspension was centrifuged and the resulting white precipitate was washed with water and ethanol. After drying overnight under vacuum at 60 °C, LPEI@ $\text{SiO}_2$  powders were obtained.

### Magnesiothermic reduction of $\text{SiO}_2$ to Si (reduced $\text{SiO}_2$ )

The as-obtained LPEI@ $\text{SiO}_2$  was subjected to thermal treatment at 800 °C under air for 3 h after being heated from room temperature to 800 °C over the course of 5 h to remove the LPEI components and to generate the nanostructured  $\text{SiO}_2$ . Next,  $\text{SiO}_2$  and magnesium powders (at a mol ratio of 1:2) were manually ground using an agate mortar to form a gray mixture. The mixture was then placed on a stainless plate and transferred into a tube furnace. The temperature was increased to a specific value by heating at 10 °C/min and maintained for a specific amount of time under an atmospheric pressure of flowing Ar. After the reaction was completed, the product was cooled to room temperature and then treated with HCl solution (1 mol/L). The suspension was then filtered, washed with water and ethanol, and finally dried at 60 °C overnight under vacuum, presenting the reduced  $\text{SiO}_2$ .

### Modification of reduced $\text{SiO}_2$ with Ag

A suspension was prepared by stirring 0.10 g of reduced  $\text{SiO}_2$  powders with 50 mL of  $\text{AgNO}_3$  solution (2 mM, pH  $\sim$  9.5) for 2 h and then adding 0.1 mL of a 2% formaldehyde solution. The resulting suspension was stirred for 2 h, centrifuged, washed with water and acetone, and then the products were dried at 60 °C under vacuum.

### Electrochemical test

A slurry of Si powders (the above reduced  $\text{SiO}_2$ ) was prepared by mixing the Si powders with acetylene black

Download English Version:

<https://daneshyari.com/en/article/1557944>

Download Persian Version:

<https://daneshyari.com/article/1557944>

[Daneshyari.com](https://daneshyari.com)