



## Full paper

# A novel approach to synthesize micrometer-sized porous silicon as a high performance anode for lithium-ion batteries

Haiping Jia<sup>a</sup>, Jianming Zheng<sup>a</sup>, Junhua Song<sup>a</sup>, Langli Luo<sup>b</sup>, Ran Yi<sup>a</sup>, Luis Estevez<sup>a</sup>, Wengao Zhao<sup>a</sup>, Rajankumar Patel<sup>a</sup>, Xiaolin Li<sup>a</sup>, Ji-Guang Zhang<sup>a,\*</sup>

<sup>a</sup> Energy and Environmental Directorate, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354, USA

<sup>b</sup> Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99354, USA

## ARTICLE INFO

## Keywords:

Silicon  
Anode  
Porous structure  
Nano pores  
Micrometer-sized silicon  
Li ion batteries

## ABSTRACT

Porous structured silicon (p-Si) has been recognized as one of the most promising anodes for Li-ion batteries. However, many available methods to synthesize p-Si are difficult to scale up due to their high production cost. Here we introduce a new approach to obtain spherical micrometer-sized silicon with unique porous structure by using a microemulsion of the cost-effective silica nanoparticles and magnesiothermic reduction method. The spherical micron-sized p-Si particles prepared by this approach consist of highly aligned nano-sized silicon and exhibit a tap density close to that of bulk Si particles. They have demonstrated significantly improved electrochemical stability compared to nano-Si. Well controlled void space and a highly graphitic carbon coating on the p-Si particles enable good stability of the structure and low overall resistance, thus resulting in a Si-based anode with high capacity ( $\sim 1467 \text{ mAh g}^{-1}$  at  $2.6 \text{ A g}^{-1}$ ), enhanced cycle life (370 cycles with 83% capacity retention), and high rate capability ( $\sim 650 \text{ mAh g}^{-1}$  at  $11 \text{ A g}^{-1}$ ). This approach may also be generalized to prepare other hierarchical structured high capacity anode materials for constructing high energy density lithium ion batteries.

## 1. Introduction

The increasing demand for high-energy storage systems for applications such as electric vehicles, portable electronics, and stationary energy storage, is spurring the development of high-energy-density (gravimetric and volumetric) and long lifespan lithium-ion batteries (LIBs) [1–3]. In this regard, silicon (Si) has been extensively studied as a high-capacity anode for next-generation high-energy LIBs [4,5]. Si has the highest theoretical capacity of  $4200 \text{ mAh g}^{-1}$  (practical: ca.  $3579 \text{ mAh g}^{-1}$ ) compared to the conventional carbonaceous anode materials  $372 \text{ mAh g}^{-1}$  [6–8]. However, it suffers a fast capacity fade due to its large volume change and pulverization during lithiation and delithiation processes. The newly formed fresh surface during volume change also triggers continuous consumption of electrolyte, repeated breaking/formation of the solid electrolyte interphase (SEI), and an increase in the overall cell impedance [9–11]. There has been significant progress toward understanding and mitigating the capacity fade in Si-based anodes, such as exploiting nanostructured electrodes [12–18], surface coatings [19–23], additives [24–27], and novel binders [28–31]. These advances have paved the way for practical application of Si-based anodes for LIB applications.

The use of nanostructured materials with special morphology has

been proposed as promising strategy to improve the electrochemical performance of Si [10,32–33]. A small particle size not only decreases the diffusion length for lithium ions, but also increases the contact area between the active material and the electrolyte. In addition, solid-state diffusion of lithium can occur with nanoparticles that are impossible in bulk material. Nanoparticle lithium storage mechanisms would ensure the full lithiation of the active material, particularly at high current rates, which would promote a high specific capacity [34]. Nevertheless, the negative effects associated with nanostructures must be addressed, especially the increased electrolyte decomposition due to enlarged surface area, low thermodynamic stability, greater binder requirement, and the low packing density.

Microstructured materials have good thermodynamic stability and high tap density but suffer from limited kinetics at high current densities. In this regard, there has been a trend of combining the micron-sized silicon with nano-porosity, which can balance the advantages and disadvantages of different properties of the electrode materials. For example, Magasinski et al. [35], adopted a two-step chemical vapor deposition (CVD) process to assemble C-Si nanocomposite granules with high internal porosity, which demonstrate high reversible capacity and outstanding rate capability. However, the CVD techniques cannot meet the requirements of commercial application due to safety issues

\* Corresponding author.

E-mail address: [jiguang.zhang@pnnl.gov](mailto:jiguang.zhang@pnnl.gov) (J.-G. Zhang).

and difficulty in mass production. Cui et al. [36]. reported a novel secondary structure of silicon anodes made by assembling silicon nanoparticles using a microemulsion approach, and demonstrated high volumetric capacity and excellent cycling stability. However, the starting material of silicon nanoparticles is very expensive and the primary Si-C nanoparticles demonstrate yolk-shell structure, which is complicate to fabricate and is not favorable for lithium ion transport.

In this work, a novel approach has been developed to prepare micron sized silicon anode by using cost-effective starting material of silica (Nippon Shokubai Co., Ltd) and creating void space by the magnesiothermic reaction step which is relatively simple compared to the fabrication of the yolk-shell structure. The obtained material displays uniform mesopores within the microparticles, which are composed of nano-sized crystalline Si. The primary nanoparticles can prevent fracture and provide a fast route for lithium-ion transport, and demonstrate promising electrochemical properties. The material has a high tap density, similar to that of micron-sized bulk Si particles, due to efficient packing inside the secondary particles.

## 2. Results and discussion

The micron-sized porous silicon was synthesized via magnesiothermic reduction of microspheres of SiO<sub>2</sub> using a bottom-up microemulsion approach. As schematically illustrated in Fig. 1a, pomegranate-like microspherical silica was synthesized via an evaporation-induced assembly of waterborne colloids in a water-in-oil emulsion process. An aqueous suspension of monodisperse silica (70 nm, Fig. 1b) was emulsified into polydispersed water droplets of micrometer size in the oil phase and colloidal aggregates were produced spontaneously during the slow evaporation of water. It should be noted that silica particles were not trapped at the interface between aqueous and oil phases due to the high hydrophilicity of silica particles. During the evaporation of water, the silica particles condensed to form micron-sized silica particles. The densely packed microspherical silica was

further used as template and silicon source in a magnesiothermic reduction for the synthesis of microspherical Si particles [20]. After reduction and etching steps, the residual silicon nanocrystals form 3D porous Si particles (hereafter abbreviated as p-Si), which largely maintain the original morphology of the microspherical silica. The porous structure inside the secondary particles, which arises from the complete removal of MgO, can effectively accommodate the volume expansion of silicon upon lithiation.

The tap density of the micrometer-sized particles was significantly improved due to the close packing structure. As shown in Supplementary Fig. S1, the starting material of 70 nm silica nanoparticles has a tap density of 0.56 g cm<sup>-3</sup>, while the intermediate product of micrometer-sized silica clusters has a tap density of 0.72 g cm<sup>-3</sup>. For the silicon nanoparticles obtained from the 70 nm silica, the tap density is 0.18 g cm<sup>-3</sup>, while the tap density of micro-sized silicon clusters is as high as 0.43 g cm<sup>-3</sup>. The increase in tap density from nanostructure to microstructure is 139%. Furthermore, the tap density of the micro-Si is comparable to that of commercial (comm) microstructure silicon (1–5 μm, 0.44 g cm<sup>-3</sup>) and 378% higher than that of commercial nano-silicon (50 nm, 0.09 g cm<sup>-3</sup>). The high tap density of p-Si will lead to high volumetric capacity of the electrodes. [37]

The obtained micron-sized porous silica shows highly spherical morphology with the particle size ranging from 500 nm to 10 μm (Fig. S2a). Statistical analysis of the diameter of the silica pomegranates shows that the average particle size is ~ 5.28 μm (Fig. S3). It should be noted that different sizes of the particles can help to bring higher tap density of the material. [38] And the high-resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 1c and Fig. S4) further display the primary nanoparticles of silica tightly compacted to form the pomegranate-like microspherical silica. The resulting silicon product, as shown in Fig. 1d and Fig. S2b, basically demonstrates the same morphology as the template. Investigation into the fine structure (inset of Fig. 1d and Fig. S4) reveals an open

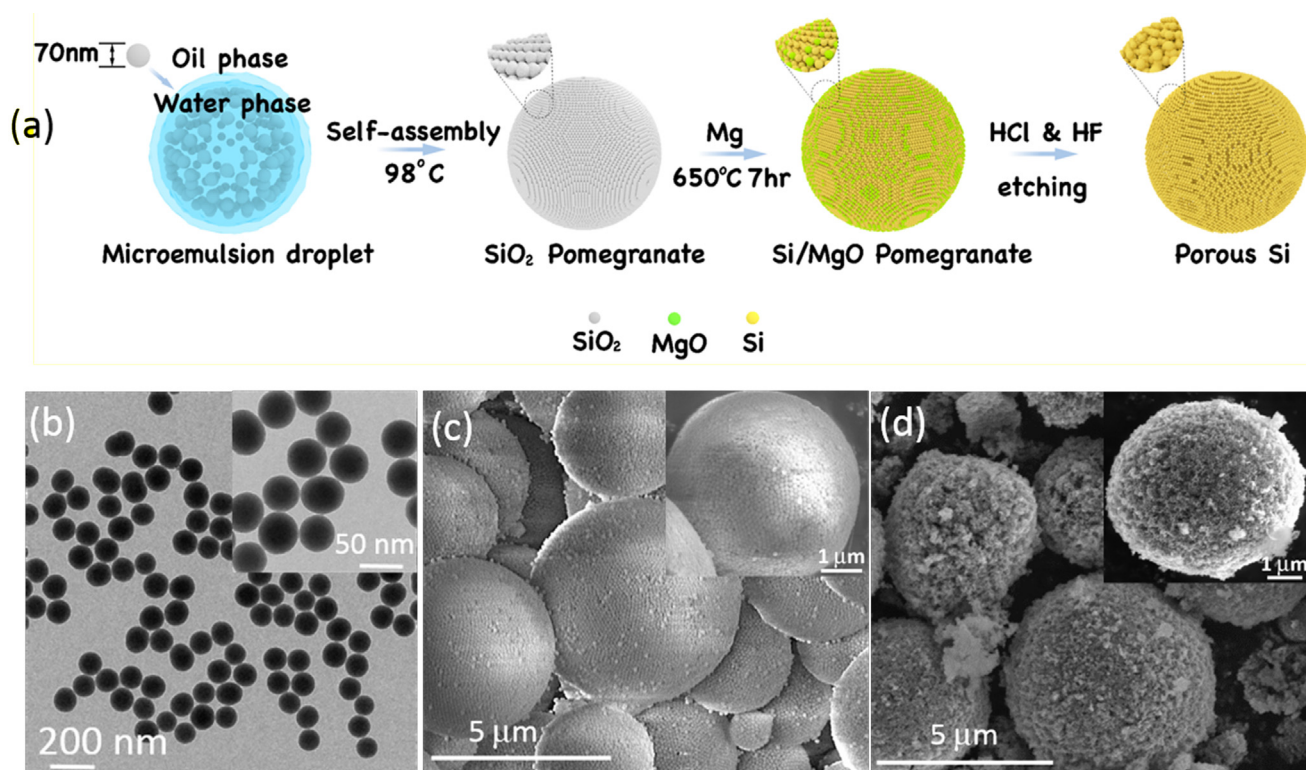


Fig. 1. a) Schematic illustration of the preparation process of the porous Si; b) TEM images of nano-SiO<sub>2</sub>. The inset shows an enlarged TEM image; c, d) SEM images of SiO<sub>2</sub> pomegranates and the obtained porous Si, respectively. The insets show magnified images of the individual microparticles.

Download English Version:

<https://daneshyari.com/en/article/7952492>

Download Persian Version:

<https://daneshyari.com/article/7952492>

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