

# Titanium Silicide Coated Porous Silicon Nanospheres as Anode Materials for Lithium Ion Batteries



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## ABSTRACT

We report on the facile synthesis of porous silicon structure *via* magnesiothermic reduction followed by coating of the surface with TiSi<sub>2</sub>. These modifications not only showed significant promise in overcoming the drastic volume change during charge and discharge cycles but also in improving the relatively low conductivity of silicon. The synthesized porous structure with a highly electrically conductive coating layer significantly enhanced the electrochemical performance in terms of cyclic stability and rate capability. The TiSi<sub>2</sub> coating layer, which has good electrical conductivity and physical strength, enhances the conductivity and maintains the Si structure during cycling. This combination of porous structure *via* magnesiothermic reduction and highly conductive TiSi<sub>2</sub> coating provides a synergistic effect, which can be seen in the improvements in electrochemical performance. This synthesis demonstrates a promising method for producing high capacity anode materials for next generation LIBs.

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## 1. Introduction

Until recently, lithium ion batteries (LIBs) have been mainly applied as power sources for small-portable devices. However, the medium to large size battery sector, which includes electric vehicles (EVs) and energy storage systems (ESS) have recently garnered increasing interest, which, in turn, has led to increasing demands for higher power density at reasonable costs [1,2]. Silicon is considered to be one of the most promising anode materials for LIBs, due to its high theoretical capacity (4200 mAh g<sup>-1</sup>), nontoxicity, low cost and abundance. On the other hand, Si anodes have been inhibited from mass market production due to intrinsic limitations, such as severe volume change and low electrical conductivity. These limitations usually result in poor cycling and rate performances, which ultimately limit its use in applications [3,4].

Numerous reports have reported on improvements in the cyclic stability of Si, by synthesizing Si into nanospheres [5], nanotubes [6–8] and nanowires [9,10], making composites with carbon

[11,12], and creating void spaces to buffer the volume expansion [13,14]. Recently, many researchers have synthesized porous structured materials which have shown better cyclic stability. These reports often state that this improvement is due to the void spaces in porous materials being able to lower the stresses that arise during volume changes. For example, the Cui group proposed a hierarchical structured silicon anode inspired by the structure of pomegranate [13]. The void spaces in between particles can make a stable SEI and alleviate the volume stress during alloying-dealloying. In addition, the Hyeon group proposed self-assembled Fe<sub>3</sub>O<sub>4</sub> nanoparticle clusters to be used as high performance anode materials [14]. These “bottom up” approaches have exhibited excellent cyclic stability and rate capability due to their elaborate design. However, “bottom-up assembly” for Si anodes usually require a toxic precursor such as SiH<sub>4</sub> or SiCl<sub>4</sub> and the synthesis methods are often complex and expensive. Therefore, some researchers have tried to synthesize porous silicon structures using top-down approaches. For example, Park et al. reported a simple route to produce micro-porous bulk Si materials by using a combination of electroless metal deposition and metal assisted chemical etching [15]. Ran Yi et al. have developed a facile route to produce interconnected micro sized porous Si using the disproportionation of SiO by heating [16]. However, although these methods show promise, impediments, such as cost and scalability, have kept these methods from becoming widespread. In contrast,

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“magnesiothermic reduction can produce porous silicon structures from silica at relatively low temperatures [17], is environmentally friendly and is inexpensive. Additionally, the morphology and structure can be easily controlled [18–24]. Recently, the number of reports using magnesiothermic reduction has been increasing at an exponential rate and synthesis of macro porous structures [18], nanosheets [19], nanowires [20], nanotubes [21], nanorods [22] hollow spheres [23] and yolk-shell structures [24].”

In addition to the volume expansion issues, silicon also suffers from its low electrical conductivity. This problem can often be somewhat mitigated by coating the surface of silicon with a conductive material. Although many possibilities, such as carbon, metal oxides, and conducting polymers, exist, the choice of coating material should be based on high conductivity, mechanical strength and chemical stability. Currently, the carbon based materials have been the main coating source but, convertible oxides have also started to gain interest as candidates for coating [25]. Among them, titanium silicide ( $\text{TiSi}_2$ ) holds much appeal due to its high electrical conductivity (resistivity  $\sim 10 \mu\Omega$ ), thermal stability, mechanical robustness, and light in weight [26]. Also,  $\text{TiSi}_2$  in C54 crystal structure rarely reacts with lithium at the low voltage (0–3 V vs.  $\text{Li}^+/\text{Li}$ ) [25,27–29]. Park et al. reported a simple route for combining titanium silicide and silicon *via* the silicothermic reduction. It exhibited a highly stable solid electrolyte interface during cycling and good rate ability [30].

Herein we present a facile way to synthesize high performance porous silicon@titanium silicide (P-Si@ $\text{TiSi}_2$ ) spheres using the magnesiothermic reduction process for  $\text{SiO}_2$ @ $\text{TiO}_2$  composite to be used as anodes in lithium ion batteries. During the reduction reaction, the  $\text{TiO}_2$  layer was first reduced to Ti and then  $\text{SiO}_2$  layer was reduced to Si. In addition, Ti and Si produced a  $\text{TiSi}_2$  layer at high temperatures [31]. The porous structure with high electrically conductive coating layer significantly enhanced the electrochemical performance.

## 2. Experimental

### 2.1. Preparation of $\text{SiO}_2$ nanoparticles (500~600 nm)

The Stöber method was used to prepare  $\text{SiO}_2$  nanoparticles. Briefly, 200 ml of absolute ethanol, 20 g of DI water, and 12 g of ammonium hydroxide solution (28~30%) were mixed and magnetically stirred for 30 mins. Then, 12 g of tetraethylorthosilicate was added to the solution. After 6 hrs,  $\text{SiO}_2$  nanoparticle was collected by centrifugation and washed with ethanol 3 times. The collected  $\text{SiO}_2$  nanoparticles were dried under vacuum at 80 °C.

### 2.2. Preparation of $\text{SiO}_2$ @ $\text{TiO}_2$ nanoparticles

500 mg of  $\text{SiO}_2$  nanoparticles were dispersed in 500 ml of a co-solvent composed of ethanol and acetonitrile (v/v = 1:1). 2.5 ml of ammonium hydroxide solution (28~30%) was then added to the solution, and stirred for 30 minutes. A titanium butoxide solution, containing 0.5 ml of titanium butoxide, 10 ml of ethanol, and 10 ml of acetonitrile, was then injected into the stirred solution and allowed to react for 2 hrs. The product was collected by centrifugation and washed with ethanol 3 times. The collected product was dried under vacuum at 80 °C.

### 2.3. Preparation of P-Si@ $\text{TiSi}_2$ nanoparticles

The as-synthesized  $\text{SiO}_2$ @ $\text{TiO}_2$  nanoparticles and magnesium powder were put in the steel boat ( $\text{SiO}_2$ @ $\text{TiO}_2$ : Mg = 1: 2.5, molar ratio). The steel boat was then put into a cylindrical sealing reactor and assembled in an argon filled glove box. The assembled

cylindrical sealing reactor was heated in a tube furnace at 700 °C for 6 hrs under an argon atmosphere. The samples were immersed in 1 M HCl for 8 hrs to selectively remove MgO and  $\text{Mg}_2\text{Si}$ . Then, the samples were washed with DI water three times and vacuum dried. For comparison, we also synthesized P-Si spheres (~600 nm) by direct magnesiothermic reduction of  $\text{SiO}_2$  spheres.

### 2.4. Characterization

X-ray diffraction (XRD) patterns were recorded using a High Power XRD from Rigaku Corporation with Cu  $K\alpha$  radiation (Model: D-MAX2500-PC). The diffraction data was collected in the  $2\theta$  range of 20° ~ 80°. The morphologies of samples were analyzed using a field emission electron microscope (FE-SEM, AURIGA, Carl Zeiss). High resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray spectroscopy (EDS) analysis were carried out on a JEOL JEM-2100F electron microscope.

### 2.5. Electrochemical measurement

The working electrode was prepared by creating a slurry composed of mixing active material (70 wt.%), super P (as a conductive agent) (15 wt.%) and polyamideimide (PAI) binder (15 wt.%). The slurry was uniformly spread onto a copper foil through a using the doctor blade method and dried in a vacuum oven at 60 °C for 1 hr. To activate the PAI binder, the as-prepared electrode was heated at 350 °C for 90 mins under an argon atmosphere and dried again in a vacuum over at 120 °C for 8 hrs. The loading level of active materials in the working electrodes is around 1.5 mg/cm<sup>2</sup>. 2016-type coin cells were assembled with the as-prepared electrode, a polypropylene separator, lithium foil as the counter electrode and 1.5 M  $\text{LiPF}_6$  solution in a 5: 25: 70 (v/v) mixture of ethylene carbonate (EC), fluoroethylene carbonate (FEC), diethyl carbonate (DEC). The assembly was performed in an argon atmosphere glove box. Electrochemical measurements were carried out using 2016-type coin cell. The galvanostatic charge-discharge experiment was performed in the potential range 0.01 ~ 1.5 V vs.  $\text{Li}^+/\text{Li}$  with a WBCS3000 cyclor (WonA Tech, Korea) at room temperature. Cyclic voltammetry (CV) was carried out from 1.5 to 0.01 V vs.  $\text{Li}^+/\text{Li}$  at a scan rate of 0.1 mV s<sup>-1</sup> using a WBCS3000 cyclor (WonA Tech, Korea). Electrochemical impedance

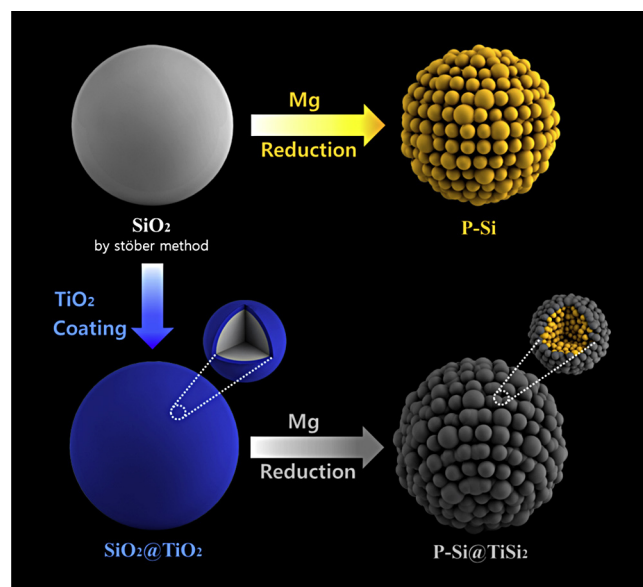


Fig. 1. Schematics of the synthesis of P-Si and P-Si@ $\text{TiSi}_2$  spheres.

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