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Synthesis of Si nanosheets by using Sodium Chloride as template for high-performance lithium-ion battery anode material

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HIGHLIGHTS

- The 2D Si nanosheets have been fabricated by using the NaCl particles as template.
- The obtained Si nanosheets have a larger area up to 10 μm^2.
- It delivers high reversible capacity about 2500 mAh g^{-1} at the current density of 0.2 A g^{-1}.
- The final capacity is 900 mAh g^{-1} at 2 A g^{-1} even after 200 cycles.

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ABSTRACT

Due to the shorter path length and more channels for lithium ion diffusion and insertion, the two-dimensional (2D) Si nanosheets exhibit superior electrochemical performances in the field of electrochemical energy storage and conversion. Recently, various efforts have been focused on how to synthesize 2D Si nanosheets. However, there are many difficulties to achieve the larger area, high purity of 2D Si nanosheets. Herein, we developed a facile and scalable synthesis strategy to fabricate 2D Si nanosheets, utilizing the unique combination of the water-soluble NaCl particles as the sacrificial template and the hydrolyzed tetraethyl orthosilicate as the silica source, and assisting with the magnesium reduction method. Importantly, the obtained Si nanosheets have a larger area up to 10 μm^2. Through combining with reduced graphene oxides (rGO), the Si nanosheets@rGO composite electrode exhibits excellent electrochemical performances. It delivers high reversible capacity about 2500 mAh g^{-1} at the current density of 0.2 A g^{-1}, as well as an excellent rate capability over 900 mAh g^{-1} at 2 A g^{-1} even after 200 cycles.

1. Introduction

The increasing need to reduce greenhouse gas emission and the effective untilization of renewable energy are urgently requiring advanced energy storage devices. Currently, Li-ion batteries are the major energy storage system to address it and are applicable to day-to-day electronic products and electric vehicles in spite of research efforts on new types of rechargeable batteries. Nevertheless, the present Li-ion batteries are not sufficient to meet the increasing demand for higher energy density [1–4]. Today's Li-ion batteries mostly use graphite as anode with a maximum theoretical specific capacity value of 372 mAh g^{-1}, which limits their use in high capacity systems. As an earth-abundant material, Silicon is one of the most promising candidates for next-generation rechargeable batteries materials due to their high theoretical specific capacity (~4200 mAh g^{-1} in form of $Li_{4.4}Si$ at room temperature), low working potential and environmental friendliness [5–9]. In spite of these advantages described above, silicon anodes have been delivering limited applications because it undergoes an enormous (~400%) volume expansion via an alloying reaction process during lithiation, which results in pulverization and capacity fading [5–10].

Based on the aforementioned issues, silicon anodes have been primarily mitigated by nanostructure and surface engineering strategies, because nanostructures can accommodate large mechanical stress from alloying reaction due to the high surface-to-volume ratio [10]. Along with distinctive features of nanostructured, including excellent mechanical durability, extraordinary electronic properties, and compatibility with existing technologies, their electrochemical performances have been significantly improved since past decades [11–13]. Actually,

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the diversely textured silicon nanomaterials, such as nanoparticles [14–19], nanotubes [20–23], nanowires [6,24–26] and 3D porous structures [27–30] have been extensively explored for advanced battery anodes. However, two-dimensional (2D) Si nanosheets, as an important nanostructure, have been barely researched as anode materials in Li-ion batteries, in spite of such advantages as easy accessibility of lithium ions, compatibility with other materials, and small volume expansion. What's more, the Si nanosheets have a shorter transport path length in the direction of perpendicular to 2D plane and more channels for lithium ion diffusion and insertion [31–34].

Different from the layered structure materials, such as graphite and molybdic sulfide, the typical exfoliation methods are not suitable for the preparation of the 2D Si nanosheets due to its diamond structure. In general, in order to obtain the 2D Si, most of the researchers have to resort to the typical chemical decomposition of silanes [35,36] or sputtering [37,38] to prepare Si thin film on diverse substrates, which have exhibited excellent electrochemical performances. Recently, Lu et al. reported a graphene oxide-based template method to synthesize 2D Si nanosheets with a low yield and poor electrochemical properties. On the other hand, the minisize graphene oxide template leads to synthesizing of a small area 2D Si nanosheets [32]. Moreover, Kim et al. demonstrated a more scalable approach to produce Si nanosheets from sand, which combined with reduced graphene oxide as coating material. And the resulting Si nanosheets were tore out into smaller nanosized sheets and showed largely stacked structures, which cause detrimental effects on the performance of LIBs including lower Coulombic efficiency and drastic capacity decay [31]. In addition, Soojin Park's group found that a natural clay with silicate containing layered structures can be exfoliated by molten salts and used as 2D SiO_2 source to produce 2D Si nanosheets [33,34]. However, due to the multiple elements of clay, it is difficult to remove the useless or harmful elements. So, it is still an urgency to find a feasible and cost-effective method of synthesizing large area and high purity 2D Si nanostructures with improved electrochemical performance at present. Nevertheless, as far as we know, this work will be very difficult and full of challenge.

Herein, we developed a facile and scalable synthesis strategy to fabricate 2D Si nanosheets. In this process, we employed the unique combination of the water-soluble NaCl particles as the template and the hydrolyzed tetraethyl orthosilicate (TEOS) as the silica source, and assisting with the magnesium (Mg) reduction method, to fabricate 2D Si nanosheets. We found that the recrystallized NaCl have large surface, which contributes to forming a large area SiO_2 nanosheets via a self-assembly process on the surface of NaCl. In the following metal magnesium reduction, the morphology of Si nanosheets can completely be preserved. Finally, combining with the reduced graphene oxides (rGO), this Si nanosheets@rGO composite electrode exhibits extremely durable cycling performance and improved rate performance, which demonstrates that the 2D Si nanosheets synthesized via this method will be a potential anode material for next generation high performance LIBs.

2. Experimental

2.1. The synthesis of Si nanosheets

All reagents are of analytical grade without any further purification. Tetraethyl orthosilicate (TEOS, AR, grade), Magnesium powder (Mg, 100–200 mesh), Sodium Chloride (NaCl, AR, grade), and Ammonium Hydroxide (AR, 25–28%) were purchased in Sinopharm (Sinopharm Chemical Reagent Co., Ltd, China). In this experiment, we developed a facile and scalable two-steps synthesis strategy, which contains crystal and chemical reduction process. Firstly, the silica nanosheets were prepared using NaCl as template. The detail process is as follows. 1 g NaCl, 20 ml ethanol, 4 ml deionized water and 0.1 ml ammonium hydroxide were mixed in one beaker. Next, 20 ml ethanol and 0.2 ml TEOS were mixed in another beaker. After fully stirring, the two beakers mixed slowly. Followed by 12 h stirring, the mixture solutions were poured into the petri dish to evaporate the ethanol and water at 60 °C. The obtained white crystals in the petri dish were heat-treated at 500 °C for 2 h. After removing the NaCl by deionized water treatment, a light green powder can be obtained, and that is the silica nanosheets. The photograph of the products can see Fig. S1 (supporting information).

Secondly, the obtain silica nanosheets were reduced by magnesiothermic reduction methods. Magnesium powder and silica nanosheets with a weight ratio of 1:1 were added into a sealed metal container (Fig. S7, supporting information). Then, the container was heated at 650 °C for 6 h in a tube furnace under Ar atmosphere. Finally, the resulting nut-brown powder was etched with 1 M HCl and 10% HF acid, and the expected Si nanosheets can be achieved.

2.2. The preparation of Si nanosheets@rGO composites

To obtain the reduced graphene oxide (rGO), a novel double-steps microwave radiation method was used [39]. The initial step started from microwave heating of commercially available expandable graphite, which was followed by oxidation and intercalation of an oxidant and sulfuric acid. Afterwards, the second microwave irradiation process was applied. This process leads to effective exfoliation and reduction of graphite oxide. Next, the Si nanosheets were directly dispersed in deionize water with the assistance of a surfactant (sodium dodecylbenzenesulfonate) and sonication. After mixed together, the mixed solution, with the ratio of mass weight 7:3, was treated by vacuum filtration, and the composite electrode of Si nanosheets@rGO was successfully achieved, as shown the inset image in Fig. 4a. Even bent to some extent, the composite paper can preserve the initial state without any fragmentation and breaking. And the paper-like composite electrodes can be readily cut as needed with a razorblade into free-standing platelets.

For comparison, the bare Si nanosheets electrode was prepared by typical process: active materials (Si nanosheets), conductivity agent (carbon black), and binder (polyvinylidene fluoride, PVDF) in a weight ratio of 8:1:1 were blended with *N*-methylpyrrolidone as solvent. Electrode film prepared by coating the mixture on a copper foil was first vacuum-dried at 80 °C for 4 h and then at 120 °C for 12 h.

2.3. Material and electrode characterization

SEM (SEM, TESCAN, VEGA 3) was used to characterize the morphology of the obtained products. Transmission electron microscope (TEM, JEM-3000F, JEOL), micro-Raman spectroscope (WITec excited by λ = 633 nm laser) and X-ray diffraction (XRD, D/MAX 2500) with Cu-Ka Radiation were employed to visualize internal crystalline structures. X-ray diffraction (XRD) patterns were collected from the powder sample (D/Max 2500 v, Japan Rigaku).

To evaluate the electrochemical performance of the silicon nanosheets, the obtained Si nanosheets@rGO composite electrodes were cut into desired size and assembled into 2032-type coin cells in which Celgard 2400 and Li foil were used as separators and counter/reference electrodes. The electrolyte used was lithium hexafl uorophosphate (1 M, $LiPF_6$), dissolved in 1/1/1 (volume rate) ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl carbonate (DMC). Particularly, the cells were assembled in an argon-filled glove box. Cyclic voltammetry (CV) curves were achieved with an electrochemistry system (CHI 660D, China). The constant current charge and discharge measurements in a voltage range between 0.01 and 1.5 V (vs Li/Li^+) were conducted using Neware Technology (NEWARE BTS-5V 5 mA, Neware Technology Co, Ltd., China).

3. Results and discussion

The synthesis process of Si nanosheets is schematically presented in Fig. 1. This fabrication process principally consists of *in situ* synthesis of