



Facile synthesis of reduced graphene oxide-porous silicon composite as superior anode material for lithium-ion battery anodes



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HIGHLIGHTS

- Both porous Si from rice husks and rGO have been introduced into the composite.
- The composite exhibits good rate and cycling performance.
- Waste material can be converted into potential sources for future technological applications.

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ABSTRACT

We report a new method for synthesizing reduced graphene oxide (rGO)-porous silicon composite for lithium-ion battery anodes. Rice husks were used as a raw material source for the synthesis of porous Si through magnesiothermic reduction process. The as-obtained composite exhibits good rate and cycling performance taking advantage of the porous structure of silicon inheriting from rice husks and the outstanding characteristic of graphene. A considerably high delithiation capacity of 907 mA h g⁻¹ can be retained even at a rate of 16 A g⁻¹. A discharge capacity of 830 mA h g⁻¹ at a current density of 1 A g⁻¹ was delivered after 200 cycles. This may contribute to the further advancement of Si-based composite anode design.

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1. Introduction

Lithium ion batteries (LIBs) have found a wide variety of applications in popular portable electronics [1,2]. They are also important power sources for electric vehicles (EVs) or hybrid electrical vehicles (HEVs) and renewable energy storage stations because of higher energy density, power density, and long cycle life than other comparable battery systems [2,3]. To meet such requirements, electrode materials of LIBs must have high specific capacities and satisfactory rate performance. Silicon (Si) has recently received great attention as an LIBs anode owing to its highest theoretical

capacity around 4000 mA h g⁻¹ [1,4], which is about ten times higher than that of graphite (372 mA h g⁻¹). Unfortunately, Si suffers from severe capacity fading due to huge volume change (>300%) during charging and discharging processes and low intrinsic electrical conductivity [5,6]. Some effective strategies, mainly including fabricating Si nanostructures [7–9] and nanocomposites [10–16], have been suggested to improve the overall performance of Si anodes. However, most of these involved complicated and costly processes.

Graphene, a two-dimensional carbon nanomaterial with high electronic conductivity, mechanical strength and flexibility, has been utilized to design Si-based anode materials for LIBs [17–19] and other electrochemical energy storage devices [20].

Herein, we report a facile method for preparing reduced graphene oxide (rGO)-porous silicon composite. Porous Si nanoparticles from rice husks have been uniformly inserted into graphene by combining a condensation reaction and subsequent

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thermal treatment. The porous structure and graphene act as elastic buffers against volume changes during cycling. In addition, graphene also plays the roles of an effective electronically conductive network. As a result, the rate performance and cycling stability of the composite are significantly improved compared to those of pristine porous Si.

2. Experimental

2.1. Materials

Rice husks used were obtained as a by-product of rice harvested in the suburbs of Chengde in the People's Republic of China. Graphite flakes (<20 μm , synthetic) was commercially obtained from Sigma-Aldrich. Other reagents, including HCl, HF, ethanol, magnesium powder, H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$, P_2O_5 , KMnO_4 , formaldehyde(37% w/w), melamine, sodium alginate (China Medicine Co., Ltd.) were at least of analytical grade and used as received.

2.2. Preparation of porous Si

Rice husks were treated according to previous report by Refs. [4,21]. In a typical preparing process, Rice husks were first leached with a 10% (w/v) HCl solution and calcined at 700 $^\circ\text{C}$ for 2 h to produce high-quality silica. Then 1.0 g of the pretreated silica and 1.0 g of magnesium were thoroughly mixed and introduced into a steel boat in an argon-filled glove box, and then heated to 650 $^\circ\text{C}$ with a ramping rate of 5 $^\circ\text{C}$ and kept for 3 h in a tube furnace flowing Ar gas. The collected dark brown mixture was etched in 1 M HCl solution (HCl: H_2O : EtOH ratio = 0.66:4.72:8.88 in molar ratio) for 5 h at room temperature, then immersed in HF solution (HF: H_2O : EtOH = 1.05:1.11:6.45 in molar ratio) for 10 min to remove residual silica. After drying under vacuum at 60 $^\circ\text{C}$ for 12 h, porous Si powders were obtained.

2.3. Preparation of graphene oxide

The synthesis of Graphene oxide (GO) was described in our group's previous report [22]. Typically, graphite powder (5.0 g) was added to a hot (ca. 80 $^\circ\text{C}$) and concentrated H_2SO_4 solution (7.5 mL) containing $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g) and P_2O_5 (2.5 g). The mixed solution was stirred continuously for ca. 3 h. After cooled down to room temperature, the dark blue mixture was diluted with water, filtered, and washed with water until the waste solution reached neutral pH. Pre-oxidized graphite powder was collected and dried in air at room temperature overnight. Then, pre-oxidized graphite (1.0 g) was added to concentrated H_2SO_4 (23 mL) incubated in an ice-water bath (0 $^\circ\text{C}$). KMnO_4 (3.0 g) was then added to the mixture under stirring slowly, so that the temperature of the solution was controlled below 20 $^\circ\text{C}$ during the addition procedure. The mixture was then stirred at 35 $^\circ\text{C}$ for 2 h, to which distilled water (46 mL) was added for dilution. After 15 min, the reaction was terminated by the addition of distilled water (140 mL) and 30% H_2O_2 solution (2.5 mL). It was clearly observed that the color of the mixture rapidly changed to bright yellow upon the formation of GO. To remove metal ions, the mixture was filtered and washed in succession with 1:10 HCl solution (v/v) and further purified by dialysis for a week. Finally, the resulting graphite oxide was diluted into a 300 mL brown dispersion (4.0 mg mL^{-1}).

2.4. Preparation of rGO-porous Si composite

In a typical synthesis of the composites, 200 mg porous Si powders were dispersed in 100 mL water by sonication in a water bath. The as-prepared GO dispersion was diluted to 1.0 mg mL^{-1} .

After the exfoliation of the aqueous dispersion (1.0 mg mL^{-1}) was achieved by sonication for 30 min, 40 mL of GO aqueous dispersion was mixed with the 100 mL of silicon aqueous dispersion and sonicated for another 30 min.

Meanwhile, 1.0 g of melamine and 1.77 mL of formaldehyde aqueous solution were added into 15 mL water. The solution was heated at 70 $^\circ\text{C}$ until it turned transparent. Then, the mixture of GO and porous Si powders was introduced to this transparent solution and stirred at 98 $^\circ\text{C}$ for 3 h. During this process, a condensation reaction between melamine resin and GO sheets took place. Both porous Si and GO have been functionalized by melamine resin. The precipitate was washed with water and dried at 60 $^\circ\text{C}$ under vacuum. Finally, the rGO-porous Si composite was obtained by a heat treatment at 800 $^\circ\text{C}$ for 4 h with a ramping rate of 1 $^\circ\text{C}/\text{min}$ under Ar atmosphere (main procedures were illustrated in Scheme 1). rGO sample without porous Si was prepared according to the same procedure to estimate the practical specific capacity of Si.

2.5. Structural and electrochemical characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The accelerating voltage was set at 40 kV with 30 mA flux at a scanning rate of 8 $^\circ \text{min}^{-1}$ in the 2θ range of 20–70 $^\circ$. Scanning electron microscope (SEM) images were performed on a XL 30 ESEM FEG scanning electron microscope integrated with an EDAX system at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were carried out on a Hitachi-600 TEM with an accelerating voltage of 100 kV. The nitrogen adsorption-desorption measurements were performed on a Quantachrome ASiQwin-Autosorb Iq Station 2 and the bath temperature was 77.35 K (The outgas Temp. is 473.15 K). Thermogravimetric analysis (TGA) of the composites was conducted in air at a heating rate of 10 $^\circ\text{C min}^{-1}$ from 30 $^\circ\text{C}$ to 750 $^\circ\text{C}$ using a thermal analyzer (TGA50H).

For the electrode fabrication, rGO-porous Si composite or porous Si, acetylene black, and sodium alginate with a mass ratio of 60:20:20 were mixed into a homogeneous slurry with mortar and pestle, and then the obtained slurry was casted onto copper current collector (18- μm -thick Cu foil; Kejing Group) using the doctor blade technique. The coating was dried at 120 $^\circ\text{C}$ under vacuum followed by roll pressing. The electrode was punched according to CR-2032 coin cell dimension. The active material loading is in the range of 0.30–0.35 mg cm^{-2} . The electrolyte consisted of a solution of 1 M LiPF_6 in EC/DEC (1:1 v/v) plus 1 wt% vinylene carbonate (VC) provided by Guangzhou Tinci Materials Technology Co. Ltd. Polypropylene (Celgard 2400) were utilized as separators and pure lithium metal foil was used as counter electrode. 2032 type coin cells were assembled in an argon-filled glovebox ($\text{O}_2 < 1 \text{ ppm}$, $\text{H}_2\text{O} < 1 \text{ ppm}$). The cells were tested on a multi-channel battery test system (NEWARE CT-3008) with galvanostatic charge and discharge in the voltage ranges of 0.01–1.0 V vs. Li^+/Li at room temperature. Electrochemical impedance spectral (EIS) measurements and cyclic voltammetry were recorded on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China). EIS tests were carried out with a small AC perturbation pulse of 5 mV and the frequency ranges between 100 KHz and 0.01 Hz.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the typical XRD patterns of the rGO-porous Si nanocomposite and pristine porous Si from rice husks. Both

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