



A two-dimensional nitrogen-rich carbon/silicon composite as high performance anode material for lithium ion batteries

Tiansheng Mu, Pengjian Zuo*, Shuaifeng Lou, Qingrui Pan, Qin Li, Chunyu Du, Yunzhi Gao, Xinqun Cheng, Yulin Ma, Geping Yin*

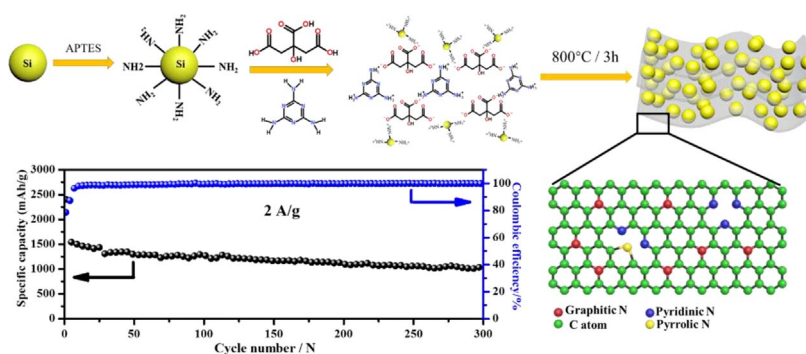
MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, Harbin Institute of Technology, Harbin 150001, China



HIGHLIGHTS

- NRC/Si composite is prepared through a facile self-assembly process.
- NRC/Si composite possesses a two-dimensional structure.
- Rich-nitrogen doping improves the electronic conductivity of the composites.
- NRC/Si anode exhibits high reversible capacity and excellent rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

The two-dimensional (2D) carbon material shows great superiority in improving the electrochemical performance of silicon-based anode for lithium ion batteries. We synthesize a nitrogen-rich carbon/silicon composite (NRC/Si) with a graphene-like structure by an amino-carboxyl self-assembly of the citric acid, melamine and Si-NH₂. The NRC/Si composite with a two-dimensional structure can effectively buffer the volume change of silicon material during cycling. Moreover, the rich-nitrogen doping improves the electronic conductivity and facilitates the charge transfer during charge and discharge process. The NRC/Si as anode material for lithium ion batteries shows good cycle stability and rate capability, delivering a reversible capacity of 1000 mA h g⁻¹ after 300 cycles at 2 A g⁻¹ and 572 mA h g⁻¹ even at 5 A g⁻¹, respectively. In addition, the synthesis method of the NRC/Si composite is cost-effective, environmentally friendly and industrially scalable, which makes it very promising to obtain the high-performance anode materials in lithium ion batteries.

1. Introduction

Lithium ion batteries (LIBs) are being applied as the dominating power sources for the portable communication devices, electric vehicles and smart grid systems [1,2]. The growing demands in high energy density, long cycle life and excellent rate capability stimulate the

development of high performance electrode materials for LIBs [3]. For traditional graphite anodes, the theoretical capacity is only 372 mA h g⁻¹, which severely limits the development of LIBs [4–8]. Silicon is one of the most promising anode materials due to its exceptionally high theoretical capacity of 4200 mA h g⁻¹, which is more than ten times higher than that of a commercial graphite [2,9].

* Corresponding author.

E-mail addresses: zuopj@hit.edu.cn (P. Zuo), yingeping@hit.edu.cn (G. Yin).

Additionally, natural abundance and comparable working potential with graphite further ensure the promising application of silicon-based anode materials [10]. However, silicon suffers from the low conductivity and the large volume change during the lithiation and delithiation process, resulting in the electrode pulverization and gradual loss of electric contact between active materials and current collector [11,12]. Moreover, the solid electrolyte interphase (SEI) is repeatedly formed on the exposed surface caused by the pulverization of active particles, leading to rapid consumption of electrolyte. All of these problems cause poor cycling and rate performance of silicon-based anode materials [13–16].

In the past decades, many efforts have been devoted to improving the electrochemical performance of silicon-based anode materials. Typically, a strategy is to reduce the particle size of silicon to nanoscale, which can release the structural stress caused by large volume changes [2,17]. Various nanostructured silicon materials have been successfully synthesized, such as nanowires [18,19], quantum dot [20], etc. However, the rate capability and cycling performance of nanostructured silicon materials are still not satisfied [21]. Great efforts have been made to prepare the nanocomposite of silicon with carbon [22], metallic oxide [23–25], etc. Thereinto, silicon/carbon composites have been widely studied due to their enhanced electrical conductivity and cycle stability. Various carbonaceous materials including amorphous carbon [26], carbon nanotube [27,28], graphene and graphene oxide [14,29–36], etc. have been employed for silicon/carbon anode composites. Graphene-based silicon/carbon composite shows the outstanding flexibility, electrical conductivity and excellent mechanical strength [36,37]. Guo et al. developed an electrostatic attraction self-assembly approach to fabricate a composite of silicon nanoparticles encapsulated into graphene [34]. Nitrogen-doping into carbon material can enhance the electrical conductivity and energy storage ability [38,39]. Therefore, encapsulating nano-silicon using nitrogen-doped graphene-based material will further improve the electrochemical performance of silicon/carbon composites. Chen et al. synthesized the silicon/nitrogen-doped graphene microspheres, which demonstrated a capacity retention of 96.1% after 150 cycles [40]. Compared to the graphene, the preparation of graphene-like carbon nanosheets is very facile and low-cost. Liu et al. reported a graphene-like silicon nanocomposites derived from a liquid polyacrylonitrile precursor, and the discharge capacity remained at 819 mA h g⁻¹ after 50 cycles [41]. The electrochemical performance of this kind of silicon anode material should be further improved to meet the practical application.

Herein, we report the 2D nitrogen-rich carbon/silicon (NRC/Si) composite via a facile self-assembly process. The obtained NRC/Si with a typical two-dimensional structure shows superior cycle performance and excellent rate capability. Typically, a high specific capacity of 1700 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ with the initial Coulombic efficiency of 75.3%, are achieved, and the composite can remain a reversible capacity of 1000 mA h g⁻¹ after 300 cycles at 2 A g⁻¹. In addition, the citric acid and melamine precursors are non-toxic, environment friendly and low-cost, and the synthesis strategy is very beneficial for the scalable fabrication of high-performance silicon-based anode materials for lithium ion batteries.

2. Experimental section

2.1. Material synthesis

2.1.1. Preparation of nano-Si-NH₂

The nano-Si-NH₂ was prepared according to the previously reported procedure [42]. 500 mg of nano-sized silicon powder (40–160 nm, Shanghai ST-NANO Science & Technology Co., Ltd., China) was firstly dispersed into 200 mL ethanol by 2 h sonication. Subsequently, 2 mL concentrated ammonia solution (25%wt) and 10 mL water were slowly added into the dispersion, and then 0.5 mL APTES was added immediately. The reaction was carried out at 25 °C with magnetic stirring

for 2 h. Nano-Si-NH₂ was collected by centrifugation, and it was washed several times by ethanol. The obtained nano-Si-NH₂ was dried at 40 °C for ten hours.

2.1.2. Preparation of NRC/Si

A certain amount of melamine was dissolved in 200 mL water at 100 °C. The solution was denoted as A. Citric acid was dissolved in 200 mL deionized water, and the molar ratio of melamine and citric acid used in the experiment is 3:1. Then 0.5 g nano-Si-NH₂ was dispersed into the citric acid solution by water bath sonication for 30 min. The obtained solution was denoted as B. The B was added dropwise into A, and the temperature of the solution decreased to room temperature gradually. The precursor was obtained by centrifugation after stirring for 24 h. The final product was obtained after the precursor was calcined at 800 °C for 3 h. Here, we performed two different proportions according to the weight of the raw materials. NRC/Si-1 was obtained using the 1.0 g citric acid and 1.9673 g melamine, and sample NRC/Si-2 was prepared by using 2.0 g citric acid and 3.9346 g melamine.

2.2. Characterization

The crystalline structures of the samples were obtained by X-ray powder diffractometer (Empyrean) using Cu-K α from 10° to 80°. X-ray photoelectron spectra (XPS) was carried out using a Physical Electronics PHI model 5700 instrument, and the C1s binding energy at 284.6 eV was used as a reference. Raman spectra were obtained by a Raman system (HR800, JY Company) with a 457.9 nm laser. The N₂ adsorption/desorption isotherms were performed using 3H-2000PS2 (Beishide Instrument Technology Co., Ltd), and the pore size distribution was calculated by the Barrett-Joyner-Halenda method. The I_D/I_G ratio was calculated by fitting the area ratio of the corresponding D-band and G-band. The weight content of silicon in the composite was determined from the weight loss curves measured under an air atmosphere on a thermogravimetric analysis (Netzsch STA449F3 Jupiter). The surface morphology and structure of the samples were studied by scanning electron microscopy (Helios Nanolab 600i) and transmission electron microscopy (Hitachi, Japan).

2.3. Electrochemical measurements

The working electrode was prepared by mixing 80 wt% active material, 10 wt% Super P and 10 wt% carboxymethyl cellulose (CMC) in aqueous solution. The resulting slurries were cast onto copper current collector, and then dried at 80 °C for 12 h. The areal loading of electrode active materials for each circular disk with 14 mm in diameter here is approximately 1.0 mg/cm². The specific capacity is based on the NRC/Si composite. The electrochemical tests were conducted by assembling coin-type half cells (CR2025) in an argon-filled glovebox. The liquid electrolyte was 1 M LiPF₆ dissolved in a 1:1:1 mixture of ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC), containing 10 wt% fluoroethylene carbonate (FEC). The galvanostatic charge and discharge tests were carried out by using the NEWARE-BTS-5 V/5 mA instrument (Neware Co., Ltd., Shenzhen, China) in a voltage range between 0.01 and 1.50 V. The cyclic voltammetry test was conducted using a CHI660D electrochemical workstation between 0.01 and 1.5 V at a scan rate of 0.1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was conducted by using a CHI660D electrochemical workstation in the frequency range from 0.01 Hz to 1 × 10⁵ Hz. All electrochemical experiments were done at room temperature. The electronic conductivity measurements were carried out on a SB120/2 Conductivity Meter (Shanghai Qianfeng Electronic Instrument Co., Ltd.) by a four-wire method. The samples were compressed into a cylinder with a radius of 15 mm and a height of 2 mm under a pressure of 10 MPa.

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