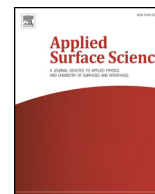




ELSEVIER

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Facile electrostatic self-assembly of silicon/reduced graphene oxide porous composite by silica assist as high performance anode for Li-ion battery

Ming-Shan Wang^{a,*}, Zhi-Qiang Wang^a, Ran Jia^a, Yi Yang^a, Fang-Yu Zhu^a, Zhen-Liang Yang^b, Yun Huang^a, Xing Li^{a,*}, Wu Xu^{c,*}

^a The Center of New Energy Materials and Technology, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu, Sichuan 610500, PR China

^b Institute of Materials, China Academy of Engineering Physics, Mianyang, Sichuan 621908, PR China

^c Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA

ARTICLE INFO

Keywords:

Silicon
Reduced graphene oxide
Electrostatic self-assembly
Silica
Lithium ion battery

ABSTRACT

Silicon(Si)/graphene composite has been regarded as one of the most promising candidates for next generation anode materials with high power and energy density in lithium ion batteries. Introduction of graphene in Si anodes could improve the electronic conductivity, suppress the severe volume expansion of Si, and facilitate the formation of stable solid electrolyte interphase, etc. However, traditionally mechanical mixing of Si and graphene cannot realize uniform distribution of Si particles on the graphene sheets, which would largely weaken the effectiveness of the graphene in the composite. In this work, nano-Si/reduced graphene oxide porous composite (p Si/rGO) has been fabricated by a facile electrostatic self-assembly approach via using SiO₂ as the sacrificial template. Compared with the simply mechanically mixed nano-Si and rGO (Si/rGO), the nano-Si particles could be more uniformly dispersed among the rGO sheets in the p Si/rGO, which significantly increases its electronic conductivity. Moreover, the drastic volume expansion of nano-Si during repeated lithiation/delithiation cycles also has been effectively accommodated by the large number of pores left after removing the SiO₂ template in the composite. Thus, the p Si/rGO presented largely enhanced electrochemical performances, showing a high reversible capacity up to 1849 mA h g⁻¹ at 0.2 A g⁻¹ with good capacity retention, and high rate capability (535 mA h g⁻¹ at 2 A g⁻¹).

1. Introduction

Since the commercialization in 1990s, Li-ion batteries (LIBs) have been extensively used in portable devices, electronic devices and electric vehicles due to their advantages of high energy density, long cycling performance, low self-discharge compared with other secondary batteries such as lead-acid batteries, nickel-cadmium batteries [1–4]. However, with the increasing demand for higher power and high energy density LIBs, the conventional graphite anode, on account of its low theoretical specific capacity (372 mA h g⁻¹), cannot meet the increasing requirement of markets [5–7]. Silicon (Si) and its composite materials have been considered as most promising anodes to replace the commercial graphite anode for next-generation LIBs. It is well known that Si anode has many significant advantages, such as ultrahigh theoretical specific capacity (4200 mA h g⁻¹), abundant availability, low working potential (0.2 V vs Li/Li⁺), environmental benignity [8–11]. However, the practical application of Si-based anodes is hindered by some intrinsic drawbacks, i.e., low electrical conductivity, huge volume

change (~300%), severe cracking and pulverization as well as unstable solid-electrolyte interphase (SEI) film during repeated electrochemical discharge/charge cycles [12–14]. In order to address these problems, the common strategies are combining Si with different kinds of carbon framework materials, such as amorphous carbon [15,16], conductive carbon black [17,18], carbon nanotube [19,20] and graphene [21–25]. According to the research results in recent years, it is commonly accepted that mixing Si with carbon materials could not only increase the conductivity but also accommodate its severe volume expansion, thus significantly improving its electrochemical performance. Among the carbon frameworks, the graphene with the advantages of excellent electronic conductivity, flexibility, high Li⁺ diffusion efficiency (10⁻⁸ cm² s⁻¹) as well as large theoretical specific area (2630 m² g⁻¹) has been recognized as an ideal carbon matrix to overcome the above mentioned drawbacks of Si anodes [26–29]. Nevertheless, there are still great challenges for the synthesis and application of the Si/Graphene composites. First, it is not easy to realize the uniform dispersion of Si particles on the surface of the graphene sheets [30–32], which is mainly

* Corresponding authors.

E-mail addresses: wangmingshan@swpu.edu.cn (M.-S. Wang), lixing@swpu.edu.cn (X. Li), wu.xu@pnnl.gov (W. Xu).

<https://doi.org/10.1016/j.apsusc.2018.06.147>

Received 3 April 2018; Received in revised form 18 May 2018; Accepted 16 June 2018

Available online 18 June 2018

0169-4332/ © 2018 Elsevier B.V. All rights reserved.

because they contain the functional groups with the same charge repelling each other and the intrinsic Van der Waals force results in the severe aggregation of them. Second, the improved electronic conductivity, the suppressed volume expansion, and the enhanced electrochemical performances of the Si electrode would not be efficiently presented if the Si particles are not uniformly dispersed on the graphene sheets with wrinkle structures [5,23].

In this paper, silica (SiO_2) has been chosen as a sacrificial template for fabricating porous nano-silicon/reduced graphene oxide (p Si/rGO) composite in water solution by a facile electrostatic self-assembly technology. The nano-Si particles coated with a SiO_2 layer were firstly synthesized by hydrolysis of ethyl silicate. Then, the outer SiO_2 layer was further modified through grafting it with amidogen groups ($-\text{NH}_2$). As a result, the $-\text{NH}_2$ modified Si/ SiO_2 (with positive charges) could easily self-assemble with graphene oxide (GO, with negative charges) via electrostatic interactions in the aqueous solution. Finally, the p Si/rGO composite with porous microstructures and uniformly distributed Si nano particles on the wrinkle graphene sheets was obtained through freezing dry, heating treatment in argon (Ar) atmosphere and washing with HF solution step by step. The structure, electrochemical performance, and the related fundamental mechanism of the p Si/rGO composite anode were systematically investigated in this work. As a comparison, the simply mechanical mixing of nano-Si and rGO (Si/rGO) sample was also prepared and studied.

2. Experimental section

2.1. Materials

Si nanoparticles (Si NPs, average diameter ~ 50 nm) were purchased from Xuzhou Jiechuang New Material Technology Co., LTO (China). Graphene oxide powder (thickness 0.55–3.58 nm, purity > 99 wt%, layer number < 10 , size > 5 μm) was supplied by Da Ying Ju Neng Technology and Development Co., Ltd. (China). Tetraethyl orthosilicate (TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$), ammonia solution (NH_3 content 25–28% by wt.), cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$, $> 99.0\%$) and hydrofluoric acid (HF, $> 40\%$, AR) were purchased from Chengdu Kelong Chemical Reagent Factory (China). All the materials were used without further purification.

2.2. Synthesis of $-\text{NH}_2$ modified Si/ SiO_2

The purchased Si NPs were first washed by HF solution (5 wt%) for 5 min to remove the oxide layer. Then 0.4 g newly washed Si powder, 0.25 g CTAB and 3.65 g ammonia solution (25–28 wt%) were successively dispersed into a mixture of 80 g H_2O and 235 g ethanol by stirring and sonification. After that, another mixture including 1.495 g TEOS and 15 g ethanol was dropwise added into the above mixed solution under vigorously stirring. After stirring for 8 h, the Si/CTAB/ $\text{SiO}_2\text{-NH}_2$ was obtained by filtrating the above mixture and drying at

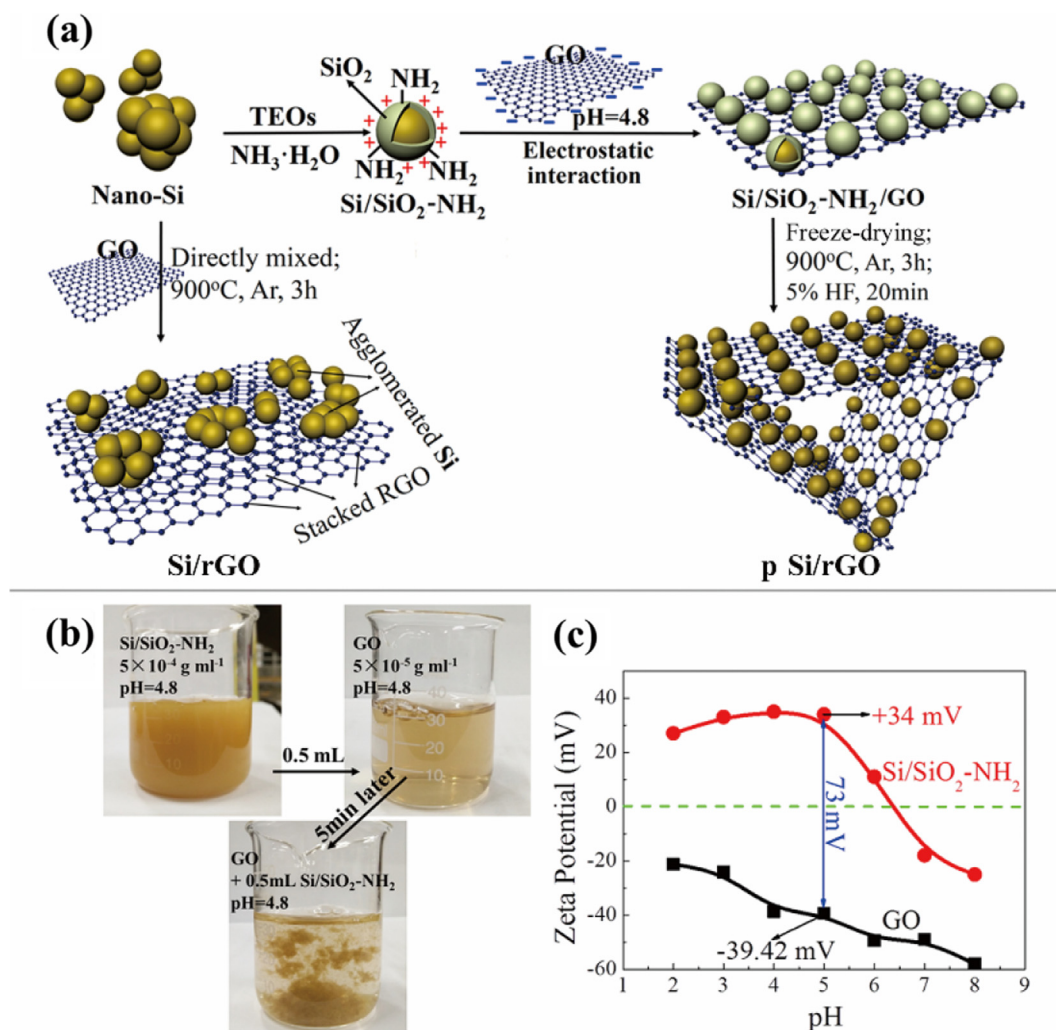


Fig. 1. (a) Schematic illustration of preparation of p Si/rGO and Si/rGO. (b) Photographs of GO solution, $\text{Si/SiO}_2\text{-NH}_2$ solution and the mixed of $\text{Si/SiO}_2\text{-NH}_2/\text{GO}$ solution at pH = 4.8. (c) Zeta potential of GO and $\text{Si/SiO}_2\text{-NH}_2$ solution under different pH values.

Download English Version:

<https://daneshyari.com/en/article/7833106>

Download Persian Version:

<https://daneshyari.com/article/7833106>

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