



In situ growth of Si nanowires on graphene sheets for Li-ion storage

Ziyang Lu^a, Jixin Zhu^a, Daohao Sim^a, Wenhui Shi^a, Yee Yan Tay^a, Jan Ma^a, Huey Hoon Hng^{a,**}, Qingyu Yan^{a,b,c,*}

^a School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

^b Energy Research Institute@NTU, Nanyang Technological University, Singapore 637459, Singapore

^c TUM CREATE Centre for Electromobility@NTU, Singapore 637459, Singapore

ARTICLE INFO

Article history:

Received 20 January 2012

Received in revised form 14 April 2012

Accepted 14 April 2012

Available online 20 April 2012

Keywords:

Li ion battery
Graphene oxides
Si nanocrystals

ABSTRACT

Si nanowires in graphene papers were successfully prepared by supercritical fluid–liquid–solid (SFLS) process, which showed high specific capacities and charge–discharge cycling stability as anode materials for Li-ion storage. The enhancement on capacity and cycling stability of the Si/graphene composite nanostructures was attributed to the presence of graphene papers in the hybrid samples that served as a highly conductive framework and absorption of volume changes of Si nanowires during the lithiation/delithiation process. This Si/graphene electrodes maintained reversible capacities of 1400 mAh g⁻¹ for the 30th cycle at a current density of 420 mA g⁻¹, which is much better as compared to that of pure Si nanowires.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Research in alternative energy sources and solutions for energy management have attracted much attention in recent years. This is due to issues including increased demands for energy coupled with rapid depletion of fossil fuels. Many efforts have been devoted to energy conversion devices [1–3] and energy storage devices [4–6]. Among them, lithium ion battery (LIB) is widely used as the power source for portable electronics [7,8]. There are numerous research efforts towards cost-effective and high-performance electrode materials [9–13]. Among the many candidate materials, silicon has received extensive attention as a promising anode material because it has the highest known theoretical capacity (4200 mAh g⁻¹ for Li₂₂Si₅) and it is highly abundant [14–18]. However, the large volume swings of 360% during the lithiation process cause the loss of electrical contacts between the silicon electrodes and the current collectors, which eventually leads to fast capacity fading [19]. In order to solve this issue, many silicon nanostructures have been prepared by various synthesis techniques [11,20], e.g., vertically aligned Si nanowires by CVD process [18], nest-like Si nanospheres were prepared via a solvothermal route [21], Si nanowires were synthesized by supercritical

fluid–liquid–solid (SFLS) process [18,22,23], and nanotubes were fabricated by reductive decomposition of silicon precursors on templates [24]. These silicon nanostructures showed high capacities and improved cycling stabilities.

Recently, it has been reported that the stability of the silicon electrode can also be improved by combining the silicon nanostructures with carbon materials due to their high conductivity and large surface area [25–33]. Graphene, a single layer of carbon atoms, attracted great attentions due to its high electrical/thermal conductivity [34–38], great mechanical strength [39] and large specific surface area [40,41]. Silicon nanoparticles have been successfully attached on graphene sheets by thermal treatment of mixture of commercial silicon nanoparticles and graphene oxides [32]. Silicon nanowires were reported as a high capacity anode material because of its large surface-to-volume ratio [18,22,23]. However, it is still a challenge to combine the silicon nanowires, which is not commercially available, with graphene sheets. In this paper, we report the in situ growth of silicon nanowires (Si NWs) onto graphene sheets as anode materials for Li-ion storage, which showed improved specific capacities and charge–discharge cycling stability as compared to that of pure Si NWs.

2. Experimental

2.1. Preparation

Graphene oxide (GO) sheets were prepared by a modified Hummer's method [42]. Firstly, a mixture of graphite (1 g), concentrated H₂SO₄ (6 ml, 98%), K₂S₂O₈ (2 g) and P₂O₅ (2 g) was heated at 80 °C

* Corresponding author at: School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. Tel.: +65 6790 4583; fax: +65 6790 9081.

** Corresponding author. Tel.: +65 6790 4583; fax: +65 6790 9081.

E-mail addresses: ASHHHng@ntu.edu.sg (H.H. Hng), AlexYan@ntu.edu.sg (Q. Yan).

for 5 h by a hotplate. And then it was cooled to room temperature and diluted with 200 ml water. After removed the acid by filtration and washing with water, this pre-oxide graphite was dried in vacuum oven at room temperature. The pre-oxide graphite and 60 ml H_2SO_4 (98%) were put into a 500-ml flask in an ice-water bath. And then 8 g KMnO_4 was added into the flask and the temperature of the water bath was increased to 35°C and standing for 2 h. After the mixture was diluted with 250 ml water, 20 ml H_2O_2 was added into the flask. The solution was turned to yellow. The resulted graphite oxide was washed by HCl aqueous (1:10) to remove the acid and metal ions. Finally the GO sheets were obtained by exfoliating the graphite oxide with the ultrasonic.

Gold nanoparticles were synthesized by sodium citrate reduction of HAuCl_4 . 100 ml of aqueous solution of 1 mM HAuCl_4 was brought to boiling under magnetic stirring. Then 2 ml solution of 5% tri-sodium citrate was added and the solution was kept on boiling for 15 min. The gold nanoparticles were washed with water by centrifugation and then dispersed in water.

To get gold nanoparticles on GO sheets, 10 ml gold nanoparticles, 0.2 mg GO sheets were mixed together. The pH value of the mixture was adjusted to 4 by HNO_3 aqueous and standing for 2 h. And then the pH value was further adjusted to 2 to sediment down the composite on a glass substrate and then dried in an oven.

Si NWs were synthesized by thermally degrading diphenylsilane (DPS) in hexane at 360°C . The glass substrate with gold/GO composite was put into the reactor, and then 20 ml hexane and 100 μl diphenylsilane were added. The temperature was increased to 360°C by the rate of $10^\circ\text{C}/\text{min}$ and stand for 2 h. After cooling down, the glass substrate was rinsed with hexane and annealed at 650°C in a tube furnace with the Ar protection. The Si NWs/graphene was cut off from the glass substrate as active materials for battery electrodes.

2.2. Characterization

Zeta-potential of the GO sheets were measured with a Zeta sizer apparatus (Malven). Fourier transform infrared (FTIR) spectra were measured in the wavenumber range of $4000\text{--}450\text{ cm}^{-1}$ at a resolution of 2 cm^{-1} by using a Perkin-Elmer Spectrum One FTIR spectrophotometer. Raman spectra were recorded on WITec confocal Raman microscopy that used a 633 nm HeNe laser. Transmission electron microscopic (TEM) observations were carried out under a JEOL-2010 electron microscope after the dilute dispersions of the particles were dropped onto carbon coated copper grids. The morphologies of the composites were investigated by using a JEOL JEM-7600F field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) patterns were acquired on a Shimadzu X-ray diffractometer ($\text{Cu K}\alpha$). Electrochemical experiments were performed by assembling two-electrode coin cells in an argon-filled glove box with Li foil as the counter electrode and 1 M LiPF_6 in EC/DEC as the electrolyte similar as previous reports [43]. The electrodes were prepared by mixing 80 wt% of the active materials, 10 wt% of Super P carbon black and 10 wt% of poly(vinylidene fluoride) binder and then coating on copper foil. The obtained electrodes were dried under vacuum at 50°C for 12 h. The cells were charged and discharged within the voltage window from 0.005 V to 1.5 V. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) analysis were performed with an electrochemical workstation (CHI 660C).

3. Results and discussion

AFM measurement showed (see Fig. 1) that the GO sheets were micro-scale size with a thickness of $\sim 0.9\text{ nm}$, indicating the single layered GO sheets were obtained. Electrophoresis measurements

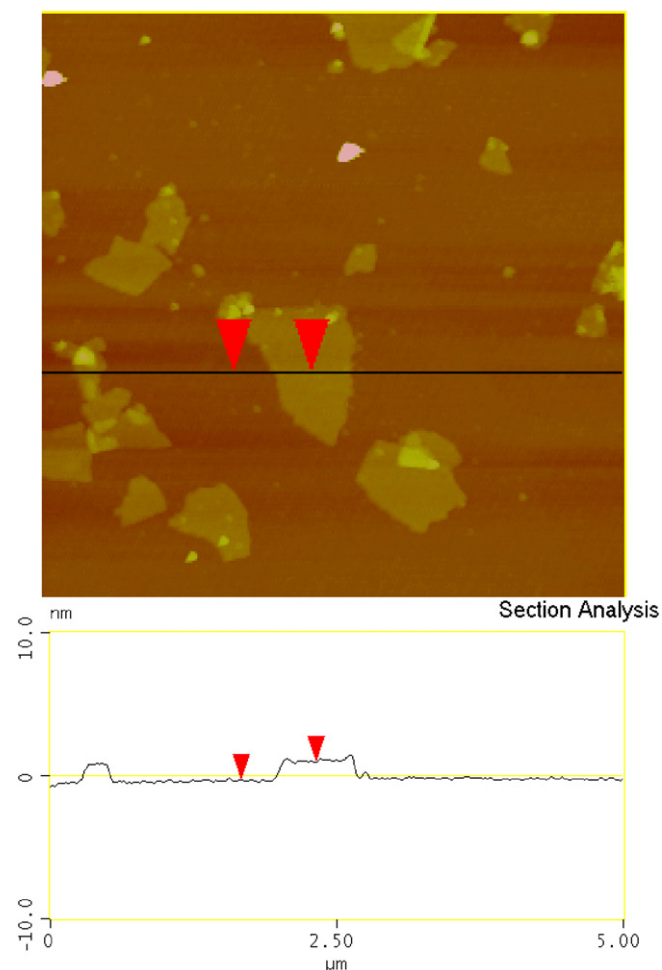


Fig. 1. AFM of a GO sheet and line profile along the black line.

were used to evaluate the surface properties of the gold nanoparticles and GO sheets (see Fig. 2a). In the pH range of 3–6, the zeta-potential of the gold nanoparticles showed negative values and the absolute values increased with the pH value, which could be attributed to the transformation of COOH to COO^- in the surface citrate ligand. At $\text{pH} = 3$ the gold nanoparticles are not colloidal stable and aggregate slowly forming blue flocs after 1 h. The zeta potential of the GO sheets was also negative in the measured pH range of 2.5–9.5, which became more negative at higher pH values.

The presence of sulfonic, carboxyl and hydroxyl groups on GO sheets were confirmed by FTIR measurements (see Fig. 2b). The FTIR spectrum of GO sheets showed characteristic absorption peaks corresponding to the $\text{C}=\text{O}$ carbonyl stretching vibration at 1731 cm^{-1} , the $\text{C}=\text{C}$ stretching at 1622 cm^{-1} , the $\text{C}-\text{OH}$ stretching at 1224 cm^{-1} , the $\text{C}-\text{O}$ stretching at 1051 cm^{-1} , and the sulfonic stretching at 1170 cm^{-1} [44,45]. Here, the sulfonic group on the GO sheets is believed to maintain the GOs sheet colloidal stable in a wide range of pH values [46], which is important for the Au nanoparticle attachment.

The attachment of the Au nanoparticles onto the GO sheets was highly sensitive to the pH value. It was indicated that at $\text{pH} > 6$, mixing Au nanoparticles with GO sheets in the aqueous solution resulted in no attachment of Au particles on the GO sheets. This is attributed to the strong electrostatic repulsion between the gold nanoparticles and GO sheets due to their high negative surface potential. At lower pH value of 4, the attachment of the Au nanoparticles onto GO sheets was successful (see Fig. 3a) due to that the surface potentials of both became less negative, which led to less

Download English Version:

<https://daneshyari.com/en/article/188568>

Download Persian Version:

<https://daneshyari.com/article/188568>

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