Enhanced electrochemical performances of silicon nanotube bundles anode coated with graphene layers

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A B S T R A C T

Significant enhancement in electrochemical performances has been achieved in silicon nanotube bundles (Si NBs) via coating with graphene layers (denoted as Si NBs@G), which could be a promising anode material in Li-ions batteries. The synthesized Si NBs@G have tubular structure with a diameter of around 200 nm and a thickness about 80 nm and the tube walls are composed of Si nanocrystals with a size about several nanometers. Galvanostatic charge-discharge measurements showed that the Si NBs@G displayed gradual increasing in capacity after first 100 cycles and finally reached a capacity of $\sim$765 mAh g^{-1} at 600 cycles, which was almost fivefold the capacity of the parent Si NBs without graphene coating. The graphene outerlayer is considered to serve as the mechanical protecting layer to enhance structural sustainability of Si NBs anode by forming stable solid electrolyte interface. In addition, the formation of Li-rich Li$_{15}$Si$_4$ crystallites also contributes to the capacity improvement.

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1. Introduction

Battery demands for transport and grid applications are expected to be boosted in the years to come [1]. Of all batteries, high energy lithium ion batteries are promising for consumer electronics, electric-drive vehicles and grid-scale stationary energy storage [2]. Silicon has been considered to be an attractive alloy-type anode material because of its highest known theoretical capacity of 4200 mAh g^{-1} with the formation of Li$_{4.4}$Si alloy [3], which is ten times higher than that of traditional graphite anode [4]. Unfortunately, utilization of silicon-containing anode materials for lithium-ion batteries is usually limited by manufacturing cost, their intrinsic low electric conductivity, and serious volume changes during cycling [5]. In recent years, various approaches have been employed to overcome the limitations of silicon materials. Nanostructured silicon ranging from nanowires, nanofilms, nanotubes to nanoparticles and their composites, in which the strain can be relaxed easily without mechanical fracture because of their smaller size and available surrounding free spaces, have been exploited widely to alleviate the structure deterioration efficiently [6–10]. Si nanotube bundles (NBs) have been successfully synthesized at large scale in our previous work [11] via a

magnesiothermic reduction method [12]. However, structural collapse still occurred during prolonged electrochemical reactions for these long Si tubes with length larger than several micrometers, hence resulting in unsatisfactory electrochemical performances. Recent work by Wu et al. developed a smart way to preserve the low dimensional morphology of Si via coating the tubes with amorphous SiO$_2$ layer, which served as a mechanical protecting layer helping to form stable solid electrolyte interphase (SEI), thus giving rise to better cycle performance [13].

In the present study, strong and Li acceptable graphene layers were coated on Si NBs aiming to improve the structural sustainability and electrochemical performances. X-ray diffractometry (XRD), Raman spectrometry, scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) were employed to investigate the structure and morphology of the as-prepared Si NBs@G as well as the structural evolution after cycling in cell. Electrochemical performances of Si NBs@G served as anode materials were investigated with comparison to the parent Si NBs.

2. Experimental

2.1. Sample preparation

The synthetic processes of Si NBs@G were illustrated schematically in Fig. 1. We used the hydroxylapaptite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, HAP) nanobelt bundles as sacrificial templates, which were
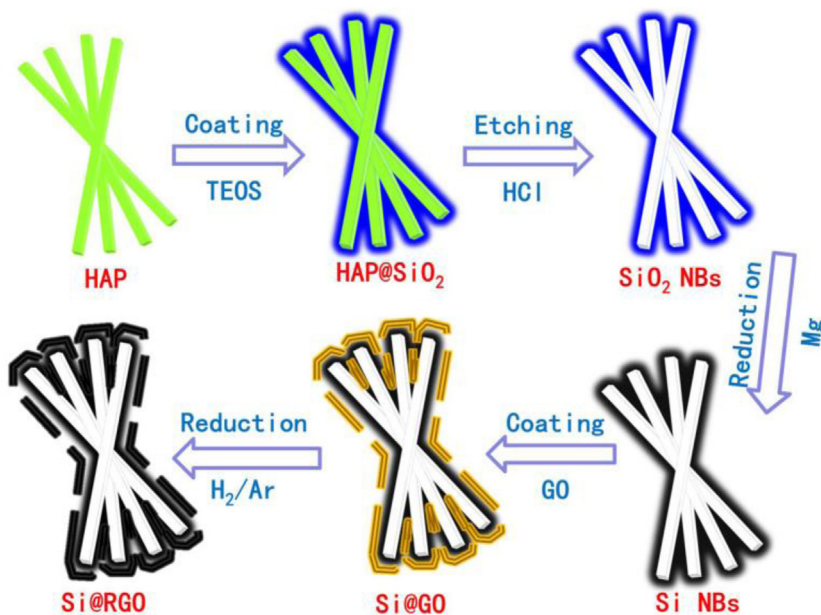
Fig. 1. Schematic illustration of the synthetic routes for Si NBs@G. HAP NBs were used as sacrificial templates, then silica was coated on the HAP NBs to form HAP@SiO₂. SiO₂ NBs were obtained after etching of HAP NBs, magnesiothermic reduction was then applied to convert SiO₂ NBs to Si NBs. on Si NBs. Finally, graphene oxide layers were coated on Si NBs and reduced to from Si NBs@G.

prepared by a hydrothermal method. Then silica was coated on the HAP NBs(indexed as HAP@SiO₂). After etching of HAP cores by HCl solution, SiO₂ NBs were obtained, followed by a magnesiothermic reduction (using Mg metals as reductant) to convert SiO₂ NBs to Si NBs. Si NBs were then treated with (3-aminopropyl)-triethoxysilane (APTES) to fabricate graphene oxide layers on Si NBs. Finally, graphene layers coated Si NBs can be obtained after reduction treatment using H₂/Ar. The experimental details of each step were described as following.

Details of synthesis of Si NBs have been reported elsewhere[11]. Typically, HAP nanobelt bundles were prepared by adding NaH₂PO₄·H₂O and CaCl₂ one after another to the solution composed of polyethyleneimine, maleic acid and urea, followed by thermal treatment at 120 °C for 2 days. HAP@SiO₂ core–shell composites were synthesized using tetraethoxysilane (TEOS) as source material. After removing the HAP template by 1 M HCl solution, the as-obtained SiO₂ NBs were finally converted to Si NBs through magnesiothermic reduction at 650 °C for 2 h using magnesium powders (molar ratio of Mg to Si was 2:1).

The graphene oxide (GO) was prepared by a modified Hummers method[14]. 1 g graphite powders and 0.8 g NaNO₃ were added to 23 mL concentrated H₂SO₄. Then, 3 g KMnO₄ was added gradually with stirring in an ice–water bath and the mixture was further stirred at room temperature for 5 days. The solution was diluted by 200 mL distilled water, during which the temperature of the solution was increased up to 98 °C. After staying for 15 min, 10 mL of 30% H₂O₂ was added to the solution, leading to the formation of GO plates. The products were then centrifuged and washed with 5% HCl solution, distilled water and ethanol for several times. Finally, the dark brown GO plates were dispersed in ethanol for further use.

APTES was used as coupling reagent for the fabrication of graphene layers on Si NBs according to others references [15,16]. Si NBs (0.2 g) and APTES (2 mL) were mixed in ethanol (30 mL) and stirred overnight. After filtration, the pretreated Si NBs were mixed with certain amount of GO solution (mass ratio Si: GO = 1:0.3) in ethanol under ultrasound and stirring at room

temperature for 3 h. Thereafter, the mixed solution was transferred to an agate mortar placed on an 80 °C heating platform. The moderate heating associated with gentle lapping using an agate pestle could eventually remove the ethanol in the solution, and thus Si NBs@GO powders were obtained. Finally, the Si NBs@GO was reduced by Ar/H₂ gas (600 °C overnight) to form Si NBs @G.

2.2. Structural and morphological characterization

The crystal structure and the phase purity of as-prepared Si NBs and Si NBs@G samples were examined using powder X-ray diffractometer (XRD Ultima IV) with Cu$_{K\alpha}$ radiation operating at 40 kV and 40 mA. Raman spectrum was obtained using a THERMO FISHER DXR micro-Raman spectrometer with an excitation wavelength of 532 nm. Microstructures were measured by TEM (JEOL 2100F) and SEM (Hitachi S4800) both equipped with Oxford energy disperse spectroscopy (EDS) system. FEI Tecnai G2 F20 TEM equipped with a Gatan Enfina spectrometer was used to perform electron energy-loss spectrometry (EELS) analysis.

2.3. Electrochemical evaluations

The electrodes were prepared by mixing of Si NBs@G active material, acetylene black and polyvinylidene fluride (PVDF) binder (the mass ratio was 7:2:1) to form slurry in N-methyl-2-pyrrolidone (NMP). The slurry was then cast on a Cu foil and a doctor blade with a gap opening of 120 μm was used to define the maximum thickness of the casted layer. The film was dried at 80 °C in vacuum, followed by compressing under 10 MPa pressure before assembling. The cells were assembled in an argon-filled glovebox with the concentrations of moisture and oxygen below 1 ppm. The electrolyte used was 1 M LiPF₆ in a 50:50 mass ratio ethylene carbonate (EC):dimethyl carbonate (DMC) solvent. Electrochemical investigations were conducted using a CT 2001 battery tester. Cyclic voltammetry (CV) was carried out in a voltage range of 0–1.5 V with a scan rate of 0.5 mV s⁻¹. All of the electrochemical