Binder-free Si nanoparticles@carbon nanofiber fabric as energy storage material

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ABSTRACT

A nonwoven nanofiber fabric with paper-like qualities composed of Si nanoparticles and carbon as binder-free anode electrode is reported. The nanofiber fabrics are prepared by convenient electrospinning technique, in which, the Si nanoparticles are uniformly confined in the carbon nanofibers. The high strength and flexibility of the nanofiber fabrics are beneficial for alleviating the structural deformation and facilitating ion transports throughout the whole composited electrodes. Due to the absence of binder, the less weight, higher energy density, and excellent electrical conductivity anodes can be attained. These traits make the composited nanofiber fabrics excellent used as a binder-free, mechanically flexible, high energy storage anode material in the next generation of rechargeable lithium ions batteries.

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1. Introduction

The development of lightweight, long-lasting lithium-ion batteries is of great technological importance for critical applications, such as portable electronic devices, low- or zero-emission hybrid electrical and electrical vehicles [1–6]. Increasing the specific capacity of lithium-ion battery anodes is considered an attractive route to lower battery weight and volume [7–12]. The low discharge potential and high theoretical capacity of Si has triggered significant research efforts on Si-based anodes [13,14]. Unfortunately, the practical application of silicon as anode material is seriously hampered by the low intrinsic electric conductivity and large volume changes during lithium insertion and extraction, and this result in dramatic pulverization of silicon particles and electrical disconnection from the current collector, leading to rapid capacity fading upon cycling [15]. Versatile strategies have been developed to circumvent these drawbacks. So, one of the challenges associated with the use of high-capacity Si anodes is how to increase capacity retention with long-time battery cycling [7,16].

As is well known, in lithium-ion battery anodes, particles of the active material are held together by polymeric binders, which

are electrochemically inactive and commonly required to provide mechanical connections among active materials, conductive additives. The insulating binders reduce the overall energy density by adding weight to the electrodes and lead to poor electron transfer on cycling [17,18]. Thus, the elimination of binders will be an alternative approach to improve Si anodes performance. Hitherto, various efforts have been made to obtain binder-free Si composited nanostructure electrodes. For example, a fabric Si@C composited nanowires has been successfully synthesized by super critical-fluid-liquid-solid (SFLS) process [19]. Si nanoparticle-decorated Si nanowire networks as binder-free electrodes have been reported [20], where Si nanoparticles electrically contact with current collectors via vertically grown silicon nanowires. And Si-graphene paper composites prepared by vacuum filtration method [21,22] or plasma-enhanced chemical vapor deposition (PECVD) method [23]. However, these methods require costly specific equipment and multi-step operations, or even employ dangerous reaction conditions. At the same time, scale-up and industrial implementation of these Si nanostructures still lag behind and further improvements in overall performance, scalability, and the reduction of cost are considerably required.

Considering the shortcomings aforementioned, herein, we use a conventional electrospinning technique to develop Si nanoparticles and carbon composited nanofibers fabric for binder-free anode electrodes. Albeit–Zhang [24–26] and Chen [27] have fabricated
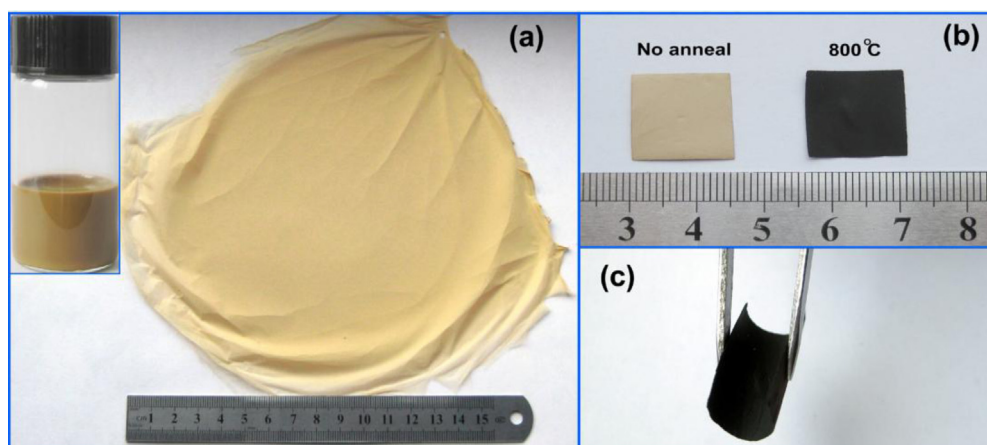
Fig. 1. (a) Photograph of SiNPs@PAN nanofiber fabric and the inset is the homogeneous SiNPs/PAN electrospinning solution. (b) As-prepared SiNPs@PAN and SiNPs@C (annealed at 800 °C under a reducing atmosphere) nanofiber fabrics, respectively. (c) The mechanically flexible Si-NPs@C nanofiber fabrics.

Si@C composited nanofibers, yet the tedious metal current collector or polymer binder were introduced into their half cells, significantly reduce the energy density and intrinsic electric conductivity. These defects result in the ultimate capacity decay and limit the development of innovative and facile techniques for preparing advanced binder-free flexible robust material for next generation lithium ion battery.

For our composited nanofiber fabrics, the carbon component act not only as a compromiser facilitating electron percolation against the low intrinsic electric conductivity of active Si nanoparticles but also serve as structure cushion to alleviate the dramatic volume expansion. As there is no binder in the electrodes, the compact lithium ion batteries with less weight and higher energy density can be achieved. Moreover, Si nanoparticles are uniformly distributed in the highly conductive carbon network, assuring all the Si nanoparticles can participate in the lithiation/delithiation process and preventing the Si nanoparticles from agglomerating thus further preserve the morphology integrity, avoiding the general pronounced capacity fading. In the last, the continuous nanofibers construct three-dimensional scaffold architecture, rendering a well-developed porous structure with high mechanical strength and superior flexibility. The porous structure can efficiently facilitate electrolyte infiltration and faster ion transport throughout the whole electrodes. These traits make the Si nanoparticles@carbon nanofiber fabrics can be served as a binder-free, mechanically flexible, high energy storage anode material in the next generation of rechargeable lithium ions batteries.

2. Experimental

Si nanoparticles with sizes ∼50 nm and polyacrylonitrile (PAN) with a large molecular weight of 150,000 were purchased from Sigma–Aldrich Chemical Company Inc (United States), N,N-dimethylformamide (DMF) from Xi Long Chemical Company Inc (China), Sodium dodecylbenzenesulfonate (SDBS) from Sinopharm Chemical Reagent Co., Ltd (China). All these chemicals were used as received without any further purification. First, the Si Nanoparticles were dispersed in DMF solution with 1% by weight SDBS as a surfactant under super ultrasonic treatment. Then, a homogenous yellowish dispersion solution was received. Second, a certain scale of PAN (Si:PAN ∼7:13 in wt%) mix with the received homogeneous solution together, and under constant mechanical stirring for 24 h, followed by super ultrasonic treatment for 2 h. Finally, a yellow viscous well-distributed solution of Si nanoparticles/PAN was obtained, which is presented in the inset image of Fig. 1. The

dispersion concentration of Si nanoparticles is about 10 mg mL^{-1} and the solution can stable for several months but not sediment.

The precursor solution was then delivered into the metallic needle, which was clamped by a programmable syringe pump for electrospinning. A high voltage power supply (about 15 KV) was connected to the metallic needle, and an aluminum foil as the grounded collecting screen was placed ∼15 cm to the needle tip. A constant flow rate of 0.5 mL h^{-1}, and the precursor solution was jetted toward the aluminum foil form Si nanoparticles@PAN nanofibers. At last, the dense composited nanofiber fabric was collected on the target, as shown in Fig. 1a. The obtained nanofibers fabric was torn down from the aluminum foil, and be cut with razor-blade into 1.5 cm × 1.5 cm platelet. To obtain the carbonized composited nanofiber fabrics, the platelet were heated in a tube furnace at 800 °C for 2 h under the flowing gas (5% hydrogen and 95% argon) environment.

SEM characterization SEM (LEO 1550 Gemini), and a transmission electron microcopy (HRTEM, JEOL, 2100) was used to observe the as-prepared Si Nanoparticles@C nanofiber. Raman spectrum was tested using a Renishaw inVia microscope Raman system with a laser operating at λ = 633 nm as excitation source. Thermogravimetric analysis (NETZSCH, TG209F3) was employed to calculate the mass content of Si in the composite.

For the electrochemical characterization, standard CR2032 coin cells were assembled in an Ar-filled glove box (Mikrouna, China). The Si nanoparticles@C composited nanofiber fabrics were used as working electrode without any conducting material, binding agent and metal current collector. The electrolyte was 1.0 M LiPF$_6$ in solution of 1:1 (w/w) ethylene carbonate: diethyl carbonate (Novolyte Technologies). Discharge/charge capacity of the fabricated electrodes was determined by galvanostatic cycling the half cells over the potential range between 0.01 V and 1.5 V in a battery tester (NEWARE BTS-5V 5 mA, Neware Technology Co., Ltd, China). Cyclic Voltammetry curves were scanned using an electrochemistry workstation (Chen Hua Shanghai Corp., China).

3. Results and discussion

Fig. 1a shows photograph of Si nanoparticles@PAN fabric over 150 cm^2 produced by electrospinning. It is a facile method to yield high output, which can be freely controlled according to our requirement. The pale yellow of as-prepared nanofiber fabric is attributed to the Si nanoparticles homogeneously distributed in the PAN precursor electrospinning solution, as shown in the inset of Fig. 1a. After annealing at 800 °C under a reducing atmosphere, the