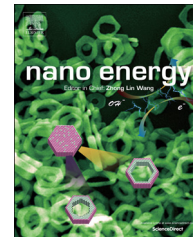


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RAPID COMMUNICATION

Encapsulated within graphene shell silicon nanoparticles anchored on vertically aligned graphene trees as lithium ion battery anodes

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Abstract

Silicon has been regarded as one of the most promising anode material for the next generation lithium ion battery. Unfortunately, the structure damage caused by the volume change of silicon and the continual interfacial reaction due to the electrolyte remain two major challenges. Here, we design a novel kind of *in-situ* growth binder-free silicon-based anodes. The adaptable silicon nanoparticles were encapsulated in graphene nanosheets (SiNPs@GNS). Simultaneously, the SiNPs@GNS composites anchored on vertically aligned graphene trees with loose intersecting leaves (GrTr). In the resulting samples, the GNS shells, as adaptable sealed wraps, could synergistically accommodate the volume change of the wrapped SiNPs, thus effectively avoiding the direct contact between encapsulated silicon and the electrolyte and enabling the interfacial and structural stabilization of encapsulated SiNPs during cycling. The GrTrs directly grown on current collector act as supporters of SiNPs, which ensure their dispersion uniformity and supply three dimensional short transportation paths for both Li ions and electrons. The *in-situ* growth of SiNPs@GNS-GrTr composites were proximately used as anodes in LIBs without adhesives and other complex brushing processes of the active material. The composite material exhibits a high capacity (1528 mAh g⁻¹ at 150 mA/g), relatively good cycle stability (88.6% after 50 cycles), and fast charge/discharge rate (412 mAh g⁻¹ at 8 A/g). The uniquely designed structure of the composites, which provide an ultra-thin, flexible GNS shell to accommodate the changes in volume, introduces large efficient areas, good

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conductivity, three dimensional transportation paths for both Li ions and electrons, and contributes to its excellent performance.

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Introduction

Rechargeable lithium ion battery (LIB) was the main power source for automotive and stationary energy storage devices from small-scale portable electronic devices to large-scale electric vehicles [1-4]. High energy density, excellent cycling stability and long cycle life are appreciated factors for the commercial applications of LIB. From the viewpoint of electrode materials, Silicon (Si) has attracted significant attention as a promising anode material for the following reasons. First, Si has the highest theoretical gravimetric $\sim 4200 \text{ mAh g}^{-1}$ (lithiated to $\text{Li}_{4.4}\text{Si}$), volumetric capacity $\sim 9786 \text{ mAh/cm}^3$ (based on the initial volume of silicon) [5,6] and relatively low discharge voltage platform (below 0.4 V) [7]. Second, Si is the second most abundant element in the earth's crust (about 28% calculated by mass) and is a kind of environmentally benign material. Unfortunately, the bottleneck for the commercial applications of Si is its dramatic volume change (greater than 300%) that commonly occurs during the lithiation and delithiation process [8]. Two effects that could result in degradation performance of Si will appear once the ceaseless volume change occurs [5,9-11]: (1) severe disintegration of electrode structure and the subsequent electrical disconnection from current collector, which usually cause the capacity fading and unstable cycle capability. (2) Solid electrolyte interphase (SEI) layers will continually form on the surface of pulverized Silicon, which increases the intrinsic resistance step-by-step and the coulomb efficiency decreased gradually [12].

Based on the context above, lots of efforts center on the stabilizing of Si structures and isolating the active material of Si from electrolyte have been attempted. Different designs reported in the previous studies can be classified into three main groups: (1) proceeding from stabilizing of Si structures, active materials were prepared into nanostructures, such as Si nanoparticles [13-16], Si nanowires [17-19], Si nanotubes [6,20,21] and porous silicon frameworks [22,23] to improve the cycling performance and effectively reduce fracture. In this way, the volume expansion could be accommodated in some extent. The electrical contact between the active material and the current collector was guaranteed. However, the surfaces of silicon nanostructures are still directly exposed to the electrolyte, and thus the continual formation of unstable SEI film remains a problem. (2) Proceeding from isolating the active material of Si from electrolyte, wrapping of Si nanostructures with a thin light layer is further considered one of the most promising solutions to both of the challenges. Wrapping materials commonly used includes metal, metal oxide and amorphous carbon, such as Al_2O_3 -coated Cu-Si nanocable arrays [24], SiO_x -Si nanotubes [6], amorphous carbon-coated Si nanowires [19,25,26], Si nanotubes [21], Si particles [13,14,27,28], amorphous carbon shell-sheltered Si yolks [29], carbon nanofiber-protected Si nanoparticles [27], polymer-coated Si nanowires

[25] and N-doped graphitic layer-sheathed Si nanowires [25], graphene wrapped silicon nano-wire paper [9]. Most of the designs demonstrate good electrochemical properties. However, some of the coatings will easily fracture if the void space for volume expansion was not enough or the coatings were nonelastic, namely, the inside active materials will in-turn contact with electrolyte. Based on the above discussions, graphene with good elasticity, superior electrical conductivity and exceptionally high surface area ($> 2600 \text{ m}^2/\text{g}$) [30,31] was employed as wrapping materials to meet both of the challenges [32,33]. Therefore, a design that encapsulated active materials with small sized Si nanostructures, elastic coatings, good distribution and well connection with current collector was desired.

Herein, we design a loose and adaptable kind of *in-situ* growth binder-free silicon based anode. As shown in Scheme 1, three dimensional (3D) tree-like structure graphene nanosheets (GNS) (namely "graphene tree"-GrTr) vertically aligned on copper foil current collectors. Silicon nanoparticles (SiNPs) were uniformly sandwiched or encapsulated in the leaves of graphene tree, thus formed the SiNPs@GNS-GrTr structure. Within this design, some special features are analyzed as follows. First, silicon was prepared into nanosized structures to avoid pulverization by reducing the absolute volume change [9,24-27]. Second, SiNPs were encapsulated into graphene shells with sufficient elasticity to accommodate the strain associated with volume change and effectively isolate the SiNPs from electrolyte [9,19,22,34,35]. So, the direct contact of SiNPs with electrolyte was avoided and the integrity of SiNPs was guaranteed. In addition, the interleaving growth of SiNPs@GNS sheets formed a 3D tree like composite, which supply a mechanically robust, flexible and loose internal structure to accommodate the volume change of single SiNPs@GNS sheets. Namely, the synthesized SiNPs@GNS-GrTr could switch freely between a contracted state and expanded state without breaking the internal structure. This novel structure plays a pivotal role in the electrochemistry performance of the material. The electrodes exhibit (1) a high reversible capacity value of 1528 mAh g^{-1} at 150 mA/g , (2) relatively good cycle stability (88.6% after 50 cycles) and (3) fast charge/discharge rate (412 mAh g^{-1} at 8 A/g).

Materials and methods

Synthesis of VAGNs

The synthesis of the freestanding graphene tree composites was performed in a microwave plasma enhanced chemical vapor deposition system (MPECVD) equipped with a 2 kW, 2.45 GHz microwave source. The rectangular microwave waveguide couples the MW power in a quartz tube to generate the plasma. Copper foils ($18 \mu\text{m}$ thick), which are typically used as current collectors in Li ion batteries,

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