



# Polyaniline-encapsulated silicon on three-dimensional carbon nanotubes foam with enhanced electrochemical performance for lithium-ion batteries



Xiaoming Zhou<sup>a,b,1</sup>, Yang Liu<sup>a,b,1</sup>, Chunyu Du<sup>a,b,\*</sup>, Yang Ren<sup>a,b</sup>, Tiansheng Mu<sup>a,b</sup>, Pengjian Zuo<sup>a,b</sup>, Geping Yin<sup>a,b</sup>, Yulin Ma<sup>a,b</sup>, Xinqun Cheng<sup>a,b</sup>, Yunzhi Gao<sup>a,b</sup>

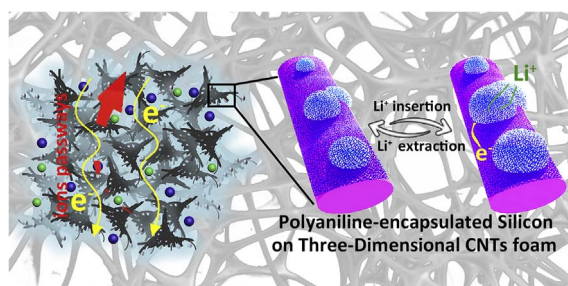
<sup>a</sup> MITT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, Harbin Institute of Technology, Harbin 150001, China

<sup>b</sup> Institute of Advanced Chemical Power Sources, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

## HIGHLIGHTS

- A PANI-Si@CNTs foam anode is fabricated based on the melamine foam.
- The 3D CNTs matrix boosts electronic/ionic transport and reaction kinetics.
- The core-sheath structure accommodates the volume change of Si during cycling.
- The composite exhibits high cycle stability and enhanced rate capability.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Carbon nanotubes foam  
Silicon anode  
Core-sheath structure  
Lithium-ion battery

## ABSTRACT

Seeking free volume around nanostructures for silicon-based anodes has been a crucial strategy to improve cycling and rate performance in the next generation Li-ion batteries. Herein, through a simple pyrolysis and in-situ polymerization approach, the low cost commercially available melamine foam as a soft template converts carbon nanotubes into highly dispersed and three-dimensionally interconnected framework with encapsulated silicon/polyaniline hierarchical nanoarchitecture. This unique core-sheath structure based on carbon nanotubes foam integrates a large number of mesoporous, thus providing well-accessible space for electrolyte wetting, whereas the carbon nanotubes matrix serves as conductive thoroughfares for electron transport. Meanwhile, the outer polyaniline coated on silicon nanoparticles provides effective space for volume expansion of silicon, further inhibiting the active material escape from the current collector. As expected, the PANI-Si@CNTs foam exhibits a high initial specific capacity of 1954 mAh g<sup>-1</sup> and retains 727 mAh g<sup>-1</sup> after 100 cycles at 100 mA g<sup>-1</sup>, which can be attributed to highly electrical conductivity of carbon nanotubes and protective layer of polyaniline sheath, together with three-dimensionally interconnected porous skeleton. This facile structure can pave a way for large scale synthesis of high durable silicon-based anodes or other electrode materials with huge volume expansion.

## 1. Introduction

Silicon, as one of the most abundant elements in earth, has been the

most desirable choice as a promising anode material for rechargeable Li-ion batteries (LIBs), mainly due to: (i) the high theoretical specific capacity (4200 mAh g<sup>-1</sup> corresponding to Li<sub>4.4</sub>Si) [1]; (ii) the similar

\* Corresponding author. Harbin Institute of Technology, School of Chemical Engineering and Technology, 92# Xidazhi Street, Harbin, Heilongjiang 150001, China.

E-mail address: [cydu@hit.edu.cn](mailto:cydu@hit.edu.cn) (C. Du).

<sup>1</sup> The two authors have equally contributed to the manuscript.

properties with carbon in the same group [2]; (iii) the relatively lower discharge voltage ( $\sim 0.37$  V after alloying with lithium), which is higher than that of current graphite (about 0.15 V), reducing risk of anode lithium plating. Unfortunately, the major bottleneck of silicon-based anodes is the lattice volume expansion (360% upon full lithiation) during lithiation-delithiation process [3] (only 9% for graphite). This expansion results in the pulverization of silicon anodes, loss of electrical contact, and regeneration of solid electrolyte interphase (SEI), eventually leading to the dramatic deterioration of electrochemical performance. In addition, the low intrinsic electrical conductivity of silicon ( $1.56 \times 10^{-3} \text{ S m}^{-1}$  at 20 °C) [4] and poor diffusivity of lithium ions ( $\sim 10^{-14}$ – $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ ) [5] significantly degenerate the charge-discharge behaviors of silicon anode.

To tackle these challenges, a series of strategies have been implemented, such as using amorphous silicon [6], silicon oxides [7–9], low-dimensional silicon (nanoparticles [10–12], nanowires [13] and nanotubes [14,15]), porous and hollow structures [16,17], silicon-carbon composites [18,19] and so on. Nanoscale silicon ( $< 150$  nm) can mitigate volume expansion within a certain scope by accommodating the strain of silicon and a series of related literature are reported [20–22]. Nonetheless, nano silicon can not be directly applied owing to its poor conductivity. The acetylene black as conductive additive is indispensably added but the uniform dispersion of silicon nanoparticles and acetylene black is difficult in processing, resulting in the agglomeration of silicon and uneven reactions during cycling. Encapsulating silicon in conductive carbon and/or polymer protective coatings is an elaborately intelligent design. Recently, Cui et al. proposed double walled hollow [23], yolk-shell [24], Si-hydrogel [25], self-healing [26], pomegranate-like [27] and conformal graphene cages [28] nanostructures. The advantages of these nanostructures are prominent because the volume change of silicon can be easily relaxed by the inward internal void space and the outward carbon or conductive polymer can provide fast electron and ion transport channels. As a further step, three dimensional (3D) interconnected networks (metal foams [29], carbon sponges [30] and coaxial nanostructures [31]) have emerged for alleviating the mechanical issues and improving the overall electrochemical performance of silicon anodes. Typically, Ruoff et al. [32] prepared a 3D foam electrode by anchoring graphene-coated silicon nanoparticles on ultrathin-graphite foams to enhance silicon loading density and gravimetric capacity. Yang et al. [33] developed 3D graphene-silicon networks by commercial sponge as template and graphene oxide as building block and obtained superior reversible capacity, rate capability, and cyclability. He et al. [34] utilized the modified carbon foam with a thin titanium layer as current collector to deposit silicon film and this silicon electrode exhibited excellent electrochemical performance and high-energy density. The significant advantage of 3D interconnected electrode in enhancing electrochemical performance lies in the porous network, which would provide larger surface area for trapping the active materials and accelerate electron and ion diffusion. Therefore, it is envisaged that the 3D interconnected scaffold accompanying by the incorporation of the core-shell structure is a novel approach to validly enhance the electrochemical property of electrode. Unfortunately, current methods employing carbon (carbon nanotube or graphene) foams usually require complex steps and post-processing, which might be unsuitable for accessible and cost-effective manufacture. In this regard, it is highly desirable to large-scale fabrication of durable 3D silicon-based electrode materials.

In this paper, we develop a facile and general approach to fabricate polyaniline-encapsulated silicon on 3D carbon nanotubes foam (PANI-Si@CNTs foam), where melamine foam act as sacrifice template to obtain carbon nanotubes foam. This hierarchical structure of anode material with carbon nanotubes matrix as core, silicon nanoparticles as sandwich and polyaniline as adhesive not only constructs an interconnected conductive network but also provides sufficient buffer space for the volumetric effect of silicon nanoparticles and the indestructible scaffolds ensure stable long-term electrochemical performance. As a

consequence, the unique 3D PANI-Si@CNTs foam exhibits a high reversible capacity of  $919 \text{ mAh g}^{-1}$  in the first 10 cycles, and retains  $727 \text{ mAh g}^{-1}$  after 100 cycles, as well as enhanced-rate capability, which could be a practical candidate of anode materials for lithium ion batteries.

## 2. Experimental section

### 2.1. Preparation of CNTs foam

To improve the hydrophilicity, 0.5 g carbon nanotubes (Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences) were ultrasonically treated by the mixed acid (45 ml  $\text{H}_2\text{SO}_4$  (98%) and 15 ml  $\text{HNO}_3$  (67%)) for 2 h. After standing still for 24 h, carbon nanotubes were then filtered and washed with deionized water until the pH of filtrate was neutral. Eventually, the purified carbon nanotubes were collected and dried in vacuum oven at 100 °C for 12 h. The content of metal ion before and after acid treatment for carbon nanotubes is shown in Table S1. The purified carbon nanotubes powder, polyvinylpyrrolidone (PVP as dispersant) and deionized water with the mass ratio of 5:1:94 were added into  $\text{ZrO}_2$  vessel and wet ball-milled (pulverisette 7+, FRITS CH) at the speed of 400 rpm for 10 h. The particle-size distribution before and after ball-milling operation of carbon nanotubes is shown in Fig. S1.

Commercial melamine foam (MF) was washed with deionized water and ethanol, and then immersed into the carbon nanotubes dispersion. The resultant mixture was transferred to a hydrothermal reactor. After reacting at 150 °C for 2 h, the as-prepared foam was washed with a large amount of deionized water to remove unattached carbon nanotubes, which was subsequently carbonized at 900 °C for 2 h under argon atmosphere. After cooling to room temperature, the carbon nanotubes foam was obtained.

### 2.2. Preparation of PANI-Si@CNTs foam

The original silicon powder (30 nm) was pretreated via ball-milling at the speed of 400 rpm for 10 h under argon atmosphere to obtain uniformly dispersed nanoparticles. 20 mg silicon nanoparticles and 10 mg CNTs foam were ultrasonically dispersed into 100 ml deionized water. The hydrochloric acid aqueous solution of aniline monomer (molar mass 1:20) was dripped into the above suspension. After that, hydrochloric acid aqueous solution of ammonium persulfate (molar mass aniline: APS = 1:1) as an oxidant was added dropwise and continuously stirred in ice-water bath for 6 h until the colour of solution changed to dark green. The PANI-Si@CNTs foam was obtained after centrifugation and dried in vacuum oven. For comparison, Si@CNT foam without PANI coating composite was synthesized in the same process.

### 2.3. Characterization

Scanning electron microscopy (SEM) images were obtained from a Hitachi S-4800 microscope (Hitachi, Japan). Transmission electron microscopy (TEM), high resolution TEM (HRTEM) and select area electron diffraction (SAED) were conducted on a JEOL-2010 TEM instrument at an acceleration voltage of 200 kV. The structure of as-synthesized samples was characterized by X-ray diffraction (XRD) (Rigaku D/max IIIA, Cu K $\alpha$ ) with a scan rate of  $0.05^\circ \text{ s}^{-1}$  in the  $2\theta$  range of  $10$ – $90^\circ$ . Fourier transform infrared spectroscopy (FTIR) spectra were measured using an IFS-85 (Bruker) spectrometer. The chemical composition of samples was determined by thermal gravimetric analysis (TGA) using a Perkin-Elmer TGA 4000 instrument. The Brunauer Emmett Teller (BET) specific surface area was analyzed by nitrogen adsorption on a Micromeritics ASAP 2020 nitrogen adsorption apparatus. X-ray photoelectron spectroscopy (XPS) was recorded by an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W

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