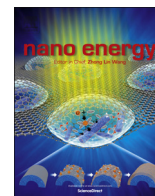




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# Rice husk-derived hierarchical silicon/nitrogen-doped carbon/carbon nanotube spheres as low-cost and high-capacity anodes for lithium-ion batteries

Yi-Chi Zhang<sup>a,b</sup>, Ya You<sup>b</sup>, Sen Xin<sup>c</sup>, Ya-Xia Yin<sup>b</sup>, Juan Zhang<sup>b</sup>, Ping Wang<sup>a</sup>,  
Xin-sheng Zheng<sup>a</sup>, Fei-Fei Cao<sup>a,\*</sup>, Yu-Guo Guo<sup>b,\*</sup>

<sup>a</sup> College of Science, Huazhong Agricultural University, Wuhan 430070, China

<sup>b</sup> Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China

<sup>c</sup> School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, China

## ARTICLE INFO

### Article history:

Received 6 April 2016

Received in revised form

22 April 2016

Accepted 24 April 2016

Available online 26 April 2016

### Keywords:

Silicon

Rice husk

Nano/micro-hierarchical structure

Electrospray

Anode material

Lithium-ion batteries

## ABSTRACT

The fabrication of silicon anode materials using biomass resources enables the effective utilization of subsidiary agricultural products in battery industries, despite the electrochemical performances of these as-synthesized silicon materials still need improvements. Using rice husk (RH) as silicon source, here we report for the first time the fabrication of silicon/nitrogen-doped carbon/carbon nanotube (SNCC) nano/micro-hierarchical structured spheres through a facile electrospray approach. The unique hierarchical hybrid structure of the composite spheres, in which the silicon nanoparticles are homogeneously encapsulated in the highly conductive, porous carbon matrix built by carbon nanotubes and nitrogen-doped carbon, contributes to fast electronic transport and prevents silicon from pulverization possessing good structure stability upon the synergistic lithiation/delithiation of the components. These SNCC spheres could deliver a high reversible specific capacity of 1380 mA h g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup>, and still maintain 1031 mA h g<sup>-1</sup> after 100 cycles. The low cost RH-derived silicon composites synthesized by a facile, scalable synthetic method turn out to be promising for the next-generation rechargeable lithium-ion batteries.

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## 1. Introduction

Silicon (Si) has attracted considerable research attention as a promising anode material for the next generation lithium-ion batteries (LIBs), because of a high theoretical capacity (Li<sub>15</sub>Si<sub>4</sub>, 3579 mA h g<sup>-1</sup>) [1], and a rich abundance [2]. However, the practical utilization of Si anode is still hindered by the fracture and pulverization problems caused by drastic volume change of Si (larger than 300%) during Li<sup>+</sup> insertion/extraction [3]. Recent pioneer works find that reducing the size of Si to the nanoscale could effectively accommodate the strain, buffer the volume change and further prevent fracture [3–6]. However, the common methods to obtain nano-Si anodes are restricted to the high-temperature pyrolysis of silane precursors and laser ablation of bulk Si [7–10], which inevitably raise energy consumption and lead to high cost of manufacture. So far, it remains desirable yet

challenging to develop a facile and scalable preparation method of nano-Si anodes to achieve optimized cost effectiveness.

Rice husk (RH), a common and high output agricultural waste, processes a high silica content (15–20 wt%), implying that it could be used as a cheap and sufficient resource for large-scale fabrication of Si materials [11]. More importantly, the silica obtained from RH is in the form of nanoparticles (NPs), making RH-derived Si promising as anode materials for LIBs [12]. Nevertheless, the RH-derived Si NPs also suffer from a low coulombic efficiency in the initial charge/discharge and limited cycle life as anode materials because of high surface reactions and low thermodynamic stability [13]. An ideal way to improve the electrochemical performances of Si nanomaterials would be fabricating nano/micro-hierarchical structure [13], since the materials on the micrometer size possess a good thermodynamic stability upon cycling. Embedding nano-sized Si into three-dimensional (3D) conductive matrix would be an effective way to improve the structure stability and form stable solid electrolyte interphase (SEI) films on surfaces. Among various Si/carbon composite materials [14–18], carbon nanotube (CNT) has been considered as a promising matrix because of the wired

\* Corresponding authors.

E-mail addresses: [caofeifei@mail.hzau.edu.cn](mailto:caofeifei@mail.hzau.edu.cn) (F.-F. Cao), [ygguo@iccas.ac.cn](mailto:ygguo@iccas.ac.cn) (Y.-G. Guo).



Fig. 1. Schematic illustration of the preparation process for SNCC nano/micro-structured spheres.

morphology, high electronic conductivity, and robust structure [19]. Additionally, it is easy for CNT to form 3D cross-linked conducting networks, ensuring effective electron transportation among active particles [14]. Combining the above two approaches, Si anode materials with nano/micro-hierarchical structure, in which CNTs are tightly intertwined between the RH-derived Si NPs, are supposed to be ideal anode materials for LIBs.

In this work, using the RH-derived Si NPs as raw material, we fabricated Si/nitrogen-doped carbon/carbon nanotube (SNCC) nano/micro-structured spheres by a polyacrylonitrile (PAN) assisted electro-spray method for the first time. RH-derived Si NPs on the sizes of  $\sim 50$  nm were homogeneously dispersed and embedded into the N-doped carbon matrix which was intertwined and threaded by CNT cross-linking networks, forming microspheres with the diameters of  $3.2 \pm 0.8$   $\mu\text{m}$ . Given the high electronic conductivity, robust structure, and improved surface/interface stability, SNCC spheres exhibit high cycling stability ( $1031 \text{ mA h g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  after 100 cycles) and excellent rate capability as anode materials for LIBs.

## 2. Experimental section

### 2.1. Materials

The RHs were obtained as by-product of rice harvested from Jingmen, Hubei, China. Multi-walled carbon nanotubes (MWCNTs) (length: 0.5–2.0  $\mu\text{m}$ , diameter  $< 50$  nm) were purchased from Shenzhen Nanotech Port Co., Ltd.. Polyacrylonitrile (PAN,  $M_w = 150,000$ ) was purchased from Sigma-Aldrich. All other reagents were purchased from Sinopharm Chemical Reagent Beijing

Co., Ltd.. Unless otherwise specified, all the reagents were used without further purification.

### 2.2. Fabrication of SNCC nano/micro-structured spheres from RHs

The RHs were firstly refluxed with 10% HCl for 2 h to remove the metal ion impurities. The leached RHs were washed by deionized water then dried, and next heated in air at  $700$   $^{\circ}\text{C}$  for 2 h with a ramp rate of  $2$   $^{\circ}\text{C min}^{-1}$  to remove organic components. Then the high-quality RH-derived nano- $\text{SiO}_2$ , denoted as RH- $\text{SiO}_2$ , was obtained. The transformation from nano- $\text{SiO}_2$  to nano-Si was conducted by magnesiothermic reduction. 2 g RH- $\text{SiO}_2$ , 2 g magnesium powder (200–300 mesh) and 20 g NaCl were fully mixed and grinded in a mortar for 40 min. The mixture was placed in a corundum crucible and heated in a tube furnace under Ar flow at  $680$   $^{\circ}\text{C}$  for 3 h with a ramp rate of  $2$   $^{\circ}\text{C min}^{-1}$ . The obtained mixture powder was soaked in 1 M HCl (molar ratio of HCl:H<sub>2</sub>O:EtOH = 0.66:4.72:8.88) for 8 h to remove MgO and MgSi<sub>2</sub>. Then the HCl-soaked powder was etched by 5% HF for 20 min to make sure the residual silica and newly formed SiO<sub>x</sub> were both removed. After drying under vacuum at  $60$   $^{\circ}\text{C}$  for 10 h, the RH-derived Si, denoted as RH-Si, was obtained. For fabrication of SNCC spheres, 12 mg HNO<sub>3</sub> pretreated MWCNTs, 6 mg sodium citrate and 120 mg RH-Si were dispersed in 4 mL of N,N-dimethylformamide (DMF) by ultrasonic treatment for 1 h. 180 mg PAN was then added to the suspension and stirred vigorously for 12 h. Subsequently, the dispersion was loaded into a syringe matching a needle with 20-gauge size. A piece of  $10 \times 10$   $\text{cm}^2$  aluminum foil was used as a product collector, and the distance between needle and collector was 15 cm. Electro-spray process was performed at a working voltage of 20 kV with the flow rate of  $0.8 \text{ mL h}^{-1}$ . After that, the

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