



# Facile high-voltage sputtering synthesis of three-dimensional hierarchical porous nitrogen-doped carbon coated Si composite for high performance lithium-ion batteries



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## HIGHLIGHTS

- 3D NPC@Si microsphere is prepared via high voltage sputtering process.
- The void space alleviates the drastic volume expansion of silicon.
- 3D NPC@Si exhibits high performance for lithium-ion batteries.

## ARTICLE INFO

### Keywords:

Three-dimensional hierarchical porous nitrogen-doped carbon  
Silicon nanoparticles  
High voltage sputtering  
Void space  
Lithium-ion batteries

## ABSTRACT

Various kinds of efforts have been devoted to ameliorate the serious volume-expansion effect and low electron conductivity of silicon-based materials in lithium ion batteries. Here, we report a facile high voltage sputtering process to prepare three-dimensional hierarchical porous nitrogen-doped carbon coated Si microsphere to significantly improve the lithium storage performance. The structure and morphology of the as-obtained samples are characterized by X-ray diffraction, transmission electron microscope and scanning electron microscope. The results indicate that the as-prepared composite is composed of silicon nanoparticles (~100 nm) coated with conductive thin carbon layer (~8.5 nm). The composite shows excellent lithium storage performance with a reversible capacity of 1565 mAh g<sup>-1</sup> after 100 cycles at a current density of 0.5 A g<sup>-1</sup>, as well as a long cycling performance at the high current density of 2 A g<sup>-1</sup>. The facile preparation process and highly silicon-loading (~78%) makes the prepared material be a great potential application in lithium-ion batteries.

## 1. Introduction

In recent years, lithium-sulfur and lithium-air batteries have been paid much attention [1–4]. In addition, sodium ion batteries and lithium-nitrogen batteries are also developing rapidly [5,6]. For traditional lithium ion battery (LIB), graphite cannot meet the needs of high energy density completely. Silicon has been regarded as one of the next generation anode materials [7], because of its high theoretical capacity (ca. 3579 mAh g<sup>-1</sup>, Li<sub>15</sub>Si<sub>4</sub>), 10 times more than graphite anodes (ca.

372 mAh g<sup>-1</sup>); Actually, the silicon anode also possesses a low and remarkable working voltage (~0.4 V vs. Li/Li<sup>+</sup>); Besides, it is cheap and abundant in the earth; Meanwhile, it can reduce the safety concerns of lithium deposits. The above mentioned advantages of silicon make it a prospective material for high energy-storage, whereas, the silicon particles are subject to large volume changes during charging and discharging, leading to material pulverization and electronic contact failure [8]. In addition, the routine electrolyte is not stable when the potential is below 1 V vs Li<sup>+</sup>/Li and form an unstable solid electrolyte

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interphase (SEI) on the silicon surface, which can crack during volume variations and expose bare silicon [9]. Which leading to a serious stability problems as an increasing number of SEI formed on newly exposed silicon surfaces, rapidly plugging the electrode pores and reducing the capacity of the batteries [10].

To overcome these technical bottlenecks, a large number of research teams reported various strategies to improve lithium storage performance of silicon anodes. One strategy is to downsize of silicon to micron or nanoscale [11,12], such as silicon nanoparticles (Si NPs) [13–15], silicon nanowires [16,17], silicon nanospheres [18,19], and double-walled silicon nanotubes [11,20]. Thanks to small particle sizes and available void space, the particles of silicon nanostructures can effectively cushion the stress of volume changes during the lithiation/delithiation process. Another approach is that the silicon is tightly embedded in the matrix [11,21,22], which possesses superior conductivity and mechanical properties, such as graphene-encapsulated silicon foam [23], silicon/single-walled carbon nanotube composite [24], silicon/graphene nanosheets [25,26], silicon/porous or hollow carbon [21,27], and silicon/carbon nanotubes [11,28–30]. These silicon-carbon composites not only enhance the electronic conductivity of silicon, but also adjust the expansion effect of silicon anode and conduce to form a stable SEI layer. However, these efforts are suffering from the low silicon loading and/or expensive production cost. In particular, in many of the reported silicon/carbon composites, the majority of silicon content is below 75% [11,21,24,25,27]. Furthermore, by introducing N, P, S, etc. heteroatom dopants can alter the band gap and/or surface property to improve the electrochemical activity of the material [31,32]. As well known, metal-organic frameworks (MOFs) are belong to a crystalline porous materials [33]. Among them, the zeolitic imidazolate framework (ZIF-8) is a good candidate for the synthesis of high specific surface area nitrogen doped porous carbon [34,35]. However, these previous studies mainly focused on these strategies respectively, rather than taking them into consideration. In view of this, it is expected that utilization of silicon embedded heteroatom doped porous carbon in conjunction with highly silicon-loading could improve the electrochemical performance of Si/C composite.

Here, we designed a simple and economic strategy to preparing three-dimensional hierarchical porous nitrogen-doped carbon coated Si (3D NPC@Si) microsphere via high voltage sputtering and subsequent heat treatment. The as-prepared 3D NPC@Si possesses several features: 1) nano-silicon can cushion the stress of volume changes to a certain extent; 2) silicon embedded carbon not only buffer the volume expansion of silicon, but also contribute to the formation of a stable SEI film due to the hierarchical porous structure and void space between silicon and carbon; 3) highly silicon-loading (~78%) can significantly improve the capacity of composites; 4) introduce heteroatom (N) doped porous carbon can alter the band gap and/or surface property to improve the electrochemical activity of the material.

## 2. Experimental

### 2.1. Preparation of ZIF-8

Generally, 1.071 g of Zinc nitrate hexahydrate (Tianjin Hongyan Chemical Co., Ltd., 99.0%) was added into 50.0 mL of methanol (Tianjin Baishi Chemical Co., Ltd., 99.5%) to form a homogeneous solution A. 2.357 g of 2-methylimidazole (Aladdin, 98%) were dissolved into 50.0 mL of methanol to obtain solution B. Solution A was quickly added into solution B and with agitated stirring for 24 h. The white precipitate (ZIF-8) was obtained by centrifugation and washing with methanol, and dried under oven at 80 °C for 10 h.

### 2.2. Synthesis of 3D NPC@Si

0.35 g of Si nanoparticles (~100 nm) (Shanghai Naiou Nano

Technology Co., Ltd., 99.9%) were ultrasonically dispersed in *N,N*-dimethyl-formamide (Shanghai Titan Scientific Co., Ltd., 99.5%) followed by addition of 0.2 g of obtained ZIF-8, and then stirring at room temperature. The mixed solution was homogenized for 10 min to obtain a dispersion. 0.2 g of polyacrylonitrile (PAN, Mw = 150,000) was added to the dispersion with continuous stirring for 1 h at 60 °C, subsequently continue stirring for 12 h at room temperature. Then, high voltage sputtering was carried out at 15 kV. A self-made sputtering apparatus was utilized, which consisted of a high voltage supplier, an injection pump, an aluminum foil receiver, and the distance from the tip nozzle to receiver was about 15 cm. The obtained yellow precursor (Si/ZIF-8/PAN composite) was collected. The resulted Si/ZIF-8/PAN was placed in tube furnace and calcinated, the products were carbonized with two steps in nitrogen atmosphere: 350 °C for 3 h and subsequent 800 °C for another 1 h. Subsequently, the obtained brown powder composites were washed for 24 h with 2 M hydrochloric acids (Tianjin Hongyan Chemical Co., Ltd.). Finally, the as-obtained NPC@Si sample was rinsed with deionized water and ethanol (Shanghai Titan Scientific Co., Ltd., 99.7%), then dried at 80 °C for 12 h in a vacuum oven. For comparison, a control experiment was executed to prepare N-doped carbon coated Si (NC@Si) by a similar procedure without adding ZIF-8.

### 2.3. Materials characterization

The crystal structure of the sample was characterized by X-ray diffraction (XRD, D8, Bruker Germany). The morphology of the samples was examined using scanning electron microscopy (SEM, ZEISS SUPRA55 VP) and transmission electron microscopy (TEM, Titan G2 60-300). The content of silicon was investigated by thermogravimetric analysis (TGA, NETZSCH STA 449F3, Germany). The surficial components content was studied using X-ray photoelectron spectroscopy (XPS, Thermo SCIENTIFIC ESCALAB 250X). The specific surface areas and porous distributions of materials were studied using nitrogen sorption measurement (Autosorb-1 Quantachrome Ins). Elemental analysis was analyzed by Vario EL III.

### 2.4. Electrochemical measurements

To test the electrochemical properties of the samples with coin-type half-cells. The working electrodes were prepared by mixing 60% of the active materials, 20% of acetylene black, and 20% of sodium alginate in deionized water to form a slurry. The resulting mixture slurry was pasted onto the copper current collector using the doctor-blade method and then dried in a vacuum oven at 80 °C for 12 h, finally punched into circular discs, the mass loading of active materials was ~0.6 mg cm<sup>-2</sup>. The batteries were assembled in an Ar-filled glove box (water and oxygen concentration were kept less than 1 ppm) with Celgard 2400 as the separator membrane. The electrolyte consisted of a 1 M LiPF<sub>6</sub> solution in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) containing 5 wt% vinylene carbonate (VC), and metal Li foil was used as the counter electrode. After standing for 12 h, a Neware BTS (R3) system was used to evaluate galvanostatic charge/discharge test between 0.01 and 1.5 V. The cyclic voltammetry (CV) curves were measured on a CHI660D electrochemical workstation between 0.01 and 1.5 V with a scan rate of 0.1 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) was performed by applying a 10 mV voltage within a frequency range between 100 kHz and 0.1 Hz on a Zahner Elektrik electrochemical workstation.

## 3. Results and discussion

The fabrication process of 3D NPC@Si microsphere is schematically illustrated in Fig. 1. Firstly, universal solvent method was used to synthesis ZIF-8. Secondly, microspheres were prepared by high voltage sputtering and a subsequent carbonizing process with the mixture of ZIF-8, Si NPs and PAN. Here, both ZIF-8 and PAN were as carbon and

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