



Novel silicon/carbon nano-branches synthesized by reacting silicon with methyl chloride: A high performing anode material in lithium ion battery



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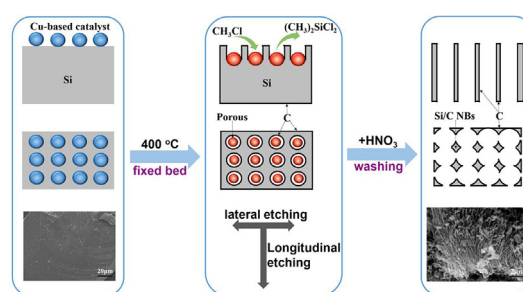
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HIGHLIGHTS

- Si/C nano-branches were prepared using bulk Si and CH₃Cl over Cu-based catalysts.
- Si/C nano-branches have the diameter of ~70 nm and the length of ~6 μm.
- Si/C nano-branches display an average specific capacity of 849 mA h g⁻¹ at 50 mA g⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

To overcome the existing technical barriers of pulverization and fast capacity fading of Si/C composite anodes in lithium ion batteries and to low their production cost, we have developed a facile method for preparing Si/C nano-branches (Si/C NBs) by reacting commercial Si microparticles directly with CH₃Cl gas over Cu-based catalyst particles followed by a simple post treatment. The samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, and Raman spectroscopy. It was found that the diameter and the length of Si/C NBs were ~70 nm and ~6 μm, respectively. When used as the anode materials for lithium ion batteries, they displayed excellent electrochemical properties with an average specific capacity of 849 mA h g⁻¹ at a current density of 50 mA g⁻¹. The much improved electrochemical performance is attributed to the unique branched nanostructure and the coated carbon layer on the surface, which can effectively increase the electrical conductivity and buffer the volume change. This work provides a simple and low-cost route to prepare Si/C anode materials with novel branched nanostructure for lithium ion batteries.

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1. Introduction

Silicon (Si)-based composite materials are very promising to replace the commercially available graphite as anode materials in lithium ion batteries because of the abundance of Si in nature, its appropriately low working potential, and high theoretical specific

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capacity of $\sim 3579 \text{ mAh g}^{-1}$ (almost 10 times higher than that of the commercial graphite anodes) [1,2]. However, the large volume change of Si ($>300\%$) during repeated lithium insertion and extraction would inevitably lead to pulverization and fast capacity fading in operation [3,4]. The cracks and pulverizations can break the solid electrolyte interphase (SEI) layer formed on Si surface, and cause continuous exposure of the freshly formed Si surface to the electrolyte and prompt further SEI formation, which will eventually result in not only extra electrolyte and lithium source consumption but also electrical insulation of the electrode [5,6].

Currently, diverse approaches are proposed and tested to overcome this difficulty, e.g., by decreasing Si particle dimensions [7–9], controlling morphologies [10–12], modifying interfaces [13,14] and by forming hybrid structures [15,16]. In these approaches, the Si/C nano-composite anodes have shown high potential in improving the overall electrochemical performance of the anodes for lithium ion batteries, because such composites combine the advantages of both carbon (e.g., proper softness and compliance, good electronic conductivity, and reasonable Li-insertion ability as well as small volume expansion) and Si (e.g., high capacity) [17]. In addition, nano-sized anode materials usually can shorten the transmission path of both Li ions and electrons, which is conducive to improve their rate performance [18]. More importantly, such kind of nanostructured materials have shown better capability to withstand stresses caused by volume changes than their bulk counterparts [7]. Recently, many efforts have been made to prepare Si and Si based nano-composites. For example, Yu and co-workers synthesized Si nanosheets from bulk Si by DC arc-discharge method, which possessed high coulombic efficiencies (above 94% except the initial few cycles) and a charge capacity of 442 mAh g^{-1} after 40 cycles at a current density of 100 mA g^{-1} [19]. Lin et al. prepared crystalline Si nanoparticles by reducing SiCl_4 and metallic magnesium in the molten AlCl_3 at 200°C , which delivered a reversible capacity of 3083 mAh g^{-1} at 1.2 A g^{-1} after 50 cycles, and 1180 mAh g^{-1} at 3 A g^{-1} over 500 cycles [20]. Lee et al. employed the metal-assisted chemical etching to fabricate hybrid silicon nanowire/graphene nanostructure which exhibited enhanced cycle performance with the retained capability of above 90% of their initial capacity after 50 cycles [21]. Wang et al. fabricated Si@graphene composites with very small particle size by the hydrothermal method using 3-aminopropyltriethoxysilane and trisodium citrate dihydrate as the reactants followed with electrostatic induced self-assembly, which exhibited outstanding lithium storage properties including extraordinary rate capability (566 mAh g^{-1} at 20 A g^{-1}) and remarkable cycling stability (0.004% decay per cycle over 500 cycles) [22]. Previously, our group prepared amorphous Si/C nanospheres via chemical vapor deposition of methyltrichlorosilane (CH_3SiCl_3) at 900°C which acted as both Si and C precursors, and improved both the reversible capacity and cycling stability of the anode [23]. Also, it was observed that Si@SiO_x/C nano-composites [24], Si/graphene nano-composites [25,26], Si/C nano-composites [27] exhibited excellent cycling stability. However, the above-mentioned materials still have some critical drawbacks, such as high cost (e.g., expensive instrument [19,28] and raw materials [20,25,26,29]) and complicated processing steps (e.g., chemical etching [21,30] and magnesiothermic reduction [9]). Therefore, developing a really facile and effective method for the synthesis of Si/C nano-composites far exceeding the current ones is highly desired.

Previously, our group innovated a method for preparation of porous Si/C composites by directly reacting metallurgical-grade Si powders with CH_3Cl [31]. Here we report a significant new development which allows facile and large-scale fabrication of Si/C nano-branches (Si/C NBs) by directly reacting metallurgical-grade Si powders with CH_3Cl over Cu-based catalysts in a fixed bed

reactor, followed by a simple post-treatment. The self-made Cu-based catalysts could increase the degree of catalytic reaction between Si and CH_3Cl , while the interconnection of porous structures in the horizontal direction could be proceeded with shorter reaction time, resulting in the formation of Si/C NBs. The obtained Si/C NBs were used as anode materials in lithium ion batteries which showed outstanding electrochemical performance. The overall method is simple, energy-efficient and easy to scale-up for fabrication of Si/C nano-composites for lithium ion batteries.

2. Experimental

2.1. Material synthesis

The reaction was carried out in a conventional lab fixed-bed reactor. Typically, 10.0 g of commercial metallurgical-grade Si powder (provided by Jiangsu Hongda New Material Co., Ltd, China) and 10.0 g of self-made $\text{CuO/Cu}_2\text{O/Cu}$ catalysts were homogeneously ground in a mortar for 20 min to form a contact mass, which was then loaded in the quartz reactor. The reactor system was purged with purified N_2 for 0.5 h followed by a heating to 400°C within 1.5 h at a N_2 flow rate of 25 mL min^{-1} . Subsequently, N_2 was turned off and commercial CH_3Cl (provided by Jiangsu Hongda New Material Co., Ltd, China) with a flow rate of 25 mL min^{-1} was introduced into the reactor to react with Si at 400°C for 6, 12, 18, and 24 h, respectively. The waste contact mass (solid residue after reaction) was dissolved in nitric acid solution under stirring at 90°C for 4 h to recover the metal compounds. After filtrated, washed with distilled water and absolute ethanol, and dried in vacuum at 80°C for 10 h, nanostructured dendritic Si/C composites were obtained, which were denoted as Si/C NBs-6 h, Si/C NBs-12 h, Si/C NBs-18 h, and Si/C NBs-24 h, respectively.

2.2. Characterization

X-ray diffraction patterns (XRD) were recorded on a PANalytical X'Pert PRO MPD using the $\text{K}\alpha$ radiation of Cu ($\lambda = 1.5418 \text{ \AA}$). The microscopic features of the samples were observed by field-emission scanning electron microscopy (SEM) (JSM-7001F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2010F, JEOL, Tokyo, Japan). For SEM analysis of cycled electrodes, the cell was disassembled in an argon-filled glove box, and then the cycled electrodes were washed by dimethyl carbonate and dried at room temperature in argon gas. A Raman spectroscopy (Renishaw inVia plus, England) with an excitation wavelength of 514.5 nm and a beam spot size of $1\text{--}2 \text{ }\mu\text{m}$ was used to characterize sample. Thermogravimetric (TG) analysis was carried out on an EXSTAR TG/DTA 6300 (Seiko Instruments, Japan) using a heating rate of $10^\circ\text{C min}^{-1}$ in air (200 mL min^{-1}). Statistical analysis of branch diameters was carried out using Nano Measurer software.

2.3. Electrochemical measurement

The working electrode was prepared by mixing the active materials, acetylene black, and alginic acid sodium salt in a weight ratio of 80:10:10 with water as a solvent. The resulting slurries were cast onto copper current collectors. The foils were rolled into $25 \text{ }\mu\text{m}$ thin sheets, dried at 40°C for 24 h, further cut into disks with a diameter of ca. 14 mm , and then dried at 120°C under vacuum for 24 h. CR2016 coin-type cells were assembled in an argon-filled glove box with lithium foils as the counter electrodes and polypropylene macroporous films (Celgard 2400) as separators. The liquid electrolyte was 1 mol L^{-1} LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The galvanostatic charge and discharge tests were carried out at room

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