



# Nanocomposites of silicon and carbon derived from coal tar pitch: Cheap anode materials for lithium-ion batteries with long cycle life and enhanced capacity

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## ABSTRACT

From energy and environmental consideration, an industrial waste product, coal tar pitch (CTP), is used as the carbon source for Si/AC composite. We exploited a facile sintering method to largely scale up Si/amorphous carbon nanocomposite. The composites with 20 wt.% silicon with PVdF binder exhibited stable lithium storage ability for prolonged cycling. The composite anode delivered a capacity of 400.3 mAh g<sup>-1</sup> with a high capacity retention of 71.3% after 1000 cycles. Various methods are used to investigate the reason for the outstanding cyclability. The results indicate that the silicon nanoparticles are wrapped by amorphous SiO<sub>x</sub> and AC in Si/AC composite. This uniform structure is very favorable to lithium storage, the SiO<sub>x</sub> and AC layers can supply sufficient conductivity and strong elasticity to suppress the stress resulting from the reaction of Si with Li during charge/discharge process.

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## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) are currently playing a critical role in energy storage technologies. Due to their overwhelming advantages, including high gravimetric and volumetric capacity, LIBs have successfully been used in various portable electronic devices and mobile applications [1,2]. With the ever increasing power requirements for real-life applications and the concerning of the environment, it is necessary to improve the performance of the electrode materials in the same time to lower the costs, achieve large-scale production, and use industry waste materials as active materials [3,4].

Graphite is the conventional anode material for commercial LIBs, in which every six-carbon atom can be intercalated with one lithium atom at maximum, with just over 10% volume expansion. It shows high reversibility and stable capacity with prolonged cycling, but the reversible capacity has reached its theoretical limit (~372 mAh g<sup>-1</sup>). Development of high capacity anodes to meet the demand is therefore imperative. Many materials with improved storage capacity have recently aroused great interest, such as silicon (3579 mAh g<sup>-1</sup>) [5–7], and tin (994 mAh g<sup>-1</sup>) [8–11]. Silicon shows great advantages over the other candidates owing to its appealing features including exceptionally high theoretical capacity, lower voltage plateau, non-toxicity, low cost, and abundance. However, it generally suffers from enormous volume expansion

(328%) during the lithiation and de-lithiation processes, causing the cracking and pulverization of active materials, followed by disintegration of the electrode and eventually leading to rapid capacity fading. Large-volume change severely restricts practical applications [12–24]. In recent years, some strategies devoted to nanostructured silicon can alleviate the volume expansion to some extent. These include chemical vapor deposition [15,16], the template method [17,18], and chemical reactions [19,20]. Nevertheless, the synthesis processes are complicated, expensive, and difficult to industrialize. The other effective tactic to overcome the volume changes is by means of an active/conductive matrix to form a composite [21–26]. Therefore, incorporating silicon to optimize carbon anode is a feasible and desirable solution to realize the high energy density needed for some practical applications [27]. The silicon content of the composite could significantly affect the overall properties of the electrode. If the composite were Si-rich, the electrode would definitely undergo large volume changes. It is evident that a Si-poor composite should go through less volume change and deliver better capacity retention to the electrodes [28]. Based on this principle, Si/C composite with a relatively low proportion of silicon is an excellent candidate to substitute for graphite anode in large-scale applications. Furthermore, from a commercial viewpoint, it is crucial to utilize a simple, green, and low-priced synthesis method, one that is also based on cheap and abundant raw materials. Coal tar pitch (CTP) as an industrial by-product, composed of cyclical hydrocarbons of various molecular weights and configurations. It has significant health hazards and environmental concerns. In China, the output of CTP was up to 8.7 million tons during the first 4 months of 2012 [29]. Recycling this low-cost waste into a

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promising active material for energy storage could be of great benefit to both the environmental issues and the energy challenges, and help to achieve green and sustainable energy development. Several previous works based on CTP have been devoted to its applications in LIBs and supercapacitors [30–32]. Previous works, however, only focused on activated carbon materials, which showed slightly lower capacity than the already commercialized carbon. To date, there is still no report on using CTP as a cheap carbon precursor for Si/C composites. More recently, polymer binders attract wide attention, which have been shown can greatly influence the performance of Si-based composite electrodes. Compared with conventional poly(vinylidene fluoride) (PVdF), the polymers with carboxy groups, such as polyacrylic acid (PAA) and carboxymethyl cellulose (CMC), can react with hydroxyl functionalities on the both carbon and silicon surfaces to confine the active material to the binder, which is responsible for the improvement of the electrode [33]. Remarkable progress has been made recently, alginate sodium (AS), a new kind of bio-derived binder with higher content of carboxylic group, can result in a large number of possible binder-Si/binder-C bonds and eventually much better cycling performance [34]. Here, we present a facile sintering method to synthesize Si/amorphous carbon (AC) composite materials, which is easy to be scaled up. Certain amounts of silicon were introduced into AC derived from CTP. Furthermore, the binder effects have been revealed to determine lithium storage performances of the Si/AC.

## 2. Experimental

### 2.1. Material synthesis

The Si/AC composites were fabricated by pyrolyzing a mixture of silicon nanoparticles (50–100 nm; Nanostructured and Amorphous Materials Inc.) and coal tar pitch (CTP) (Bao Steel Ltd., China). To obtain an evenly dispersed Si/CTP mixture, the CTP was initially dissolved in N-methyl-2-pyrrolidone (NMP) (Sigma–Aldrich) under stirring for 1 h, and the Si nanoparticles were dispersed in NMP by ultrasonication for 30 min, before the silicon dispersion was added into the CTP solution. The blend was fully mixed by stirring for 5 h. The resultant solution was heated to 150 °C for 1 h in order to evaporate the NMP, which can be collected for reuse. The prepared mixture was sintered in a tube furnace at 850 °C for 5 h under flowing argon atmosphere. After the pyrolyzation, the composites (Si/AC), which consisted of silicon encapsulated by amorphous carbon (AC), were fabricated by naturally cooling the sample to room temperature under argon atmosphere. Two samples were fabricated with different weight ratios of Si to AC (estimated values were Si:C = 20:80 and 50:50), which are denoted as 0.2 Si/AC and 0.5 Si/AC.

### 2.2. Structural characterization

The samples were characterized by field-emission scanning electron microscopy (FESEM; JEOL7500), transmission electron microscopy (TEM; JEOL JEM-2100F), and powder X-ray diffraction (XRD; GBC MMA) with Cu K $\alpha$  radiation. Raman spectra were collected by a 10 mW helium/neon laser at 632.8 nm excitation, which was filtered by a neutral density filter to reduce the laser intensity and a charge-coupled detector (CCD). Thermogravimetric analysis (TGA) was performed in air with the help of a SETARAM thermogravimetric analyzer (France). The X-ray photoelectron spectra (XPS) experiment was carried out using Al K $\alpha$  radiation and fixed analyser transmission mode. The pass energy was 60 eV for the survey spectra and 20 eV for specific elements.

### 2.3. Electrochemical tests

The tests were conducted by assembling coin-type half cells in an argon-filled glove box. Lithium foil was employed as both reference and counter electrode. The working electrode consisted of 70 wt.% active material (AC, bare Si, 0.2 Si/AC, and 0.5 Si/AC, respectively), 20 wt.% black carbon, and 10 wt.% binder (polyvinylidene difluoride (PVdF), sodium carboxymethyl cellulose (CMC), or alginate sodium (AS)). The electrolyte was 1.0 M LiPF $_6$  in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Electrochemical cycling of electrodes was conducted at 200 mA g $^{-1}$  for galvanostatic measurements in the 10 mV to 1.2 V (vs. Li/Li $^+$ ) voltage window. Cyclic voltammetry was performed using a Biologic VMP-3 electrochemical workstation between 0.01 and 1.2 V at a scan rate of 0.1 mV s $^{-1}$ .

## 3. Results and discussion

The composites proposed here has similar structure as the seeds (Si nanoparticles) in the pulp (AC) of kiwi fruit as shown in Fig. 1. Two samples were fabricated with different weight ratios of Si to AC (estimated values of Si:C = 20:80 and 50:50), which are denoted as 0.2 Si/AC and 0.5 Si/AC. It is apparent that the addition of silicon to Si/C composite can effectively improve the capacity of the anode. On the other hand, when silicon nanoparticles are anchored to the carbon matrix, the carbon in the Si/C hybrid materials not only can modify the unstable solid electrolyte interphase (SEI) layer of Si into a robust and flexible one that can accommodate the mechanical strains induced by the volume changes [36], but also can effectively buffer the volume expansion and enhance the conductivity of Si, thus preventing the degradation of the electrode integrity [15,21,22]. Combining carbon with an appropriate amount of Si can eventually ensure higher capacity and stable performance over long cycling.

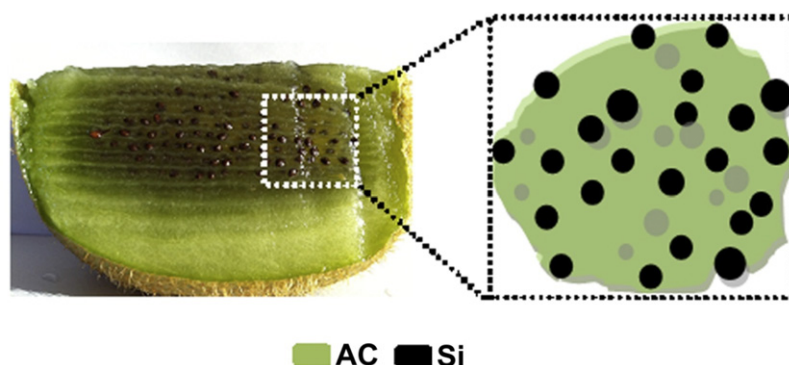


Fig. 1. Schematic illustration of the design of the materials with kiwi fruit as model.

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