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A-few-second synthesis of silicon nanoparticles by gas-evaporation and their self-supporting electrodes based on carbon nanotube matrix for lithium secondary battery anodes

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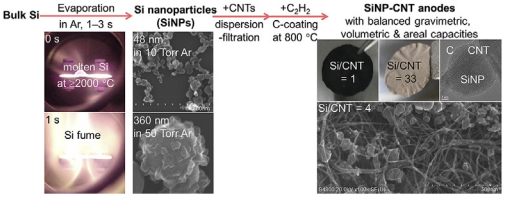
HIGHLIGHTS

- Si nanoparticles (SiNPs) were synthesized by gas-evaporation of bulk Si in a few s.
- SiNPs were obtained with controlled diameters (48–360 nm) at high yields (20–60%).
- Self-supporting SiNP-CNT electrodes were obtained by co-dispersion and filtration.
- Carbon coating significantly enhanced the anode performance of the electrodes.
- Balanced capacities of 618 mAh/g_{film}, 230 mAh/cm^3, and 0.644 mAh/cm^2 were realized.

GRAPHICAL ABSTRACT



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ABSTRACT

Rapid gas-evaporation method is proposed and developed, which yields Si nanoparticles (SiNPs) in a few seconds at high yields of 20%–60% from inexpensive and safe bulk Si. Such rapid process is realized by heating the Si source to a temperature ≥2000 °C, much higher than the melting point of Si (1414 °C). The size of SiNPs is controlled at tens to hundreds nanometers simply by the Ar gas pressure during the evaporation process. Self-supporting films are fabricated simply by co-dispersion and filtration of the SiNPs and carbon nanotubes (CNTs) without using binders nor metal foils. The half-cell tests showed the improved performances of the SiNP-CNT composite films as anode when coated with graphitic carbon layer. Their performances are evaluated with various SiNP sizes and Si/CNT ratios systematically. The SiNP-CNT film with a Si/CNT mass ratio of 4 realizes the balanced film-based capacities of 618 mAh/g_{film}, 230 mAh/cm^3, and 0.644 mAh/cm^2 with a moderate Si-based performance of 863 mAh/g_{Si} at the 100th cycle.

1. Introduction

To efficiently use renewable energy for sustainable and affluent society, it is important to develop high-performance electric energy storage devices. Lithium ion batteries (LIBs) have become popular

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because of their high energy and power densities with good cycle performance. The state-of-the-art LIB is consisted of cathode (27.2 mass%), anode (30.6 mass%), separator (3.2 mass%), electrolyte (9.1 mass%), and passive components/housing (17.2 mass%) [1], and the anode is consisted of active materials, polymer binders, conductive additives, and current collector of copper foils (21 mass% of anode). To enhance the energy density of the total device, it is important to make anodes using emerging active materials with high theoretical capacities at high mass fractions and non-capacitive materials (such as binders or current collectors) at low mass fractions [2,3].

Silicon (Si) is an attractive anode material due to its ten-times higher theoretical capacity (3580 and 4200 mAh/g_{Si} with $Li_{15}Si_4$ and $Li_{22}Si_5$) than the conventional graphite (372 mAh/g_C with LiC_6). However, it suffers from the rapid capacity fade due to the large volume change (up to ~4 times) during the charge and discharge process. The volume change causes the pulverization of Si, structure collapse of the entire electrode, and continuous solid electrolyte interphase (SEI) growth. Many studies have shown that Si nanometer-scale structures such as nanowires [4,5], hollow structures [6,7], porous structures [8,9] and thin films [10–12] can accommodate the large volume change and retain the high capacity. However, most of these nanostructures are fabricated through complicated processes using expensive and/or unsafe source materials such as silane [4–7] with Si loads much smaller than the thick and heavy current collectors of Cu foils (typically ~18 μm and 16 mg/cm^2 [13]).

High performance electrodes have been reported for Si-carbon nanocomposites [14–18]; carbon-matrix can accommodate volume expansion, enhance electric conductivity, and make stable SEI layer with inert carbon-layer on Si. Especially, graphene oxide and carbon nanotubes (CNTs) can easily form self-supporting nanocomposite films with active materials such by filtration [2,3,19], realizing high gravimetric capacities based on both active material (Si) and total electrode (including binders, conductive fillers, and current collectors) [19–24]. But they use silane as the Si source [20,21] or (commercial) SiNPs by unknown production methods [19,22–25]. To practically realize high capacity LIBs with Si-based anodes, it is highly important to realize self-supporting electrodes with high Si contents using inexpensive and safe Si source via simple and rapid processes.

Aiming at high throughput fabrication of practically thick Si anodes using inexpensive and safe source materials, we have reported the rapid vapor deposition (RVD) of porous Si and Si-Cu alloy films of 0.7–0.8 mg$_{Si}$/cm^2 (equivalent to 3–4 μm thick bulk Si) in ≤1 min directly on Cu current collectors [26,27]. Such high deposition rate was achieved by heating Si sources to ≥2000 °C (well above the melting point of 1414 °C) under low-pressure Ar (~0.1 Torr). These films showed good cycle performance for all the gravimetric, volumetric, and areal capacities (1250 mAh/g_{film}, 1956 mAh/cm^3, and 0.96 mAh/cm^2, respectively) at the 100th cycle [27]. But these anodes were built on the heavy current collector of Cu. On the other hand, we have realized semi-continuous production of CNTs (FWCNTs) by fluidized-bed chemical vapor deposition (FBCVD) [28,29]; 200–400 μm-long few-wall CNTs (FWCNTs) with average diameters of 7–11 nm and specific surface areas of ~400 m^2/g are synthesized with carbon purity of ≥99 mass% and carbon yield of 40–70%. The FWCNTs herein are much longer (with high aspect ratio) than the commercially available CNTs, and easily yield binder-free self-supporting composite papers such as the activated carbon (90 mass%)-CNT electrode for supercapacitors [30,31], MnO_2 (60–90 mass%)-CNT pseudocapacitive electrodes [32], and $LiCoO_2$ (99 mass%)-CNT cathode, graphite (99 mass%)-CNT anode, and their full-cell LIBs [3].

In this work, we report rapid and high yield production of SiNPs in a few seconds at 20%–60% from bulk Si by our original RVD process customized for SiNPs instead of porous Si films. And we realized self-supporting SiNP-CNT films via the simple co-dispersion and co-filtration process of the SiNPs and the long CNTs by FBCVD. With the aid of carbon coating by CVD [33], the SiNP-CNT composite films realized balanced gravimetric, volumetric, and areal capacities.

2. Experimental

2.1. Synthesis of SiNPs by rapid gas-evaporation method

We plan to use inexpensive, bulk Si source such as disposed Si solar cells and metallurgical grade Si in future. But in this work, Si wafer (B-doped, resistivity: 0.5–1.0 Ω cm, thickness: 625 μm) was used as the well-defined Si source. Its piece was treated with 5 mass % hydrogen fluoride (HF) solution for 1 min to remove native oxide layer, and then rinsed with purified water. The gas-evaporation apparatus is schematically shown in Fig. 1a. The Si source

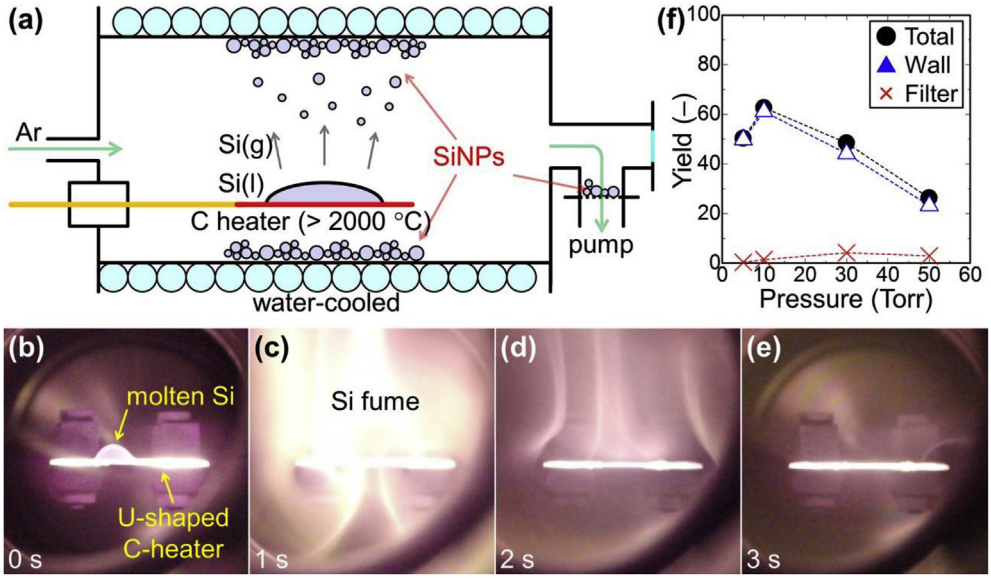

Fig. 1. Synthesis of SiNPs by rapid gas-evaporation method. (a) A schematic of the gas-evaporation apparatus. (b–e) Photographs of the rapid Si evaporation process in 10 Torr Ar taken at different time t after Si melts. (f) Yields of SiNPs at different P_{Ar}. The video (Movie S1) during the gas-evaporation process can be viewed online.