



Embedding nano-silicon in graphene nanosheets by plasma assisted milling for high capacity anode materials in lithium ion batteries



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H I G H L I G H T S

- Discharge-plasma assisted milling is used to produce a nano-Si/graphene nanosheets composite.
- Nano-Si are homogeneously embedded in the *in-situ* formed graphene nanosheets.
- The graphene nanosheets much enhance the cycling stability and rate capability.
- Full cell with good performance demonstrates a satisfying utilization of the composite.

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The lithium storage performance of silicon (Si) is improved substantially by forming composite of nano-Si particles embedded homogeneously in graphene nanosheets (GNs) using a simple discharge plasma assisted milling (P-milling) method. The synergistic effect of the rapid heating of the plasma and the mechanical ball mill grinding with nano-Si as nanomiller converted the graphite powder to GNs with the integration of nano-Si particles in the *in-situ* formed GNs. This composite structure inhibits the agglomeration of nano-Si and improves electronic conductivity. The cycling stability and rate capability are enhanced, with a stable reversible capacity of 976 mAhg⁻¹ at 50 mA g⁻¹ for the P-milled 20 h nano-Si/GNs composite. A full cell containing a commercial LiMn₂O₄ cathode is assembled and demonstrated a satisfying utilization of the P-milled nano-Si/GNs composite anode with stable working potential. This composite shows promise for application in lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs) are important power sources in a variety of applications, including portable electronic devices and home electronics, and their use is now being expanded to EV. These applications require LIBs with high energy density [1,2]. Much effort has therefore been devoted to developing higher capacity anode materials to substitute currently used graphite anodes with low theoretical capacity limitation (372 mAhg⁻¹) [3,4]. Many metals and semiconductor materials, which can react reversibly with lithium, such as Al, Si, Ge, Sn, Sb, have therefore attracted great interest as alternatives [5]. Among these, Si-based materials are the most promising alternative because of their low cost, natural abundance and especially their highest theoretical capacity

(4200 mAhg⁻¹, corresponding to the Li₂₂Si₅ alloy) [6–8]. However, poor cycleability, which is caused by structural failure and pulverization because of the huge volume change (>300%) of Si during Li⁺ insertion and removal, hinders its practical application [9]. In addition, the low intrinsic electronic conductivity of Si usually leads to an inferior rate of performance and lower reversible capacity.

Much effort has been made to solve these problems. The most common approach is to prepare composites with nano-Si particles/clusters dispersed uniformly in a carbonaceous matrix. The matrix is able to buffer the large volume expansion and enhance Si conductivity during cycling [10–13]. Different kinds of carbonaceous materials combined with nano-Si, such as graphite [14–16], pyrolysed carbon [17], mesoporous carbon [18], and carbon nanotubes [19] have been investigated using this approach. A new type of carbonaceous material, graphene nanosheets (GNs, 3–6 nm in thickness) [20], possess superior electrical conductivity, good flexibility, and chemical stability [21,22]. They are therefore a

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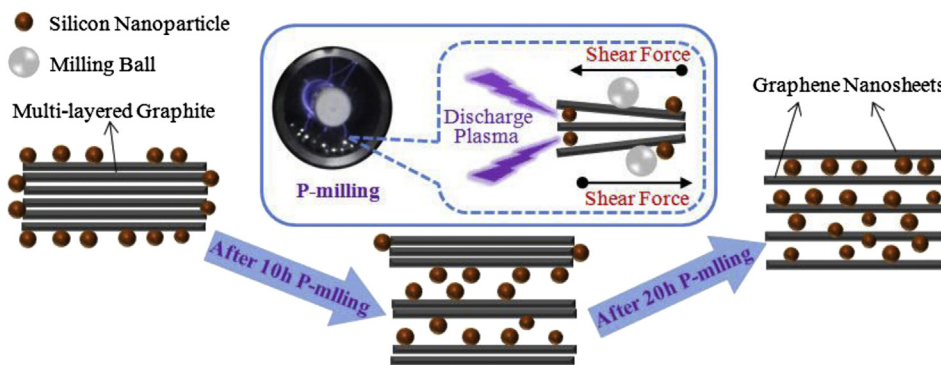


Fig. 1. Schematic illustration of nano-Si/GNs composites preparation by P-milling.

suitable matrix or additive for Si-based composite anode materials [23]. GNs have been produced by several techniques, including the mechanical peeling-off of graphite [24,25], chemical vapor deposition (CVD) [24,26], and chemical or thermal reduction from graphite oxide [27,28]. However, for Si-based anode materials, many difficulties still exist in the utilization of graphene by the mechanical peeling-off of graphite and CVD which may be complex and expensive for mass production. Widely reported preparation routes for Si/GNs composites based on graphite oxide require harsh conditions such as strong oxidizing and reducing reagents, high temperature, and precise times and reactant ratios, leading to a laborious and time-consuming preparation process [24,29,30]. It is also difficult to obtain highly dispersed nano-Si particles in the as-prepared GNs, which is a key factor in achieving good performance [27,31], by simply mechanical blending.

Dielectric barrier discharge plasma assisted milling (P-milling) is different from conventional mechanical milling in that it has a synergistic effect of the rapid heating of the discharge plasma and the impact stress of mechanical milling. This method has been used successfully to prepare Sn/graphite composite anodes for LIBs [32], where Sn particles could be refined rapidly and be well-dispersed in the graphite matrix. This leads to an enhanced cyclic performance of the LIB anode. GNs have not been synthesized in P-milled Sn–C composite materials [32,33]. Here, we report on a one-step synthesis method for the efficient production of nano-Si/GNs composites on a large scale by P-milling. We have used rigid nano-Si particles as nanomillers to peel GNs from micro-sized graphite *in-situ* in the P-milling process. The presence of GNs, as well as the high-dispersion state of nano-Si particles in the GN matrix enhances the cycling stability and rate capability of the composite electrodes.

2. Experimental

2.1. Material preparation

Nano-Si powder (99.9% purity, 50–100 nm in size, Xuzhou Jiechuang New Material Technology Co., Ltd) and natural graphite (99.9% purity, 30 μm in size, Shanghai Colloid Chemical Plant) were used as raw materials. A 30:70 mass ratio of nano-Si to graphite powder was mixed and placed in a stainless steel vial with stainless steel balls. The mass ratio of ball to powder was 50:1. The powder mixture was treated by P-milling for 5, 10 and 20 h without pre-treatment to produce nano-Si/graphite composite samples termed P-5h, P-10h, and P-20h, respectively. Milling was conducted under pure argon atmosphere with a vibration type ball mill (milling cylinder vibration with double amplitude of 7 mm and frequency of 24 Hz). Details of the P-milling have been described previously [32,34,35]. For comparison, nano-Si powder was mixed with

graphite by manual grinding in air to obtain a nano-Si/graphite mixture sample termed P-0h.

2.2. Material characterization

Materials were characterized using an XRD (Philips) with Cu-K α radiation, a laser Raman spectrometer (Horiba) with 632.81 nm laser, a field emission SEM (Carl Zeiss Supra 40), and a TEM (JEOL

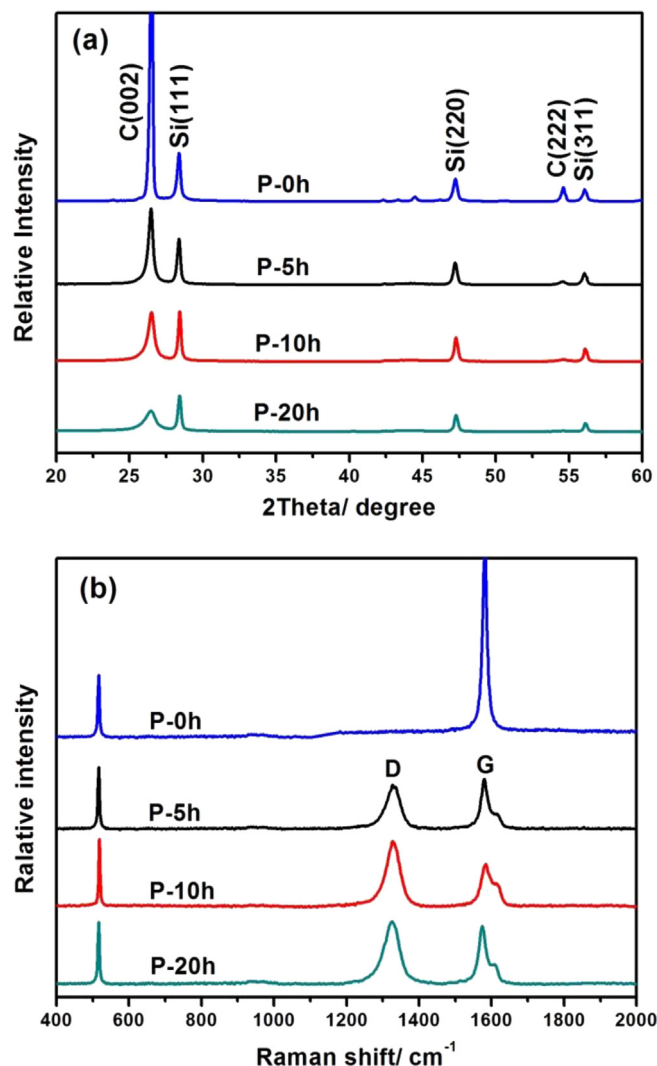


Fig. 2. (a) XRD and (b) Raman spectra for P-5h, P-10h, and P-20h nano-Si/graphite composites. Nano-Si/graphite P-0h mixture provided for comparison.

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