A novel anode material for lithium-ion batteries: silicon nanoparticles and graphene composite films

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Abstract. Silicon nanoparticles (Si NPs), with tremendous theoretical capacity, have been extensively studied how to be combined with graphene to form stable anodes for lithium-ion batteries. In this paper, a novel approach, chemical vapor deposition (CVD), is proposed to synthesis Si NPs and graphene composite film anode. Si NP s are well dispersed with carbon nanotubes in N methyl pyrrolidone solvent, spin-coated onto Cu foil as substrates to grow graphene, and successively and diversely embedded in graphene film, which is fabricated into anodes for lithium-ion batteries with high capacity of 1115.2 mAh/g. It is demonstrated a possible and promising method to prepare anode material for lithium-ion batteries.

1. Introduction

Because of high energy, long cycle life and low cost, lithium-ion batteries have become the preferred batteries for most portable electronic devices [1]. Although graphite is widely used in lithium-ion battery anode materials, its relatively low specific capacity (372 mAh/g) and poor charge-discharge capacity severely limit the lithium storage performance of lithium-ion batteries [2,3]. However, the excellent electrical and mechanical properties of low-dimensional carbon materials can be expected to be applied to lithium-ion batteries to improve the lithium storage capacity of materials. Graphene and carbon nanotube are the most remarkable carbon materials and their lithium storage capacity is much higher than that of traditional graphite materials. Graphene and carbon nanotube have excellent physical and chemical properties such as conductivity, thermal conductivity, and mechanical strength [4-8]. They have become one of the most promising anode materials for lithium-ion batteries.

In order to further improve the energy density of lithium-ion batteries, scientists have been trying to find anode materials with higher theoretical specific capacity, such as transition metal oxides, Fe-based ferrites, lithium titanate and silicon [9-11]. Among them, silicon is considered as one of the most ideal anode materials due to its ultrahigh theoretical specific capacity (4200 mAh/g) and similar operating voltage compared with graphite anode [12]. Nevertheless, the low electrical conductivity and huge volume change of silicon in the process of alloying and dealloying will lead to collapse of anode, sharp decline of reversible specific capacity and poor cycling performance [13]. Compared with silicon, silicon nanomaterials have higher cycle stability and reversible capacity [14,15]. A great number of
studies have been performed about silicon nanomaterials as the anode material for lithium-ion batteries, such as the zero-dimensional silicon nanoparticle [16,17], one-dimensional silicon nanowire [18,19], and two-dimensional silicon film [20,21]. The reducing of silicon particle size will promote the rapid diffusion of lithium-ion, shorten the transmission path between the silicon nanoparticles and the electron in the electrolyte, and reduce the transmission time [15]. As a result, the silicon nanoparticles can effectively improve the charge-discharge performance of lithium-ion batteries. However, the enormous bulk variation still exists and obstruct the long-term stability of silicon-made anodes. It has been proved that graphene, such as graphene oxide [22], graphene paper [23], contributes to hoist reversible capacity and cycling stability. The anode made of silicon nanoparticles embedded in the interlayers of graphene paper had as high as 2200 mAh/g after 50 cycles, showing robust cycling stability. The silicon nanoparticles and graphene composite anodes show their advantages to improve the electrochemical performance of lithium-ion batteries [24-27].

In this paper, using the carbon nanomaterials, such as graphene [28], as the carbon matrix, copper foil as the catalytic substrate and methane as the carbon source, the silicon nanoparticles/graphene composites were directly grown on the copper foil by chemical vapour deposition method. Unlike the physical combination between carbon and silicon [22,23], the effective contact between the silicon nanoparticles/graphene composite films and the copper foil collector was achieved without the use of binder, which would improve the energy density of lithium-ion batteries. The addition of carbon nanotubes could not only effectively disperse silicon nanoparticles on graphene, but also improve the electrical conductivity and cycle stability of the composite materials. By continuously optimizing the experimental conditions and process parameters, the composite graphene films were successfully applied to the anode of lithium-ion batteries, and it had good electrochemical performance and excellent reversible capacity, which would further promote the application of graphene and silicon nanoparticles composite films in the lithium-ion battery anode materials.

2. Materials and methods

2.1. Materials
Commercial silicon nanoparticles (Si NPs, 99.9%, Aladdin) with a radius of about 30 nm were used as the active material of silicon, and copper foil (Alfa Aesar) with purity of 99.8% was used as the catalytic substrate.

2.2. Preparation of composite materials of silicon nanoparticles and graphene films

![Figure 1](image-url)

**Figure 1.** The schematic of the progress of Si NPs/graphene composite anode.

A certain mass of silicon nanoparticles was decentralized in N methyl pyrrolidone solvent (NMP) to prepare different concentrations of Si NPs/NMP dispersions. The dispersion was treated by ultrasonic unit to make Si NPs disperse sufficiently in the NMP. To avoid the agglomeration of Si NPs, carbon nanotubes were introduced as an auxiliary dispersing agent. Then, the dispersion was spin-coated onto the surface of polished copper foils. To remove NMP, the spin-coated copper foils were placed in the oven for 10 min under 100°C. Next, the copper foil coated with silicon nanoparticles was placed in the heating zone of the single temperature zone tube furnace. After the tube was pumped to basic vacuum and cleaned three times, the hydrogen gas, at 50 sccm, was passed into the tube as carrier gas. The temperature of graphene growth zone was raised to 1000°C, while the CH₄ with a flow rate of 0.2
sccm was used as the carbon source. After 5 min, turn off the CH₄ carbon source and lower the chamber temperature to room temperature under H₂ atmosphere as shown in figure 1.

2.3. Assembly of lithium-ion battery
The anode materials of the lithium-ion battery could be directly grown on the copper foil catalytic substrate, so no conductive agent and binder were needed. The electrochemical performance test was carried out with CR-2032 type button type lithium ion battery. The cathode material was lithium iron phosphate (LiFePO₄). The electrolyte was a mixed solution of ethylene carbonate (EC) and dimethyl-carbonate (DMC) (volume ratio of 1:1) with 1M lithium hexafluorophosphate (LiPF₆). And the membrane was Celgard 2320 porous polypropylene film. The working electrode, diaphragm, metal lithium slice and filling material (foam nickel) were placed in the battery shell in the argon glove box, and a proper amount of electrolyte was injected. The battery was sealed by an encapsulation machine.

3. Results and discussion

![Figure 2](image)

Figure 2. SEM pictures and Raman spectra of Si NPs/graphene composite film with Si NPs of 3 mg/ml in (a) and (d), 5mg/ml in (b) and (e) and 8mg/ml in (c) and (f), respectively.

Different concentrates of Si NPs/NMP dispersions were prepared and spin-coated on electrochemically polished Cu foil at 5000 rpm, on which Si NPs/graphene composite films were prepared by CVD method. Individual particle can be observed on the composite film as shown in figures 2(a), 2(b) and 2(c). When the concentrate of Si NPs increasing from 3 mg/ml to 8 mg/ml, the particles on the film share less space with each and even the unwanted agglomeration of silicon particles comes into being, which would impair the performance of Si NPs/graphene film in terms of storing Li and cycling stability. Besides, the unting of Si NPs also causes influence on the composite
film quality. The Raman Spectra of Si NPs/graphene film with various Si NP concentration, displayed in figures 2(d), 2(e) and 2(f), imply that high concentration of Si NP would cause rising of D peak and descending of 2D peak, which signifies more defects turn up on the graphene. Each Si NP would lead to a hole and more edge on graphene film and consequently introduce more defects on the film. In Raman spectrum of graphene, D peak represents the defect of graphene film and is directly related with the amount of edge in the film [29], which may explain more Si NPs would increase the area of D peak.

Figure 3. SEM surface profile picture of Si NPs/graphene composite film prepared with 3 mg/ml Si NPs and MWCNT of (a) 1 mg/ml, (b) 1.5 mg/ml, (c) 2 mg/ml, (d) 3 mg/ml, (e) 4 mg/ml and (f) 5 mg/ml.

For Si having ideal ultrahigh capacity 4200 mAh/g [15], more Si NPs mean more capacity to store Li. While, high concentrate of Si NPs would have negative effect to Si NPs/graphene composite film. Hence, in this work, multi-walled carbon nanotubes (MWCNT) were hired as extra auxiliary dispersing agent to further improve the dispersion of Si NPs and the quality of composite graphene film. Different concentration of MWCNT were attempted to apply in 3 mg/ml Si NPs/graphene composite film. The surface profiles of films with several concentrate MWCNT were exhibited in figure 3, by which it implies that the dispersion effect of MWCNT seems has weak correlation with the amount of MWCNT in the fabricated composite films. Before the importing of MWCNT, the surface of composite film, showed in figure 2(a), still smooth and flat in space areas. Conversely, the surface SEM pictures displayed in figure 3 commonly exhibit fibrous feature among particles. Taking Raman spectra of Si NPs/graphene film with MWCNT of different concentration in figure 4 into consideration, the quantity of MWCNT appears to help enhancing the Raman signal of graphene and D peak, representing the defect level of graphene film, looks like to be depressed by introducing MWCNT. This may due to the addition of MWCNT because graphene and carbon nanotube share the similar Raman spectrum. On the other hand, excess MWCNT would increase specific surface area of as-grown composite film, which may give rise to higher consuming of Li⁺ to form surface electrolyte
interphase film at the anode and cause descending energy density of the lithium-ion batteries.

**Figure 4.** Raman spectra Si NPs/graphene composite film prepared with different concentrates of MWCNT.

**Figure 5.** SEM pictures and Raman spectra of Si NPs/graphene composite film with 0.5 mg/ml MWCNT and Si NPs of 3 mg/ml in (a) and (b), 5 mg/ml in (c) and (d) and 8 mg/ml in (e) and (f), respectively.

Thus, lower concentration of MWCNT, 0.5 mg/ml, was tried adding into the dispersion solution and turned out similar with the anti-agglomeration effect of higher concentration. Figure 5 is the
characterization of graphene composite films prepared under different concentration of Si NPs with 0.5 mg/ml of MWCNT in dispersion solution. Figures 5(a), 5(c) and 5(e) represent the dispersions of 3 mg/ml Si NPs, 5 mg/ml Si NPs and 8 mg/ml Si NPs in NMP with 0.5 mg/ml of MWCNT, respectively. When the concentration of Si NPs increases, the gaps among the particles get obviously smaller. However, compared with those without MWCNT in figure 2, the dispersion of the Si NPs on film remained high quality. It seems that the addition of MWCNT successfully retains certain gap among Si NPs on the film and MWCNT has contribution to prevent the occurrence of agglomeration. According to Raman spectra in figures 5(b), 5(d) and 5(f), the ratio of intensity of D peak and G peak decreases from 1.31 down to 1.20 and then increases to 1.39 again. Besides, the ratio of integral of 2D peak and G peak greatly boosts from 0.56 up to 2.33 and declines to 1.91, which infers that the quality of the composite films varies with the concentration of Si NPs and 5 mg/ml Si NPs with 0.5 mg/ml MWCNT reach the balance between the dispersion effect of Si NPs and the quality of graphene.

To further study the electrochemical lithium storage capacity of silicon nanoparticles and graphene composite films applied to the anode of lithium-ion batteries, cyclic voltammetry was carried out on the as-prepared lithium-ion batteries. Graphene composite films prepared with 5 mg/ml Si NPs and 0.5 mg/ml MWCNT/NMP dispersions, the combination with best graphene quality, was used as anode materials for lithium-ion batteries. Figure 6 shows the CV test results with 6 times cycles. In the charge process of the first cycle, an obvious peak appears at 1.1 V, which corresponds to the irreversible decomposition of the electrolyte and the formation of solid electrolyte interfacial and will disappear in later cycles. The reversible capacity retains 1115.2 mAh/g after 6 cycles, which almost 3 times than the theoretical specific capacity of the graphite electrode (372 mAh/g). In the discharging process, the oxidation peaks at 1.0 V correspond to the process of lithium-ions de-intercalating from the silicon nanoparticles and graphene composite films. It is remarkable that the cyclic voltammograms of the two electrodes are almost identical in shape starting from the second cycle, which shows that the solid electrolyte interface and stable structure have formed on the electrode surface. The spike near 0 V appearing in each cycle, may be related to the intercalation of lithium-ions into the silicon nanoparticles and graphene composite film electrodes. However, the composite anode was found malfunctioned after 6 cycles, which indicated the unsteady structure of the composite anode. From the surface profile of the anode in figure 3(c), although the Si NPs seems embedded well in graphene film, the graphene film turns out too thin to keep Si NPs in its positions in long-term cycles.

4. Conclusions
In conclusion, we have successfully synthesized the silicon nanoparticles and graphene composite
films with integrity and uniformity by chemical vapor deposition. And the composite films can be applied as the anode of lithium-ion batteries. The addition of MWCNT can effectively resist the agglomeration of Si NPs and improve the dispersion among Si NPs. Different concentrations of Si NPs and MWCNT were attempt and turned out that 5 mg/mL Si NPs with 0.5 mg/mL MWCNT dispersed in NMP were the best combination. Then, the prepared composite film was assembled as the anode of a CR-2032 button lithium ion battery and the reversible capacity of the anode reached 1115.2 mAh/g after 6 cycles, which inferred the capacity potential of such composite film anode. However, the anode lost performance after 6 cycles due to its fragile structure. In future, further studies on the reversible capacity and cycle stability of silicon nanoparticles and graphene composite films still need to be done.

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