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# Enhancement of the Cyclability of a Si/Graphite@Graphene composite as anode for Lithium-ion batteries

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## ABSTRACT

Si/Graphite@Graphene composite has been prepared by an improved spray-drying method followed by heating treatment. While the thermal deposition of the precursor is determined by thermogravimetric analysis (TG-DTA), the structure of the composite is revealed by X-ray diffraction (XRD). Meanwhile, the presence of graphene is demonstrated by fourier transform infrared spectra (FI-IR) and Raman spectra studies. And scanning electron microscopy (SEM) and transmission electron microscope (TEM) images illustrate the morphology of the as-prepared material. The Si/Graphite@Graphene composite shows an enhanced electrochemical performance. At 50 mA $g^{-1}$, the Si/Graphite@Graphene sample exhibits a high initial charge capacity of 820.7 mAh $g^{-1}$, with a high initial columbic efficiency of 77.98%, the composite can still deliver high initial charge capacity of 766.2 mAh $g^{-1}$ at 500 mA $g^{-1}$, and shows superior cyclic and rate performance. Moreover, it has low impedance, which indicates that it could be used as a promising anode material for Li-ion batteries.

## 1. Introduction

There is an ever-increasing demand for batteries exhibiting higher energy and power densities due to the continued growing energy storage needs for portable electronic devices and electrical vehicles (EV) [1,2]. But the commercial anode graphite for Li-ion batteries is limited by its low theoretical capacity (372 mAh $g^{-1}$), which cannot meet the ever increasing energy density requirements for applications [3–5]. In this regard, Si-based material is a highly promising anode material for high-power lithium ion batteries because it has high theoretical specific capacity (4 200 mAh $g^{-1}$), low lithiation/delithiation voltage (0.02~0.6 V vs. Li/$Li^+$) and low cost [6–8].

However, the low electronic conductivity and especially fast capacity fading owing to the huge volume change (~320%) during the charge/discharge processes for pure Si, severely hindered its practical application in lithium ion batteries [9,10]. And several strategies, including other metal addition [11,12], nanostructure design (nanowires [13,14], nanotubes [15,16], Si nanoparticles [17], hollow materials [18], thin film [19,20], porous materials [21], carbon-based composite [22–24] and other methods [25,26], have been adopted to address these problems. Among these researches, carbon matrixes have been considered to buffer large volume expansion/shrinkage during the charge/discharge processes, increase the electronic conductivity and enhance the electrochemical performance. Due to its superior electronic conductivity, large specific surface area, excellent structural flexibility, high surface to volume ratio, as well as urchin thickness, graphene becomes a spotlight in fields of energy conversion [27,28]. Meanwhile, Graphene is an ideal 2D support, similar to the conventional carbon matrix, which can also provide a matrix for nano-Si particles [29,30].

In this paper, we propose a facile spray-drying technology to prepare micron-sized spherical or spherical-like Si/Graphite@Graphene composites as anode material for lithium ion batteries. The effect of graphene on structure, morphology and electrochemical performance of Si/Graphite@Graphene anode materials was investigated.

## 2. Experimental

### 2.1. Preparation of Graphene oxide and Si/Graphite@Graphene

Graphene oxide was synthesized via an improved Hummers' method [31]. Typically, 5.0 g $KNO_3$ and 5.0 g flake graphite were put into 200 mL concentrated sulfuric acid (98 *wt.*%). Then 20.0 g $KMnO_4$ was slowly added into the above system in about 20 minutes under strong stirring, and the temperature was kept below 2 °C in ethanol bath. After reacting for 2 h, the mixture was transferred into 35 °C water bath and stirred for 2 h. Subsequently, 400 mL deionized water was continuously added into mixture solution and the temperature was carefully controlled below 100 °C. The mixture was then transferred into 95 °C oil bath and stirred for

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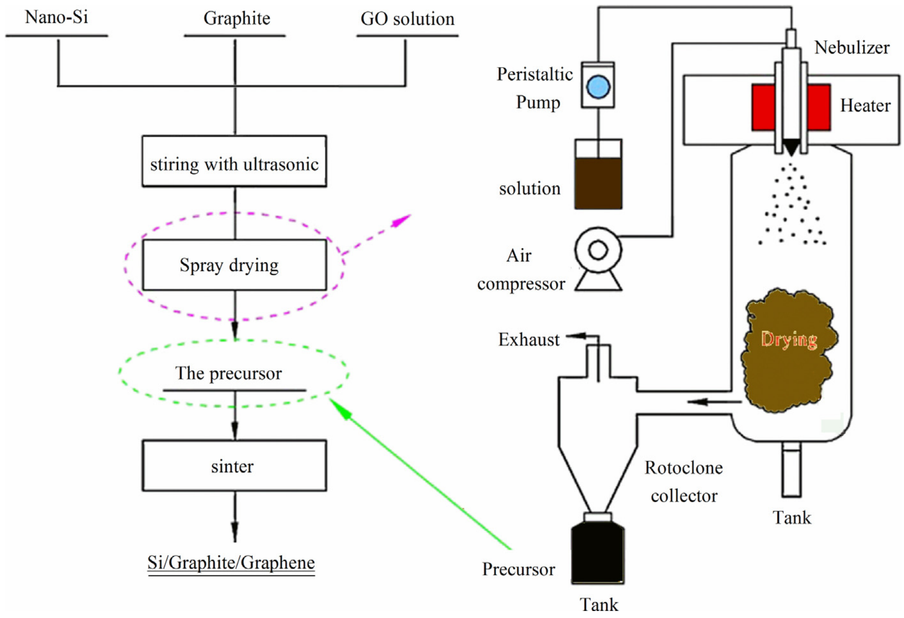

**Fig. 1.** The experimental procedure and apparatus.

2 h. Eventually, 400 mL water and 30 mL $H_2O_2$ (30 *wt*.%) were subsequently added into the mixture, and the mixture turned from dark red to bright yellow in a few minutes. After continuously stirring for 30 minutes, the solution was washed with 1 L dilute hydrochloric acid (1 *wt*.%) and about 2 L water until the pH of the solution reached a constant value of about 5.0. The graphene oxide (GO) was collected by gradient centrifuge, and dried by vacuum freeze-drying at -60 °C for 72 h to obtain GO powders.

Si/Graphite@Graphene composite was prepared via a simple spray-drying method. The weight ratio of Si, Graphite and GO was designed to 2:8:5. The experimental procedure and apparatus of spray drying are presented in Fig. 1. GO powders were dispersed into alcohol solution (5%) by ultrasonic treatment, and the GO content is ~2 mg $mL^{-1}$. Then nano-Si (~30 nm, Shuitian ST-NANO Science & Technology Co., Ltd, Shanghai, China) and graphite (~500 nm, Tianhe Graphite Co., Ltd, Qingdao, China) powders were added into the GO suspensions under vigorous stirring and dispersed uniformly. Then the mixture was dried in a spray-dryer by hot air, the inlet and outlet air temperatures were 160 °C and 110 °C. Finally, the spray dried precursor was sintered at 450 °C for 3 h under argon atmosphere in a tube furnace to yield Si/Graphite@Graphene composite.

### 2.2. Materials characterizations.

*X-ray Diffraction*.— Crystalline phase analysis of synthesized material were taken from the powder X-ray diffraction (XRD, Rint-2000,Rigaku) using Cu Kα radiation ($\lambda = 0.15406$ nm) in the range of $2\theta$=5°-80°.

*Thermal analysis*.— Thermogravimetric analysis of the spray dried powder was performed on a SDT Q600 TG (TE, USA) apparatus between room temperature and 600 °C at a heating rate of 10 °C $min^{-1}$ in argon atmosphere.

*FI-IR testing*.— Fourier transform infrared spectra (FI-IR) of the samples and graphene oxide from 400 to 4000 $cm^{-1}$ were recorded on a WQF-410 spectrophotometer (Beijing Secondary Optical Instruments, China)

*Raman testing*.—Raman spectra from 400 to 3500 $cm^{-1}$ were obtained from WiTec Alpha300 system applying 632.8 nm laser light.

*SEM testing*.— The morphology of the Si/Graphite@Graphene sample was observed by scanning electron microscopy (SEM, JEOL, JSM-5600LV).

*TEM testing*.— The microstructure of the composite was examined by a Tecnai G12 transmission electron microscope (TEM).

*Electrochemical Testing*.— Coin cells (20 mm diameter and 2.5 mm thick) were used for testing the electrochemical performance of the samples. Negative electrodes were prepared by mixing the active material, Super P and solution of the binder (5 *wt*.%, BTR Co., Ltd, Shenzhen, China) in a weight ratio of 8:1:20 to form a slurry. The slurry was coated on Cu foil and dried in an oven for 12 h at 120 °C. The electrochemical cells used a single lithium metal foil as the counter electrode, a polypropylene micro-porous film as the separator and 1 M $LiPF_6$ in EC:EMC:DMC (1:1:1, v/v/v) as the electrolyte. Cells were assembled in an argon-filled glove box. The cells were charged and discharged using a Neware battery tester (Neware, Shenzhen) in the cut-off potential ranges of 0.01-2.00 V. The electrochemical impedance spectroscopy was carried out with a CHI660A electrochemical analyzer and recorded by applying an AC voltage of 5 mV amplitude in the 0.01 -$10^5$ Hz frequency range.

## 3. Results and discussion

TG/DTA was performed for the spray dried precursor and the profiles are shown in Fig. 2. The TG curve presents three steps of weight loss and DTA curve displays two main corresponding endothermic peaks. The first step occurs between room temperature and 100 °C, which is mainly attributed to the removal of physically absorbed and crystallized water, corresponding to a small endothermic peak around 50 °C. The following step between 100 and 280 °C is resulted from the decomposition of GO to form graphene. So there is a main endothermic peak at 250 °C in the DTA curve. The final small weight loss from 280 to 600 °C may be due to the further reduction of GO. Above 350 °C, the change of weight loss becomes insignificant when the temperature is further increased to 600 °C, which indicates the full reduction of GO, and 450 °C was chosen to be the reduction temperature. The graphene content in Si/Graphite@Graphene was estimated to 19.95% at 450 °C,