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Short communication

# Facile synthesis of binder-free reduced graphene oxide/silicon anode for high-performance lithium ion batteries

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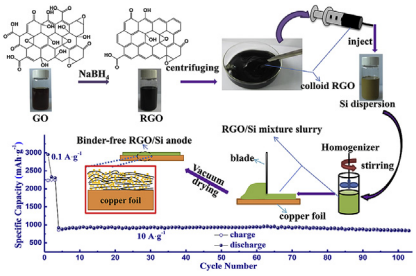
## HIGHLIGHTS

- A binder-free RGO/Si composite anode was fabricated by a straightforward coating method.
- The composite anode possesses a unique multi-layered architecture.
- The composite anode exhibits a high reversible capacity and excellent cycle performance.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A novel binder-free reduced graphene oxide/silicon (RGO/Si) composite anode has been fabricated by a facile doctor-blade coating method. The relatively low C/O ratio plays an important role for the fabrication of the bind-free multilayered RGO/Si electrode with silicon nanoparticles encapsulating among the RGO sheet layers. The RGO provides the electron transport pathway and prevents the electrode fracture caused by the volume changes of active silicon particles during cycling. The RGO/Si composite anode with a silicon content of 66.7% delivers a reversible capacity of 1931 mAh $g^{-1}$ at 0.2 A $g^{-1}$ and still remains 92% of the initial capacity after 50 cycles.



## 1. Introduction

As a promising alternative to the commercial graphite anode for lithium ion batteries (LIBs), silicon (Si) has attracted considerable attentions because of its high theoretical capacity of 4200 mAh $g^{-1}$ corresponding to the formation of $Li_{4.4}Si$, relatively low charge/discharge potential plateaus, natural abundance and environmental friendliness [1–3]. Unfortunately, silicon undergoes a dramatic volume change (>300%) and significant structure stress during the lithiation and delithiation processes, leading to a severe cracking/pulverization of the electrodes and a consequently rapid capacity decay during the repeated cycling [4]. Many efforts have been made to enhance the electrochemical performance in terms of alleviating the pulverization of electrode and enhancing the electrical conductivity of silicon-based composite. Nanostructured Si, such as Si nanowires [5–7], Si nanotubes [8,9] and hollow Si nanospheres [10] have shown superior electrochemical

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performance compared with micro-sized Si particles. An introduction of second phase as matrix is further considered to obtain high stability of Si-based anodes, such as various silicon/carbon nanocomposites [11–13], where carbon matrix can not only improve the conductivity of electrodes, but suppress the huge volume change of silicon. In addition, the utilization of electrolyte additive and new binder has also been reported to improve the electrochemical performance of the silicon anode materials [14–16].

Recently, graphene-family materials have attracted much attention as anode materials for lithium ion batteries thanks to the excellent mechanical and electronic properties derived from the graphene precursor [17–19]. Various nanostructured composites of silicon and graphene-family materials, which can be defined as the silicon/graphene-based materials, have been synthesized by different routes such as mechanical blending [20–22], thermal reduction [20,23,24], chemical vapor deposition [25] and cross-linked interactions [26], showing the improved electrochemical performance in comparison with pristine silicon. In addition, conventional fabrication of LIB electrodes usually need an addition of polymeric binder to maintain close contact among the active materials, even between the particles with metal current collector, which will not only reduce the overall storage capacity of electrodes, but decrease the available reaction area of the active materials and thus increase the electrochemical polarization of the electrodes. As an important member of the graphene-family materials, the reduced graphene oxide (RGO) has been used in the fabrication of binder-free Si-based electrode [27–32]. Wang and coworkers obtained a binder-free, free-standing RGO/silicon thin film by a filtration of RGO/Si nanoparticles suspension and subsequent heat treatment in argon [27]. However, a low capacity was delivered due to the low conductivity of the free-standing electrode caused by the lack of metallic current collector. Chang and coworkers assembled the alternating Si/RGO layers on porous Ni foams and obtained a binder-free alternating Si/RGO anode with a multilayered nanostructure, which showed a high capacity and excellent stability [29]. Unfortunately, this architecture of alternating Si/RGO layers obtained from a multiple deposition of Si and GO was quite complicated for commercial application.

Herein, a colloid RGO was obtained to fabricate a binder-free Si/RGO composite anode with a multilayered structure by a simple one-step coating method. In this unique nanoarchitecture, the flexible RGO sheets can not only effectively accommodate the volume change of silicon particles encapsulated among RGO layers, but also provide an electronic conductive network for the binder-free composite electrode. The rational structural and electrical integrity of the binder-free electrode make it behave a superior electrochemical performance for lithium ion batteries.

## 2. Experimental

### 2.1. Preparation of colloid RGO

Graphite oxide (GO) was synthesized by a modified Hummers method in a two-step oxidation process [33]. To prepare RGO, 400 mg GO was firstly dispersed in 400 mL ultrapure water with sonication for 2 h to form a stable GO dispersion. Under vigorous stirring, 4 g $NaBH_4$ was then added in GO suspension to react at 80 °C for 5 h. After cooling down to room temperature naturally, a stable, black aqueous dispersion of RGO was obtained. The obtained RGO dispersion behaved an excellent stability, and no obvious flocculation and precipitates were found even after standing for 24 h (Fig. S1a). A black colloid RGO was collected after the repeated centrifugation with DI water. 30 mg RGO was obtained by drying 3 g RGO colloids, corresponding to a RGO content of 1 wt% in the colloids.

### 2.2. Preparation of binder-free RGO/Si composite anode

Firstly, 20 mg silicon nanoparticle powders (50–150 nm, Shanghai st-nano science and technology Co., Ltd) were dispersed in 2 g ultrapure water via 2 h sonication. 1 g colloid RGO (10 mg RGO inside) was then added into the suspension by an injector, and then the homogeneous mixture slurry containing RGO/Si nanoparticles was obtained by a PB100-SP04 homogenizer. The binder-free RGO/Si composite anode was prepared by casting the mixture slurry on a clean copper foil with a doctor blade and drying overnight in a vacuum oven at 100 °C. The electrodes were cut with a metal cutter into circular pieces with a diameter of 14 mm for the coin cell assembling. The mass loading of RGO/Si is approximately 0.136 mg $cm^{-2}$. For comparison, the RGO anodes without Si nanoparticles were also fabricated using the same method.

### 2.3. General characterization

The samples were analyzed with an X-ray powder diffractometer (Empyrean) using Cu-Kα (λ = 1.5406 Å) from 5° to 80°. Raman spectra were recorded on a Raman system (HR800, JY Company) with a 457.9 nm laser. The morphology and energy dispersive spectroscopy (EDS) were characterized on a field-emission scanning electron microscope (FESEM, FEI Helios Nanolab600i). High-resolution transmission electron microscopy (TEM, Hitachi, Japan) was used to obtain the detailed structure information. The electrical conductivity was measured using a four-point probe method (SB100A/21A, Shanghai Qianfeng Electronic Instrument Co., Ltd.) at room temperature.

### 2.4. Electrochemical measurements

The 2025 coin-type cells were assembled to evaluate the electrochemical properties of the samples. The binder-free RGO/Si composite anode was used as working electrode. In addition, pure Si electrodes were prepared by mixing Si nanoparticles, acetylene black, and sodium carboxymethyl cellulose (CMC) with a weight ratio of 8:1:1 and casting onto copper foil. Lithium foil was used as counter/reference electrode, and a Celgard 2400 microporous polypropylene membrane was used as the separator. The electrolyte was a solution of 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (EC: DEC = 1:1 v/v). The cells were assembled in a high purity argon filled glove box (moisture and oxygen levels less than 1 ppm). Galvanostatic cycling experiment was carried out on a battery test system (Neware, BST-5V5mA) with a voltage ranging from 0.01 to 1.5 V. All the measurements were carried out at room temperature.

## 3. Results and discussion

The schematic diagram of the fabrication process of binder-free RGO/Si composite anode was illustrated in Fig. 1a. A simple coating process was employed with a sharp blade to prepare the binder-free RGO/Si composite anode. Fig. 1b shows the optical images of copper foil, binder-free RGO and the RGO/Si composite anodes. There is no noticeable exfoliation for the RGO/Si active materials from the bended and folded electrodes, indicating that the integrality of the RGO/Si active particles with the current collector is well maintained even without any polymeric binder in the electrodes.

The XRD patterns of Si, graphite, GO, RGO and RGO/Si nanocomposite are shown in Fig. 2a. From the diffraction pattern of GO sample, the sharp diffraction peak at around 26.5° corresponding to