



# Preparation of sandwich-like phosphorus/reduced graphene oxide composites as anode materials for lithium-ion batteries



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## ABSTRACT

Recently, phosphorus/carbon (P/C) composites as anode materials for lithium or sodium ion batteries have attracted intense attention owing to their high capacity, fast rate capability and long cycle life. However, the preparation methods of P/C composites were usually confined to high-energy mechanical ball milling and vaporization-condensation strategies. In this work, we reported a high-pressure-assisted spraying method to synthesize a unique sandwich-like hybrid of nanosized phosphorus particles and stacked reduced graphene oxide nanosheets (P@GS composites). The P@GS composites presented a superior cycling performance with an initial discharge capacity of 1876 mAhg<sup>-1</sup> and a reversible capacity of ~990 mAhg<sup>-1</sup> after 50 cycles. The remarkable electrochemical performance of P@GS composites could be ascribed to the sandwiched structure and the cooperative effect of phosphorus (high lithium-storage capacity) and reduced graphene oxide nanosheets (stable cyclability). Furthermore, this high-pressure-assisted spraying method was well suitable for the application in production due to its continuity, low cost and simple apparatus. The superiority of the preparation method and the highly reversible lithium storage of P@GS composites offered a promising alternative for lithium-ion battery materials.

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## 1. Introduction

Comprehensive attention has been attracted to the application of lithium-ion rechargeable batteries (LIBs) in portable devices and hybrid electric vehicles (HEV) [1–3]. While moving ahead with this application, plenty of efforts have been paid to research LIBs with features of high capacity density, long cycle life and fast rate ability. Therefore, it has long been desired to innovate new electrode materials, especially anode materials, with enhanced performance.

Red phosphorus (P) comes into the public sights as a promising anode candidate because of its chemical stability, cheapness and superior theoretical specific capacity (2595 mAhg<sup>-1</sup>) [4,5]. In spite of these advantages, the popularity of red P as anode materials is hindered by two serious problems, i. e. low electronic conductivity and severe volume expansion during the intercalation and deintercalation of Li ions. These two handicaps will make electrochemical reactions difficult and cause severe pulverization of active materials [6,7]. To overcome these drawbacks, effective approaches have been adopted by introducing carbon materials to

enhance the overall electrochemical abilities of red phosphorus anodes. As to the synthesis methods of phosphorus/carbon (P/C) composites, high-energy mechanical ball milling was adopted as a common strategy [8–10]. With the effect of long and vigorous ball-milling, large raw phosphorus particles were grinded into nanosized amorphous particles. Phosphorus nanoparticles would be homogeneously dispersed on carbon matrixes (carbon black, porous carbon and multi-walled carbon nanotubes) with stable Li or Na ion reservation [8]. Qian and co-workers [9] demonstrated that the amorphous P/carbon black composites synthesized by ball milling method delivered a reversible capacity of 2355 mAhg<sup>-1</sup> (on the basis of Li<sub>3</sub>P) and 90% of the capacity was retained over 100 cycles. Kim et al. [10] manifested that the electrochemical performance of amorphous P/carbon black anodes for Na-ion batteries could also display a long and stable cycling performance. Different from high-energy ball milling, the vaporization-condensation strategy tended to attach crystalline P on porous carbon materials [11–16]. Among the various composites, a mesoporous carbon-encapsulated crystalline P composite was synthesized by Marino et al. [12], which however delivered a limited electrochemical performance. Since vaporization-condensation process had no destruction on the structure of carbon matrixes, it was effective to employ 3D porous carbon nanofibers (PCNFs) to

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fabricate a freestanding crystalline red P/PCNFs composite [16]. Due to the good conductivity and high mechanical flexibility of porous carbon fibers, the sample showed a remarkably improved cycling and rate performance.

However, there are still some noteworthy issues existing in P/C anodes. On the one hand, ball-milling and vaporization-condensation are high-energy-consuming and discontinuous methods. On the other hand, the stable cycling and rate performance of these composites needs to be improved. Thus, it is crucial to focus on the study of preparing P/C composites in facile ways and designing effective structures with highly conductive matrix to enhance electrochemical performance. To address the preparation problems, simple hand-grinding and modified quick-freezing methods had been introduced by Dou et al. [17] and Chen et al. [18], respectively. These two strategies had provided new ways with great simplicity for the preparation of P/C composites. In order to improve cycling stability and rate performance of phosphorus electrodes, graphene material, an appealing carbon material in energy technology with superior specific surface area, high conductivity and chemical stability, has been recently employed to form P/C anodes for lithium or sodium ion batteries [18–23]. Graphene nanosheets [22] was used to hybridize with phosphorus by the common ball-milling process. Although the acquired composites as anode materials delivered enhanced cycling and rate performances, further optimization of synthesis methods was still needed in order to achieve low-cost, easy-to-make and efficient preparation.

Herein, we proposed a facile high-pressure-assisted spraying strategy to realize the hybrids of reduced graphene oxide sheets (GS) and nanosized P particles with a unique sandwich-like structure. During the ultrasonication and spraying process, aqueous graphene oxide could be synchronously reduced and converted to three-dimensional crumpled and overlapped GS with P nanoparticles attaching on. For the sandwich-like structure, the exposed P nanoparticles could benefit the storage of  $\text{Li}^+$  and the existence of sandwiched GS worked as mechanical backbones and electrical highways, guaranteeing the fast electron transport [24]. More importantly, high-pressure-assisted spraying method could achieve steady and continuous preparation of P@GS composites without complex apparatuses, high-energy consumption and further filtration processes, which would offer significant convenience in production.

## 2. Experimental

### 2.1. Preparation of red phosphorus (P) and graphene oxides (GO)

Commercial red phosphorus (Tianjin Zhiyuan Chemical Reagent Co. Ltd, 99%) was firstly wet ball-milled with water under argon atmosphere at the speed of 450 rpm for 3 hours in a milling

equipment (Pulverisette7, Fritsch, Germany). And then the milled phosphorus was freeze-dried before utilizing. Natural flake graphite (Qingdao AoKe ShiMo Co. Ltd, average diameter of 10  $\mu\text{m}$ ) was used to produce graphite oxide by a modified Hummers method [25]. With the treatment of ultrasonic and freeze-drying to the graphite oxide, the GO powders were obtained successfully. Then, P and GO powders were mixed in 7:3 (mass%) after optimization of the weight ratio.

### 2.2. Preparation and structural characterization of P@GS composites

The P@GS composites were prepared by a high-pressure-assisted spraying method at a moderate temperature. The detailed routes were as followed: firstly, the mixed P and GO precursor were dispersed in acetone (Tianjin chemical factory) at a concentration of 1 mg/mL under the strong ultrasonic treatment. After the dispersion, the hybrids were transferred to a spray gun with high purity  $\text{N}_2$  at 1 bar supplying high pressure. Finally, the hybrids were sprayed to a ground collector at atmosphere of 100 °C, then the finished samples were collected from the ground collector for further characterization without any further washing processes. The morphologies and microstructures of P@GS composites were tested by field emission scanning electron microscope (FE-SEM, S-4800, Hitachi) and transmission electron microscopy (TEM, JEM-2100). The elemental information of P@GS composites was executed by an energy-dispersive X-ray spectroscopy (EDX) system. The crystallization of P@GS composites was determined by X-ray diffraction (XRD, Bruker D8 Discover) using an  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54059 \text{ \AA}$ ). The structural characterizations of the phosphorus and carbon in the composites were investigated by Raman spectra (LABRAM-HR Confocal Laser Micro-Raman spectrometer) with an Ar laser ( $\lambda = 532 \text{ nm}$ ).

### 2.3. Electrochemical tests of P@GS composites

CR2032 half-cells were selected to characterize the electrochemical performance of P@GS composites with metal lithium as counter electrodes. The anode slurry was fabricated by blending the P@GS composites, conductive agents (carbon black) and polyvinylidene fluoride (PVDF) with 8:1:1 (mass%) in N-methylpyrrolidinone (NMP). The as-prepared slurry was coated on a copper foil and dried in the vacuum oven at 60 °C for 12 h. 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1 was used as electrolyte, and Celgard 2400 membranes were acted as separators. All batteries were packaged in a glovebox and tested after aging for 24 h. The charge-discharge performances were measured by Land testing system (BT2013, Wuhan Rambo Electronic Company, Wuhan, China) at 100  $\text{mA g}^{-1}$ , and the rate capability was tested at 50, 100, 200, 500, 1000  $\text{mA g}^{-1}$ . Cyclic

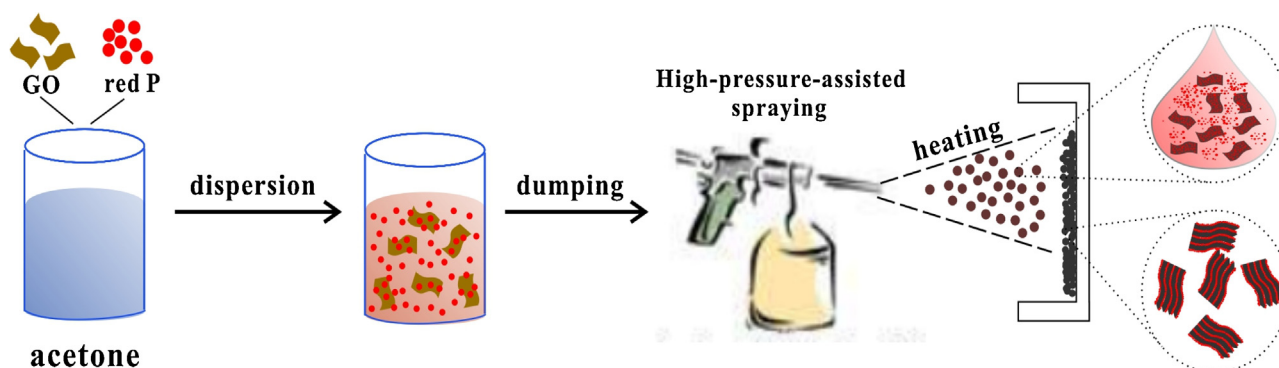


Fig. 1. Schematic diagram for the preparation of P@GS composite.

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