



Flexible phosphorus doped carbon nanosheets/nanofibers: Electrospun preparation and enhanced Li-storage properties as free-standing anodes for lithium ion batteries



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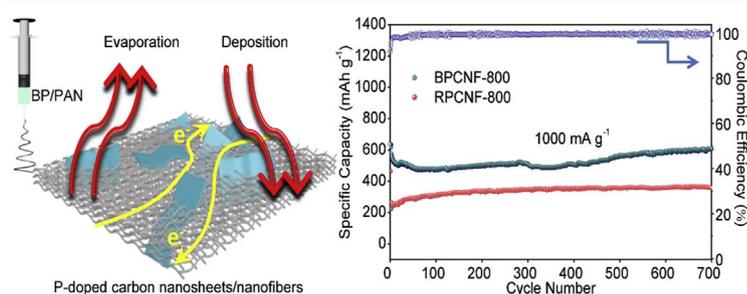
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HIGHLIGHTS

- P-doped carbon nanosheets/nanofibers were prepared by electrospinning and calcination.
- Using BP as the doping source results in a high phosphorus doping level.
- The binder-free electrode has good flexibility.
- A capacity of 1100 mAh g⁻¹ can be maintained after 550 cycles at 200 mA g⁻¹.

GRAPHICAL ABSTRACT



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ABSTRACT

The emerging wearable and foldable electronic devices drive the development of flexible lithium ion batteries (LIBs). Carbon materials are considered as one of the most promising electrode materials for LIBs due to their light weight, low cost and good structural stability against repeated deformations. However, the specific capacity, rate capability and long-term cycling performance still need to be improved for their applications in next-generation LIBs. Herein, we report a facile approach for immobilizing phosphorus into a large-area carbon nanosheets/nanofibers interwoven free-standing paper for LIBs. As an anode material for LIBs, it shows high reversible capacity of 1100 mAh g⁻¹ at a current density of 200 mA g⁻¹, excellent rate capabilities (e.g., 200 mAh g⁻¹ at 20,000 mA g⁻¹). Even at a high current density of 1000 mA g⁻¹, it still maintains a superior specific capacity of 607 mAh g⁻¹ without obvious decay.

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1. Introduction

Lithium-ion batteries have been widely regarded as the foremost rechargeable batteries for flexible devices and portable electronics mainly due to their high energy density, safety and long cycle life [1,2]. However, graphite as the commercial anode is approaching a practical capacitive limit ($\sim 372 \text{ mAh g}^{-1}$), which cannot meet the increasing demand of high-performance portable devices and electrical vehicles [3,4]. In order to overcome the capacity limitation of graphite, considerable researches have been devoted to developing alternative anode materials with high capacity and long cycle life, e.g. Si-based materials, transition metal oxides/sulfides and carbonaceous materials with functionality [5–12]. Remarkably, various nanostructured carbonaceous materials have attracted intensive attentions due to their kinetically favorable structures for ion/electron transport [13–15]. Heteroatoms (e.g. nitrogen, sulfur, and phosphorus) doping has been regarded as an effective strategy to enhance the electrochemical performance of LIBs by tailoring the electronic and chemical properties [16,17]. For example, nitrogen doped carbon has been demonstrated with improved performance for LIBs benefiting from the enhanced electrical conductivity and reactivity of carbon materials [18–20]. Phosphorus and nitrogen are in the same family, whereas the former possess higher electron-donating ability [21]. Previous studies have demonstrated that phosphorus doped (P-doped) carbon materials exhibit excellent electrocatalytic activity when they are employed as metal-free catalysts for oxygen reduction reaction [22–24]. Therefore, it is highly desirable to develop a facile and large-scale strategy towards synthesizing P-doped carbon based materials and explore their unique properties as flexible electrodes for LIBs.

To date, various methods including plasma and chemical vapor deposition are generally used to realize hetero-atoms doping [25,26]. However, those methods tend to introduce impurities or achieve only surface doping. Therefore, it is necessary to develop a facile and scale-up strategy for synthesizing P-doped carbonaceous electrode materials for LIBs. Constructing a free-standing and binder-free electrode, in which all the materials participate in the lithium storage, is favorable for the development of flexible LIBs. Flexible carbon nanofibers are one of the best option for carbon-based materials due to their one-dimensional (1D) configuration, which possesses high electronic conductivity and free-standing characteristics [27]. Moreover, the 1D nanostructure could obviously buffer the volumetric change during the repeated lithium insertion/extraction process [28,29]. To manufacture 1D nanostructured materials with small diameter, the electrospinning technique has been largely developed as a suitable and facile method to prepare large-scale 1D interwoven membranes in comparison with other methods (e.g. template-directed synthesis and self-assembly method) [30].

Herein, we report a facile strategy to fabricate flexible P-doped carbon nanosheets/nanofibers as free-standing paper using black phosphorus (BP) as doping source via electrospinning and subsequently an evaporation/deposition process. This strategy has several advantages: First, all portions of the electrode contribute to charge storage, which results in both high power and energy density. In addition, phosphorus can be uniformly doped in the carbon nanosheets/nanofibers taking advantages of the well-dispersed BP nanosheets. Furthermore, this method can be easily scale-up and thus large-area electrodes can be practically synthesized. In virtue of the above mentioned characteristics, the as-obtained phosphorus doped carbon paper shows improved lithium storage capacity (1100 mAh g^{-1} at 200 mA g^{-1}) and prolonged cycle life (607 mAh g^{-1} after 700 cycles at 1000 mA g^{-1}) compared to the un-doped carbon nanofibers as well as the phosphorus doped carbon paper using red phosphorus (RP) as doping source.

2. Experimental section

2.1. Materials preparation

2.1.1. Preparation of black phosphorus

Black phosphorus was prepared according to a previously reported method with slight modification [31]. In a typical experiment, a mixture containing 500 mg of RP, 10 mg of SnI_4 and 20 mg of Sn was sealed into an ampoule tube. The ampoule was then placed horizontally in the middle of a muffle furnace and heated to $600 \text{ }^\circ\text{C}$ within 1 h. After kept at $600 \text{ }^\circ\text{C}$ for 2 h, the furnace was then cooled down to $550 \text{ }^\circ\text{C}$ with a rate of $2 \text{ }^\circ\text{C min}^{-1}$. The temperature was further cooled down to $500 \text{ }^\circ\text{C}$ with a rate of $0.1 \text{ }^\circ\text{C min}^{-1}$ before the furnace was naturally cooled to room temperature. Finally, the as-prepared BP was collected from the ampoule tube and washed by hot chloroform and alcohol. After drying in vacuum, the BP was conserved in N_2 gas for further use.

2.1.2. Preparation of black phosphorus nanosheets

The BP nanosheets were prepared by a liquid phase exfoliation of bulk BP crystals [32]. Generally, 150 mg of bulk BP crystals was added into an agate mortar which contains 6 mL dimethylformamide (DMF) and ground for 25 min with a pestle. The resulting supernatant (2 mL) was then collected into a bottle and another 2 mL of DMF was added into the remaining mixture for further milling. The afore-mentioned process was repeated for 8 times and then 160 mL DMF was added into the collected mixture that bubbled with argon for 15 min to avoid the oxidation. Subsequently, the collected mixture was sealed with parafilm carefully and sonicated in an ice bath for 20 h. The BP nanosheets were collected by centrifuge at 8000 rpm for 6 min to remove the DMF.

2.1.3. Fabrication of P-doped carbon nanosheets/nanofibers composites using BP as doping source

198.8 mg of polyacrylonitrile (PAN, $M_w = 150,000$, Sigma-Aldrich) was dissolved in 2 mL DMF and then mixed with 101.5 mg of the as-prepared BP nanosheets. The applied working voltage, flow rate, and distance between the collector and needle were 12 kV, $6 \mu\text{L min}^{-1}$, and 10 cm, respectively. To remove the remaining DMF, the collected electrospun nanofibers (labeled as BP@PANs) were dried at $65 \text{ }^\circ\text{C}$ for 12 h in vacuum drying oven. Afterwards, the nanofibers were annealed under N_2 atmosphere at $800 \text{ }^\circ\text{C}$ (BPCNF-800) and $900 \text{ }^\circ\text{C}$ (BPCNF-900) for 1 h with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$. Another two samples with varied amounts of BP nanosheets (50.8 mg and 25.4 mg) were prepared using the same procedures and annealed under N_2 atmosphere at $800 \text{ }^\circ\text{C}$ for 1 h with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$. Correspondingly, the as-prepared two samples with 50.8 mg and 25.4 mg BP nanosheets were denoted as BPCNF-2 and BPCNF-3, respectively.

2.1.4. Fabrication of P-doped carbon nanosheets/nanofibers composites using RP as doping source

198.8 mg of PAN was dissolved in 2 mL DMF and then mixed with 101.5 mg of RP. The applied working voltage, flow rate, and distance between the collector and needle were 12 kV, $6 \mu\text{L min}^{-1}$, and 10 cm, respectively. To remove the remaining DMF, the collected electrospun nanofibers (labeled as RP@PANs) were dried at $65 \text{ }^\circ\text{C}$ for 12 h in vacuum drying oven. Afterwards, the nanofibers were annealed under N_2 atmosphere at $800 \text{ }^\circ\text{C}$ (RPCNF-800) and $900 \text{ }^\circ\text{C}$ (RPCNF-900) for 1 h with a heating rate of $1 \text{ }^\circ\text{C min}^{-1}$.

2.2. Material characterization

The morphologies of materials were determined by field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F) and dark-field scanning transmission electron microscopy (STEM, JEOL-2100F) operating at 200 kV. Energy-dispersive X-ray spectroscopy (EDX) was used for analyzing elements. Crystal structure was investigated by X-ray power diffractometer (Scintag PAD-V) with $\text{Cu K}\alpha$ irradiation. X-ray

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