A facile grinding approach to embed red phosphorus in N,P-codoped hierarchical porous carbon for superior lithium storage

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ABSTRACT Despite red phosphorous (P)-based anodes hold great promise for advanced lithium-ion batteries due to their high theoretical capacity, their practical application is hindered by poor electronic conductivity and drastic volume changes during charge-discharge processes. In order to tackle these issues, herein, a facile grinding method was developed to embed sub-micro- and nano-sized red P particles in N,P-codoped hierarchical porous carbon (NPHPC). Such a unique structure enables P@NPHPC long-cyclic stability (1120 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹) and superior rate performance (248 mA h g⁻¹ at 6400 mA g⁻¹). It is believed that our method holds great potential in scalable synthesis of P@carbon composites for future practical applications.

Keywords: red P, hierarchical porous carbon, grinding, composites, lithium-ion batteries

INTRODUCTION

The ever-growing energy needs demand the development of sustainable technologies, including both the storage and conversion of renewable energy. Lithium-ion batteries (LIBs), the predominating power sources for portable electronics in our daily life, have also been considered as the most promising energy storage devices for electric vehicles and smart grid [1,2]. At present, further improvement of LIBs' energy density is greatly hindered by the lack of high-performance electrode materials. For example, the specific capacity of the commercialized graphite-based anodes is already close to the theoretical value of 372 mA h g⁻¹, which is still relatively low [3–5]. Up to now, numerous materials have been

adopted to address the issue of low capacity. Among all of the potential candidates, phosphorus (P), a Group VA and Period III element, has attracted extensive research interest due to its high theoretical capacity (2596 mA h g⁻¹), suitable lithiation potential (0.75 V) [6], and moderate polarization (~0.4 V) [7]. Typically, P has three main allotropes, that is, white P, black P and red P. White P is flammable and toxic, while black P is unstable and unavailable for large-scale production, both of which are not suitable for lithium storage application [8,9]. Comparably, red P exhibits several fascinating features, including chemical stability, environmental benignity, natural abundance and low cost, making it one of the most attractive anodes for next-generation high energy LIBs [10,11]. However, the application of red P electrodes always encounters insuperable obstacles of poor electronic conductivity and drastic volume changes, resulting in unsatisfactory rate capability and poor cyclability [12].

To overcome the aforementioned drawbacks of red P, carbonaceous materials have been employed as hosts to compensate the conductivity of red P, thus facilitating charge transfer during the electrochemical reactions, and buffering the volume expansion of red P during cycling [13]. Although a number of delicate techniques, including electrospinning [14,15], high pressure-assisted spraying [16], vaporization-condensation [17], ball milling [18], solvothermal [19], and wet chemical processing have been applied to synthesize red P@carbon composites [20], their practical application remains a long road to go due to the following issues: (1) the exploration of carbonaceous hosts is limited to one dimensional (1D) carbon nano-

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tubes/nanofibers [21,22] and two-dimensional (2D) graphene/reduced graphene oxide (rGO) [8,16]. As a result, the obtained composites generally suffer from insufficient P/C interface, leading to unsatisfactory cycling stability. (2) The preparation of P@carbon composites generally involves special equipments, high temperature, inert atmosphere, as well as a time-consuming procedure, which are unfavorable for mass production. Moreover, hazard by-products are unavoidable for wet chemical and vaporization-condensation approaches. (3) The loading content of red P in composites remains low.

In this work, we develop a facile grinding method to embed red P within three-dimensional (3D) N,P-codoped hierarchical porous carbon (NPHPC). In contrast to the previously reported 1D and 2D carbonaceous hosts, the 3D NPHPC with high specific surface area and abundant porous structure not only enables stable P/C interface for tolerating the volume expansion of P, but also provides smooth porous channels for fast electron/ion transport and diffusion. Consequently, the P@NPHPC composite delivers a high capacity of 1120 mA h g^{-1} at 100 mA g^{-1} after 100 continuous cycles. In addition, impressive capacities of 354 and 248 mA h g^{-1} can be achieved at the current rates of 3200 and 6400 mA g^{-1} , respectively. With these enthralling properties, this method holds great potential in scalable synthesis of P@carbon composites for future practical applications.

EXPERIMENTAL SECTION

Preparation of P@NPHPC

NPHPC was prepared according to our previous report, which involves the pyrolysis of melamine polyphosphate synthesized using melamine and polyphosphoric acid as precursors [23,24]. P@NPHPC was produced by mechanically grinding NPHPC and red P (1:1 in mass ratio) in a mortar for 30 min to ensure sufficient contact between the two components.

Characterization

The morphologies of all samples were characterized by scanning electron microscopy (SEM, Zeiss Auriga Dual-Beam FIB/SEM, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) was collected using an ESCALAB MK II (Al K α radiation). X-ray powder diffraction (XRD) patterns were obtained on a D8 advance diffractometer (Cu K α radiation). Raman spectra were performed on a WITec Alpha300 (532 nm laser). Thermogravimetric analysis (TGA) was conducted on a

METTLER TGA2 in N₂ atmosphere. Brunauer-Emmett-Teller (BET) measurements were performed on a Micromeritics ASAP 2020 by N₂ sorption. The pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) mode.

Electrochemical characterizations

Coin-type cells (CR2032) were assembled in an argon-filled glovebox using pure lithium foil as the counter electrode and polypropylene film as the separator. The working electrodes were fabricated by tape casting N-methylpyrrolidone-based slurries of 80 wt% active materials, 10 wt% polyvinylidene difluoride, and 10 wt% acetylene black on Cu foils. After being dried in a vacuum oven at 100°C overnight, 1.2-cm-diameter circular electrodes were obtained using a punch machine. Mass loading of the active materials on each electrode was controlled to be 1.0–1.5 mg. Galvanostatic tests were conducted on a NEWARE battery cycler. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on a CHI 760D electrochemical analyzer.

RESULTS AND DISCUSSION

The preparation of P@NPHPC composite is schematically shown in Fig. 1a. Commercial red P with sizes of up to several micrometers (Fig. S1) was directly grinded with NPHPC, during which bulk P particles were downsized to sub-micrometer or even nanometer scales. Correspondingly, the significantly increased interfacial interactions cause the filtration of red P particles in the voids and pores of the 3D conducting NPHPC framework, leading to the formation of P@NPHPC composite [25]. SEM images illustrate that P@NPHPC has a unique interconnected framework with red P confined in the NPHPC matrix, and no bulk particles are observed (Fig. 1b and Fig. S2). This is further confirmed by the TEM images (Fig. 1c and Fig. S3), which suggest the effective capture of red P by NPHPC. Such an unusual structure is not only beneficial for improving the conductivity of red P, but also for achieving stable P/C interface for electrochemical reactions. The typical SEM image and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of P@NPHPC composite presented in Fig. 1d–h indicate the uniform loading of red P.

As shown in the XRD patterns (Fig. 2a), red P exhibits two characteristic diffraction peaks centered at about 15° and 33°, matching well with the (013) and (31 $\bar{8}$) planes of monoclinic P (JCPDS No. 44-0906), respectively [14,22]. Interestingly, these peaks become less obvious in

Figure 1 (a) Schematic illustration of the preparation of P@NPHPC composite; (b) SEM, (c) TEM, and (d–h) EDS elemental mapping images of P@NPHPC composite. The insets of (b, c) show the higher-magnification microscopic images of the composite.

P@NPHPC composite, suggesting the confinement of red P into carbon matrix and the formation of amorphous structure after grinding. Meanwhile, the broad peak centered at around 25° can be attributed to the XRD pattern of graphitic carbon [5,23]. The successful incorporation of P in NPHPC was also observed by Raman spectroscopy. As shown in Fig. 2b, the three peaks in Raman spectrum of red P in the range of $300\text{--}500\text{ cm}^{-1}$ can be assigned to B1 fundamental mode, A1 symmetric stretch motion and E1 degenerate mode [14,26]. While in P@NPHPC composite, these typical peaks of red P disappeared, and only the D band ($\sim 1330\text{ cm}^{-1}$) and G band ($\sim 1590\text{ cm}^{-1}$) of carbon were detected, which was assignable to the generation of smaller-particle size and amorphous red P after grinding [17,23]. XPS analysis substantiates the presence of phosphorous, carbon, nitrogen and oxygen elements in both NPHPC and P@NPHPC (Fig. 2c), consistent with EDS mapping shown in Fig. 1d–h.

Notably, significantly enhanced P 2p and P 2s XPS signals were recognized in P@NPHPC, attributable to its high red P content. The deconvoluted peaks of high-resolution C 1s spectra (Fig. S4a) are assigned to C–C (284.6 eV), C–N (285.6 eV), C–O (286.8 eV), and

O–C=O (289.0 eV), indicating the presence of oxygen-containing functional groups in NPHPC host [5,23]. High-resolution spectra of N 1s (Fig. S4b) can be deconvoluted into graphite-like N (401.1 eV) and pyridine-like N (398.1 eV), which signify N atom doping in NPHPC host [23]. The deconvolution of high-resolution P 2p spectra (Fig. S4c) corresponds to P–C (131.5 eV), P–O (132.8 eV), and P_2O_5 (134.1 eV) in the samples [20,21]. The dominant P_2O_5 peak in P@NPHPC originates from the large amount of oxides from the surface of red phosphorus [17]. High-resolution O 1s spectra (Fig. S4d) suggest that C=O (532.4 eV) and P=O (530.3 eV) are present in the samples [24]. TGA curve of the P@NPHPC composite illustrates a three-step mass loss (Fig. S5), where the first stage below 200°C is due to the loss of absorbed water ($\sim 12.5\%$), the second stage around $200\text{--}500^\circ\text{C}$ is probably due to the removal of external red P ($\sim 13.7\%$), and the third stage beyond 500°C is due to the sublimation of internal confined red P within the carbon framework ($\sim 40.7\%$) [13,27]. The stepwise weight loss suggests a strong P/C interface that leads to the gradual removal of red P from the composite [22]. It is worth noting that distinguished mass loss is observed at temperature higher than 500°C , indicating the internal red P

Figure 2 (a) XRD patterns and (b) Raman spectra of red P and P@NPHPC composite; (c) XPS survey spectra of NPHPC and P@NPHPC composite; (d) nitrogen adsorption/desorption isotherms and (e) pore-size distribution of red P, NPHPC and P@NPHPC. The insets in (d, e) are the enlarged profiles of P@NPHPC composite.

is more stable than the external one. The porous features of the samples were unveiled by N_2 sorption isotherms (Fig. 2d, e). NPHPC and red P exhibit a typical IV and type III isotherms, respectively, corresponding to the hierarchical porous and nonporous structures. The NPHPC shows a BET surface area of up to $1409.4 \text{ m}^2 \text{ g}^{-1}$ with a large total pore volume of $1.95 \text{ cm}^3 \text{ g}^{-1}$, and an average pore size of 5.3 nm . The fascinating porous structure enables NPHPC an idea container, where plentiful macro-/mesopores provide a large accessible area for high level red P loading, while the micropores are capable of chemically adsorbing red P to prevent the loss of electrical contact with the carbon network during electrochemical cycling [28]. It is noted that the surface area ($29 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($6.61 \text{ cm}^3 \text{ g}^{-1}$) of P@NPHPC are distinctly deceased compared with NPHPC, implying the successful restraint of red P in the NPHPC framework. Although the specific surface area of P@NPHPC is lower than that of NPHPC, the remaining void spaces are capable of acting as internal buffers for the volume expansion of red P [29]. More importantly, the compacted structure ensures good electrode integrity, and uniform and stable solid electrolyte interface (SEI) formation, both of which are advantageous to long-term cycling.

The lithium storage properties of P@NPHPC in comparison with red P were evaluated using coin-type cells. Fig. 3a depicts the first three CV curves of red P and P@NPHPC electrodes in the voltage range of $0.005\text{--}3.0 \text{ V}$ (vs. Li/Li^+), at a scan rate of 100 mV s^{-1} . As observed, both electrodes show an irreversible cathodic peak in the first cycle, corresponding to SEI formation [15]. The dramatically lower current density in red P with respect to P@NPHPC electrode could be ascribed to its low conductivity. Correspondingly, the red P electrode exhibits poor electrochemical performance in terms of low capacity and large initial capacity loss (Fig. 3b). In sharp contrast, the first discharge and charge capacities of P@NPHPC composite electrode are 2950 and 1381 mA h g^{-1} , respectively. Due to the formation of SEI layer on the electrode surface, the first coulombic efficiency (CE) of P@NPHPC is $\sim 47\%$. However, the CE of P@NPHPC electrode increases rapidly, and reaches 95% after 5 cycles (Fig. S6). Different from other crystalline red P-based anodes with flat discharge-charge plateaus, P@NPHPC shows continuous slope profiles, which is likely due to the presence of amorphous red P in NPHPC [30]. Cycling stability tests reveal that the specific capacity of P@NPHPC far exceeds that of red P electrode (Fig. 3c). After 100 cycles, a high capacity of 1120 mA h g^{-1} can be

Figure 3 (a) Representative CV cycles of the red P and P@NPHPC composite electrodes at a scan rate of 100 mV s⁻¹; (b) the initial charge-discharge profiles of the electrodes at a current density of 100 mA g⁻¹; (c) cycling stability and (d) rate performance of the electrodes tested under programmed current densities.

still retained in P@NPHPC electrode. The increase of capacity after 40 cycles is ascribed to the electrochemical activation process, which leads to an increased accessibility of Li⁺ into the inner part of the anode, and consequently more Li storage sites could be utilized [5,31]. Another attractive result is that P@NPHPC also has a superior areal capacity compared with NPHPC anode (Fig. S7), which is of pivotal for high energy density LIBs application. The rate capability of P@NPHPC electrode was evaluated under stepwise increase of the current density from 100 to 200, 400, 800, 1600, 3200 to 6400 mA g⁻¹ (Fig. 3d and Fig. S8). The corresponding discharge capacities of P@NPHPC are 928, 757, 624, 546, 470, 354, and 248 mA h g⁻¹, respectively. Upon reversing the current density back to 100 mA g⁻¹ after 80 programmed cycles, the capacity can promptly recover to 845 mA h g⁻¹, demonstrating its excellent reversibility. While the rate capacity of red P electrode is much lower than that of P@NPHPC owing to its poor conductivity. The overall performances of P@NPHPC are comparable to the recently reported P@carbon composites, such as P@rGO, P@carbon nanotubes and P@porous carbon [12,16,32], demonstrating our grinding approach is powerful for fabricating high performance P-based anodes. Such prominent lithium storage behaviors are likely

due to its unique structure. On one hand, the large BET surface area and abundant porous structure of NPHPC host guarantee high red P loading, which is beneficial for high specific capacity. At the same time, the steady P/C interface is capable of sustaining electrochemical reactions at high rates. On the other hand, the continuous 3D carbon framework can greatly improve the conductivity of the entire electrode, facilitate ion transport and diffusion, as well as buffer the volume expansion of red P during cycling.

EIS tests were performed to probe the kinetic properties of the electrodes. As shown in Fig. 4a, the Nyquist plots of both red P and P@NPHPC electrodes consist of a semi-circle in the high-medium frequency region together with an inclined line at low frequency regime. The impedances, including electrolyte resistance (R_e), surface film resistance (R_{sf}), charge-transfer resistance (R_{ct}) and Warburg resistance (W) [30], were analyzed using the equivalent circuit model presented in Fig. 4b. The simulated results for both electrodes are summarized in Fig. 4c for better comparison. It can be seen that the R_e of both electrodes are comparable, whereas the R_{sf} of P@NPHPC is lower than that of red P. This could be the results of smaller particle sizes of red P that uniformly distributed within the NPHPC matrix, thus leading to better elec-

Figure 4 (a) Nyquist plots of the red P and P@NPHPC composite electrodes; (b) schematic of the equivalent circuit for simulation; (c) simulated data of the electrodes using the equivalent circuit showing in (b).

trolyte wettability and SEI film stability in P@NPHPC electrode. More impressively, the R_{ct} of P@NPHPC (13.0 Ω) is substantially lower than that of red P electrode (94.8 Ω), indicative of greatly increased electronic conductivity and consequently a faster charge-transfer process. The considerably enhanced kinetic behaviors in P@NPHPC electrode once again suggest our grinding approach is effective for fabricating superior P@carbon composites anodes.

CONCLUSIONS

In summary, we have successfully developed a grinding approach to directly embed red P in NPHPC for LIBs. Benefiting from the fascinating porous structure of NPHPC, the grinded red P particles are evenly captured by the carbon matrix, forming steady P/C interface for electrochemical reactions. In addition, the 3D porous structure of NPHPC enables fast electron transport, short Li^+ diffusion length, and effective buffer to the large volume changes of red P. As a result, the obtained P@NPHPC electrode shows excellent lithium storage performances in terms of high specific capacity with good cyclability (1120 mA h g^{-1} after 100 cycles at 100 mA g^{-1}), and outstanding rate capability (248 mA h g^{-1} at 6400 mA g^{-1}). Given that the general method and low cost of the raw materials, P@NPHPC is believed to be a

promising candidate for energy storage devices.

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Author contributions Du Z, Sun G and Huang W designed the project. Du Z carried out the main experiments. Ai W, Yu C, Gong Y and Chen R participated in the material characterizations and analyzed

the data. Du Z, Sun G and Huang W co-wrote the paper. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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一步碾磨法快速制备红磷嵌入的氮磷共掺杂分级多孔碳复合材料及其储锂性能研究

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摘要 红磷因具有高理论储锂容量而成为新一代锂离子电池的重要候选材料, 然而其实际应用却受到导电性差以及充放电过程中体积变化大的限制。针对以上问题, 本文利用一步碾磨法制备了亚微米/纳米尺度红磷颗粒嵌入的氮、磷原子共掺杂分级多孔碳复合材料(P@NPHPC)。NPHPC三维交联的分级多孔结构为红磷负载提供了充足的空间, 促进了稳定磷/碳界面的形成, 从而有效解决了红磷作为电极材料的不足。基于此, P@NPHPC负极表现出良好的循环稳定性(100 mA g⁻¹电流密度下, 100次循环后比容量为1120 mA h g⁻¹)和优越的倍率性能(6400 mA g⁻¹电流密度下比容量为248 mA h g⁻¹)。本工作对高性能磷/碳复合材料的批量制备及实际应用具有指导意义。