Confined Amorphous Red Phosphorus in MOF-Derived N-Doped Microporous Carbon as a Superior Anode for Sodium-Ion Battery

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Red phosphorus (P) has attracted intense attention as promising anode material for high-energy density sodium-ion batteries (NIBs), owing to its high sodium storage theoretical capacity (2595 mAh g\(^{-1}\)). Nevertheless, natural insulating property and large volume variation of red P during cycling result in extremely low electrochemical activity, leading to poor electrochemical performance. Herein, the authors demonstrate a rational strategy to improve sodium storage performance of red P by confining nanosized amorphous red P into zeolitic imidazolate framework-8 (ZIF-8)-derived nitrogen-doped microporous carbon matrix (denoted as P@N-MPC). When used as anode for NIBs, the P@N-MPC composite displays a high reversible specific capacity of \(\approx 600 \text{mAh g}^{-1}\) at 0.15 A g\(^{-1}\) and improved rate capacity (=450 mAh g\(^{-1}\) at 1 A g\(^{-1}\) after 1000 cycles with an extremely low capacity fading rate of 0.02% per cycle). The superior sodium storage performance of the P@N-MPC is mainly attributed to the novel structure. The N-doped porous carbon with sub-1 nm micropore facilitates the rapid diffusion of organic electrolyte ions and improves the conductivity of the encapsulated red P. Furthermore, the porous carbon matrix can buffer the volume change of red P during repeat sodiation/desodiation process, keeping the structure intact after long cycle life.

Large energy storage systems (ESSs) require the chemical energy storage equipment with high safety and low price.[1] Li-ion batteries (LIBs) have been used as the most popular ESS, while there are still some challenges that need to be solved including safety, limited Li sources, and high cost.[2,3] Recently, Sodium-ion batteries (NIBs) have attracted great attention as a promising alternative to Li-ion batteries (LIBs) because of sodium’s high abundance, low cost, and very suitable redox potential.[4-7] However, compared with Li, Na ions insertion/extraction in the electrode shows more sluggish kinetics due to its large ions radius (Na\(^+\) is 55% larger than that of Li\(^+\)). The major challenge in advancing NIBs technology lies in seeking high performance electrode materials. Various cathode materials for NIBs have been designed and prepared, such as NaFePO_4, Na_3V_2(PO_4)_3, and NaMnO_2.[8-12] However, the development of anode materials for NIBs is in its infants.[4,13,14] It has been demonstrated that the current commercial anode materials for LIBs, graphite-based anodes are not suitable to reversibly sodium storage.[13,15,16] Therefore, it is urgent to find some alternative anode materials for NIBs with both high energy density and high power density.

Recently, phosphorus (P) has been considered as a promising anode material for NIBs, which can electrochemically react with sodium to form Na_3P and deliver a high theoretical sodium-storage capacity of 2595 mAh g\(^{-1}\), much higher than that of carbonaceous materials,[17-19] alloy-type anode materials,[20-23] metal oxides, and sulfides anode materials.[24-29] There are three main allotropes in solid phosphorus (i.e., white P, red P, and black P), among them white P is highly reactive to air and flammable and consequently, not suitable for electrochemical application in NIBs. Comparing to black P, red P has received much interest as anode material for NIBs because it is earth abundant and environment benign.[30-33] However, the practical application of red P in NIBs is severely hindered by the poor electrochemical performance, arising from the large volume change (>400%) during Na uptake/release and low electronic conductivity (=10\(^{-4}\) S cm\(^{-1}\)) of red P.[34-36] In addition, the huge volume change during charge/discharge results in the pulverization of the active materials, leading to continual formation of a very thick solid electrolyte interphase (SEI) on the surface of the active materials during cycling.[34-36] All these issues would lead to limited electrochemical activity and rapid capacity decay of red P when applied in NIBs.[37] Therefore, it is highly desirable to enhance the sodium storage performance of red P by rational design taking into account all of the abovementioned considerations.

Combinations red P with carbon-based materials have been regarded as effective strategies for enhancing the electronic...
conductivity and further improving its electrochemical properties. Recently, various types of carbon materials (i.e., carbon black–red P,[36,38] carbon nanotubes,[33,39,40] graphene,[41–43] and mesoporous carbon[44]) have been proven to be effective and facile candidates for improving the conductivity of red P and accommodating the volume change of red P because these carbon-based materials possess large specific surface area, excellent conductivity, and highly porous structure.[44] Moreover, the engineering of carbonaceous nanomaterials by heteroatoms doping (i.e., nitrogen (N), boron (B), sulfur (S), phosphorus (P), and iodine (I) doping) have been demonstrated as an effective way to tune their electrical performance and improve their energy storage performance.[42,45–48] Among them, nitrogen (N) doping in carbon is the most popular strategy that could improve the reactivity and electronic conductivity of carbon by creating extrinsic defects.[49]

In addition, to alleviate the large strain resulting from huge volume variation during cycling, the most effective solution is to downsize the red P particles to nanosize.[32,36,38,44,50] The decreased particle size could not only enhance electrochemical activity of red P owing to the size effect of nanosized particles but also shorten the diffusion time of Na⁺.[36,38,51] According to the abovementioned rational structure design, several works have presented improved electrochemical performance of porous carbon–red P composites,[36,38,44] graphene–red P composites,[42,50] and carbon nanotube–red P composites.[33] Zhu et al.[33] have presented long life of 2000 cycles of a single-wall nanotubes/red P composite as anode for NIBs, showing a reversible capacity of ≈260 mAh g⁻¹. Nevertheless, long-time cycling of more than 1000 cycles with high reversible capacity has been rarely reported in the red P-based anode materials for NIBs.

Considered about all of the abovementioned strategy, it should be wise to downsize the red P particles to <1 nm and nanoconfine the red P into heteroatom-doped porous carbon matrix, which could offer the synergistic effects of the nanosized active materials (red P), core/shell structure, heteroatom-doped porous carbon, and porous nanoarchitecture.[34] Recently, metal-organic frameworks (MOFs) have received growing attention due to the unique structure with well-defined pore size distributions consisting of linked inorganic and organic units, which display wide application in electrochemical energy storage and catalysis.[33,54] Furthermore, heteroatoms (e.g., boron, sulfur, nitrogen, and boron) contained in the organic sections of MOFs is crucial to form heteroatoms doping in the MOFs-derived carbonaceous materials, beneficial to tuning the electronic feature and surface wettability.[55,56] Zeolitic imidazole framework-8 (ZIF-8) is one typical MOF containing Zn⁺ and 2-methylimidazolate linkers, in which 2-methylimidazolate contains high content of N (~34 wt%).[57,58] After carbonization of ZIF-8, highly nitrogen-doped microporous carbon would be obtained after removing Zn in the carbon matrixes with HCl.[59]

Herein, we present a rational design and fabrication of red P/carbon composite with core/shell structure to improve the sodium storage performance of red P by confining the red P in ZIF-8-derived N-doped microporous carbon (denoted as P@N-MPC) via by a facile strategy. The unique structure combines various advantages: First, the highly nitrogen-doped microporous carbon can build up highly conductive pathways of electrons in electrodes and stabilize red P during cycling, simultaneously. Second, the uniform micropores could confine red P to nanosize, not only relieving the strain from volume variation but also enhancing the electrochemical activity. Third, the highly porous structure ensured efficient access of electrolyte to red P. Benefiting from the abovementioned synergic effects, the P@N-MPC displays superior sodium storage performance. It shows a high reversible specific capacity of ≈600 mAh g⁻¹ at a current density of 0.15 A g⁻¹ and superior cycle life of ≈450 mAh g⁻¹ at 1 A g⁻¹ after 1000 cycles with an extremely low capacity fading rate of 0.02% per cycle. Note that all these capacities are calculated based on the weight of composite. The behavior in terms of Na⁺ ion storage performance for red P is unprecedented and it shows great promise for practical application in next-generation NIBs.

**Figure 1A** displays a schematic illustration of the preparation process of P@N-MPC. The N-doped microporous carbon

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**Figure 1.** Schematic illustration of the preparation process for A) P@N-MPC and B) sodiation process of P@N-MPC.
(N-MPC) with well-defined pore size (<1 nm) was prepared by direct carbonization of ZIF-8 under N₂ atmosphere. ZIF-8 nanocrystals with a polyhedron-like morphology were prepared through reaction of Zn(NO₃)₂·6H₂O with 2-methylimidazole in methanol for 24 h, according to the previous work[58] which were then carbonized under the N₂ atmosphere. After removal of Zn via dilute HCl, highly nitrogen-doped microporous carbon (N-MPC) was fabricated owing to high nitrogen content in the organic sections in ZIF-8. Then red P was encapsulated in N-MPC to form nanosized particles with uniform size through a vaporization-condensation-conversion method.[60] After removing unconverted white P with CS₂, amorphous red P embedded in the N-MPC (P@N-MPC) was finally obtained, which is crucial to improve the structural stability of red P during cycling as shown in Figure 1B. The sub-1 nm micropores in the N-MPC can prevent the aggregation of red P, shortening the diffusion length for both ions/electrons. Furthermore, the porous structure of the N-MPC accommodates the huge volume vibration of red P during sodiation/desodiation process and the carbon matrix releases the mechanical stress resulting from the huge volume change. The P@N-MPC would guarantee stable structure after long-time sodiation/desodiation process.

Figure 2 displays the morphology of N-MPC and P@N-MPC. As shown in the Figure 2A, the obtained N-MPC presents a polyhedron-like morphology with uniform size (diameter: ≈60 nm), consistent with that of ZIF-8 nanocrystals (see Figure S1, Supporting Information). The as-prepared ZIF-8 nanocrystals display the typical X-ray diffraction (XRD) pattern, identical to the corresponding simulated data in the literature[59] (see Figure S2, Supporting Information). Figure 2B shows the transmission electron microscopy (TEM) image of the N-MPC. The N-MPC displays highly porous structure with uniform micropore size distribution (diameter of ≈0.5 nm) as shown in the high-resolution TEM (HRTEM) image (Figure 2C), which is further confirmed by the pore size distribution characterized by nitrogen absorption/desorption experiments (see Figure S3, Supporting Information). After impregnation of red P into the N-MPC (Figure 2D), the P@N-MPC shows similar morphology with the N-MPC, and no obvious red P residue appears on the surface of the N-MPC. The TEM and HRTEM images of the P@N-MPC (Figure 2E,F) reveal the microstructure. The micropores in the N-MPC matrix are partially occupied, resulting from the red P encapsulation.

The encapsulation situation of red P nanoparticles in the N-MPC is further studied via analyzing change of pore-size distribution before and after red P loading. As shown in Figure S3A (Supporting Information), the N-MPC displays the typical Type I nitrogen absorption/desorption isotherms with a high Brunauer–Emmett–Teller (BET) specific surface area of 1135.1 m² g⁻¹.[52] Additionally, the N-MPC shows a uniform narrow size distribution mainly at ≈0.5 nm as shown in Figure S3B (Supporting Information). After loading red P in the N-MPC, the BET specific surface area of the P@N-MPC decreases dramatically to 67.9 m² g⁻¹, indicating occupation of red P in the pores in the N-MPC, corresponding to much reduction in pore volume of the P@N-MPC. The distribution situation of red P in the N-MPC is further characterized by the high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and related elemental mapping of carbon, phosphorus, and nitrogen, indicating the uniform distribution of red P in the P@N-MPC (Figure 3), which is further confirmed by the energy-dispersive X-ray spectroscopy and the X-ray photoelectron spectroscopy (XPS) (see Figure S4, Supporting Information). The content of red P in the P@N-MPC and nitrogen in the N-MPC is determined to be 22.6 and 15.5 wt% via the thermogravimetric analysis (TGA) (see Figure S5, Supporting Information) and the X-ray photoelectron
spectroscopy (Figure 4A), respectively. During the TGA test in the N₂ atmosphere, the red P in the P@N-MPC would become P vapor when the test temperature reaches above the sublimation temperature of red P, while the matrix, N-MPC would be left. Via testing the weight change before and after the TGA, the weight of red P in the testing sample would be obtained as 22.6 wt% (see Figure S5, Supporting Information). For the XPS testing, the intensity of peaks in the spectroscopy is related to the weight of elements, such as carbon and nitrogen. Through comparing the intensity of the peak belonging to elemental N with the intensity of all peaks, the weight content would be calculated to be 15.5 wt% (Figure 4A). Figure 4B presents the high resolution XPS N1s spectrum of the N-MPC, which can be fitted well with three peaks, including pyridinic N (N-6), pyrrolic or pyridonic N (N-5), and quaternary N. The highly nitrogen doping is crucial to enhance the electronic conductivity of the N-MPC and further improves the sodium storage performance of the P@N-MPC.

Figure 4C,D displays the XRD patterns and Raman spectra of the P@N-MPC, the N-MPC, and commercial red P. The N-MPC shows two broad peaks at 2θ ~ 25° and 45° in the XRD pattern (Figure 4C), related to graphitic carbon with low degree of graphitization, consistent with the Raman spectrum of the N-MPC. In the case of commercial red P, the XRD pattern displays one sharp peak at 2θ ~ 15° and two broad peaks at 2θ ~ 34° and 55°, suggesting a medium-range ordered structure, which corresponds to the obvious peaks at Raman spectrum between 300 and 500 cm⁻¹ (Figure 4D). After confining red P into the N-MPC, the P@N-MPC shows combined XRD patterns of the N-MPC and the commercial red P. While the intensity of red P in XRD pattern and Raman spectrum of the P@N-MPC are much weaker than those of commercial red P, mainly resulting from downsizing of red P encapsulated in micropores to <1 nm and confinement of amorphous red P in the N-MPC.

Figure 5A shows the cyclic voltammetry (CV) curves of the first four cycles of the P@N-MPC electrode at a scan rate of 0.2 mV s⁻¹ and cycled between 0.005 and 3 V versus Na⁺/Na. The P@N-MPC presents typical CV curves of red P-based anodes. During the first sodiation process, one irreversible broad cathodic peak at ~0.75 V is observed, ascribed to the decomposition of electrolyte and formation of solid electrolyte interphase (SEI), in good agreement with the voltage profiles (see Figure S6, Supporting Information). Furthermore, another
peak appears at \( \approx 0.31 \) V during the 1st discharge process, ascribed to the sodiation of red P. Additionally, the peak potential gradually shifts to higher voltage (\( \approx 0.35 \) V) with simultaneously increased intensity during the following scan. During the charge process, the P@N-MPC displays three peaks at \( \approx 0.6 \), \( \approx 0.7 \), and 1.37 V, revealing the stepwise desodiation process.\[44]\] Moreover, the peak at \( \approx 0.6 \) V shows gradually increased peak current and gradually decreased voltage from the first scan to the fourth scan. The decreased polarization between the cathodic and anodic peaks and increased intensity of these peaks indicate the enhanced sodiation kinetics and electrochemical activity of nanosized red P (diameter: <1 nm).\[33,44]\] This process of change of CV curves during cycling is called the activation process of electrode materials, usually observed in anode materials,\[33,41,61,62\] and lithium-sulfur batteries.\[63,64\] During the continuous insertion/extraction of sodium-ion, the red P nanoparticles would realize progressive electrolyte wetting, leading to the reduced polarization and the enhanced peak intensity.\[65\] Figure 5B displays the cycle performance of the P@N-MPC at a current density of 0.15 A g\(^{-1}\). The capacity was calculated based on the mass of the P@N-MPC composite. The P@N-MPC delivers an initial discharge capacity and charge capacity of \( \approx 1312 \) and 710 mAh g\(^{-1}\), respectively, corresponding an initial Coulombic efficiency (ICE) of 54.1\%. The irreversible capacity of the first cycle is mainly attributed to the formation of SEI on the surface of the P@N-MPC nanoparticles and low ICE (around 23\%) of the N-MPC (see Figure S7, Supporting Information). However, the Coulombic efficiency (CE) of the P@N-MPC reaches almost 100\% without obvious fading after the first cycle and the reversible capacity of the P@N-MPC keeps as high as \( \approx 600 \) mAh g\(^{-1}\) after 100 cycles, indicating a very low capacity fading rate of around 0.17\% per cycle. To further confirm the enhanced electrochemical activity of nanosized red P in micropores, the rate capacity of the P@N-MPC is also tested. As shown in Figure 5C, the P@N-MPC presents reversible capacities of 684, 642, 570, 494, 470, 414, 365, 344, 315, and 291 mAh g\(^{-1}\) at the current densities of 0.3, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, and 9 A g\(^{-1}\), respectively. Moreover, when the current density recovers to 0.15 A g\(^{-1}\), the P@N-MPC can also reach a high capacity of 655 mAh g\(^{-1}\) after 100 times cycled at different current densities. To further study the long cycle life of the P@N-MPC composite, the P@N-MPC was cycled at 1 A g\(^{-1}\) for 1000 cycles (Figure 5D). It delivers a high reversible capacity of 450 mAh g\(^{-1}\) after 1000 cycles with ultrahigh CE of almost constant 100\% during the long-cycle life, displaying an extremely low capacity deterioration rate of 0.02\% per cycle. To our best knowledge, the superior electrochemical performance of the P@N-MPC in terms of Na-ion storage for red P is unprecedented. As show in Figure S8 (Supporting Information), the P@N-MPC shows improved capacity retention at the low and higher current densities compared with several previous works, including red P/carbon nanofibers composites,\[47\] red P/carbon black composites,\[36,38\] red P/carbon nanotubes composites,\[33,39,40\] and red P/graphene composites.\[41–43,50\] In the case of long-life cycle more than 500 cycles, only one work was reported by Zhu et al.\[33\] up to now, displaying 250 mAg h\(^{-1}\) after 2000 cycles. Compared with the Zhu et al.’s...
work, the P@N-MPC shows the higher capacity after 1000 cycles as discussed above. The highly improved electrochemical performance indicates that confining red P nanoparticles in N-doped microporous carbon is an effective approach to improve the electrochemical performance of red P-based anode materials for NIBs.[33,35,42,44]

The high rate capacity and ultralong cycle life of the P@N-MPC is mainly attributed to the unique structure, amorphous red P encapsulated in highly nitrogen-doped microporous carbon. First, encapsulation of the nanosized red P particles in microporous carbon is crucial to stabilize the electrodes against the huge volume change of red P during cycling and form stable SEI layer on the surface of electrodes, finally guaranteeing excellent cycling stability with high Coulombic efficiency. As shown in Figure S9 (Supporting Information), the P@N-MPC electrode maintains the original structure without fracture after 100 discharge–charge cycles. Additionally, the microporous carbon matrix with high content of nitrogen doping provides numerous pathways of ions and electrons, resulting in rapid transfer of ions/electrons along the electrodes. Furthermore, the uniform micropores restrict the size of confined red P particles to sub-1 nm, highly enhancing the electrochemical activity of red P.

In summary, we have demonstrated the rational design and fabrication of red P/carbon composite with core/shell structure by confining nanosized amorphous red P in N-doped microporous carbon as superior anodes for sodium-ion batteries via a facile strategy. The MOF-derived N-doped microporous carbon with sub-1 nm micropore is favorable for the rapid diffusion of organic electrolyte ions and the effective encapsulation of red P. Meanwhile, the porous carbon matrix could not only facilitate the transport of electrons during charge/discharge, but also accommodate the huge volume change of red P during sodiation/desodiation process. The synergy effects from such a rational design leads to enhanced electrochemical activity of red P and improved sodium storage performance. The P@N-MPC composite shows a high reversible capacity (600 mA h g\(^{-1}\) after 100 cycles at 0.15 A g\(^{-1}\)) and excellent rate performance (450 mA h g\(^{-1}\) at 1 A g\(^{-1}\) after 1000 cycles with an extremely low capacity decay rate of 0.02% per cycle). The prepared red P-based anode material shows great promise for practical application in the next-generation sodium-ion batteries. Furthermore, this special design could be extend to prepare other energy storage materials that need efficient ionic and electronic transport.

**Experimental Section**

**Synthesis of ZIF-8-Derived N-Doped Microporous Carbon (N-MPC):** ZIF-8 nanocrystals were first prepared according to the literature[38] The ZIF-8 nanocrystals were then carbonized in one tube furnace in N\(_2\) flow. The ZIF-8 was first heated up to 300 °C with a heating rate of 2 °C min\(^{-1}\) and kept for 2 h and then further heated up to 900 °C with a heating rate of 5 °C min\(^{-1}\) and maintained for 5 h. The as-prepared sample was washed with dilute HCl and then deionized water for several times to remove Zn. The ZIF-8-derived microporous carbon was finally obtained.

**Synthesis of Red P@N-MPC:** 0.5 g commercial red P (purity ≥ 99%, Sinopharm Chemical Reagent Co., Ltd.) and 2.5 g as-prepared...
microporous carbon were mixed and placed in one sealed quartz tube under vacuum. The sealed quartz tube was then heated to 900 °C and held at the temperature for 4 h, where heating rate was 4 °C min⁻¹. After cooling to 260 °C, the vessel was held at this temperature for 24 h to convert white P to red P, where cooling rate was 1 °C, the vessel was held at this temperature for 24 h to cool to 260 °C. The mass loading of the electrodes was about 1.1–1.5 mg cm⁻². The mass loading of the electrodes was mixed with acetylene black (10 wt%) and poly(vinylidene fluoride) binder (10 wt%) to make a homogeneous slurry. Then the slurry was vacuum oven overnight at 60 °C and held at the temperature for 4 h, where heating rate was 4 °C and 1. After the condensation process and drying under vacuum.

**Characterization:** XRD (TTR-III, Rigaku, Japan) was used to study the structure and elemental mapping of materials. Nitrogen adsorption/desorption isotherms were measured with an ASAP 2020 Accelerated Surface Area and Porosimetry instrument. Electrochemical Characterization: The P@N-MCP composite (80 wt%) was mixed with acetylene black (10 wt%) and poly(vinylidene fluoride) binder (10 wt%) to make a homogeneous slurry. Then the slurry was casted onto copper foil using a doctor blade, followed by drying in a vacuum oven overnight at 60 °C. The mass loading of the electrodes was about 1.1–1.5 mg cm⁻². Electrochemical test cells (2032 coin cells) for sodium-ion batteries were assembled with sodium foil as counter electrode, and glass fiber (GF/D) from Whatman as a separator. The cells were assembled in an argon-filled glove box. The galvanostatic charge–discharge tests for sodium-ion batteries were conducted between 0.001 and 2.0 V.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or www.advancedsciencenews.com.

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