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Abstract

Maintaining structural stability and alleviating the intrinsic poor conductivity of conversion-type reaction anode materials are of great importance for practical application. Introducing void space and a highly conductive host to accommodate the volume changes and enhance the conductivity would be a smart design to achieve robust construction; effective electron and ion transportation, thus, lead to prolonged cycling life and excellent rate performance. Herein, uniform yolk-shell FeP@C nanoboxes (FeP@CNBs) with the inner FeP nanoparticles completely protected by a thin and self-supported carbon shell are synthesized through a phosphidation process with yolk-shell Fe₂O₃@CNBs as a precursor. The volumetric variation of the inner FeP nanoparticles during cycling is alleviated, and the FeP nanoparticles can expand without deforming the carbon shell, thanks to the internal void space of the unique yolk-shell structure, thus preserving the electrode microstructure. Furthermore, the presence of the highly conductive carbon shell enhances the conductivity of the whole electrode. Benefiting from the unique design of the yolk-shell structure, the FeP@CNBs manifests remarkable lithium/potassium storage performance.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Yang, F., Gao, H., Hao, J., Zhang, S., Li, P., Liu, Y., Chen, J. & Guo, Z. (2019). Yolk-Shell Structured FeP@C Nanoboxes as Advanced Anode Materials for Rechargeable Lithium-/Potassium-Ion Batteries. *Advanced Functional Materials*, 29 (16), 1808291-1-1808291-8.

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Yolk-shell structured FeP@C nanoboxes as advanced anode materials for rechargeable lithium/potassium ion batteries

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Keywords: Iron phosphide, anode materials, yolk-shell structure, Lithium-ion battery, Potassium-ion battery

Abstract

Maintaining structural stability and alleviating the intrinsic poor conductivity of conversion-type reaction anode materials are of great importance for practical application. Introducing void space and a highly conductive host to accommodate the volume changes and enhance the conductivity would be a smart design to achieve robust construction, effective electron and ion transportation, thus, lead to prolonged cycling life, and excellent rate performance. Herein, uniform yolk-shell FeP@C nanoboxes (FeP@CNBs) with the inner FeP nanoparticles completely protected by a thin and self-supported carbon shell were synthesized through a phosphidation process with yolk-shell Fe₂O₃@CNBs as precursor. The volumetric variation of the inner FeP nanoparticles during cycling is alleviated and the FeP nanoparticles can expand without deforming the carbon shell, thanks to the internal void space of the unique yolk-shell

1 structure, thus preserving the electrode microstructure. Furthermore, the presence of the
2 highly conductive carbon shell enhances the conductivity of the whole electrode.
3 Benefiting from the unique design of the yolk-shell structure, the FeP@CNBs manifests
4 remarkable lithium/potassium storage performance. The as-prepared FeP@CNBs
5 electrode exhibits a high capacity of 609 mAh g⁻¹ at 100 mA g⁻¹ and excellent cycling
6 stability without any significant capacity loss in lithium-ion batteries (476 mAh g⁻¹ after
7 400 cycles at 500 mA g⁻¹). In the case of potassium-ion batteries, a reversible capacity
8 of 205 mAh g⁻¹ was retained after 300 cycles at 100 mA g⁻¹.

9 1. Introduction

10 Because of their high energy and power densities, lithium ion batteries (LIBs) have
11 been extensively investigated and widely as the power for portable electronics and
12 electrical vehicles^{[1][2][3]}. For large-scale stationary energy storage, however, such as
13 electrical grids, the limited and uneven distribution of lithium resources in the Earth's
14 crust is restricting the further development of LIBs^{[1][4]}. Recently, potassium ion
15 batteries (PIBs) have attracted tremendous attention as a potential alternative to LIBs,
16 due to the abundant potassium reserves on Earth and its low standard hydrogen potential
17 (-2.93 V versus E^0), close to that of lithium (-3.04 V versus E^0)^{[5][6]}. The large potassium
18 ion radius (1.38 Å) results in sluggish kinetics, however, during electrochemical
19 processes^{[5][7]}. Although unremitting efforts have been devoted to and great progress
20 achieved in the development of energy storage materials, there is still a long way to go
21 to achieve feasible anode materials for LIBs and PIBs with satisfactory capacity.
22 Among the various proposed anode materials, including carbonaceous materials^{[8][9]},

1 alloy materials^{[10][11]}, metal phosphides^{[12][13]}, and metal sulphides^{[14][15]}, iron phosphide
2 is one of the most appealing anode materials for both LIBs and PIBs, because of the
3 abundance of its raw materials (Fe and P) and its high theoretical capacity of ~926 mAh
4 g⁻¹^[16]. Nevertheless, FeP undergoes large volume expansion (~200 %) during the
5 lithiation/potassiation process, leading to pulverization of the electrode materials and
6 fast capacity fading during long-term cycling^[17]. What is more, the relatively low
7 electronic conductivity of FeP affects the electrochemical redox reactions to some
8 extent and leads to low utilization of the active materials^[18]. To address these issues,
9 FeP with various nanostructures have been proposed, and tuning the morphology and
10 structure has been proven to be an effective way to address the above
11 challenges.^{[19][20][21][22][23][16]} Nanostructured FeP can not only reduce the electron and
12 ions transport paths, but also buffers the strain resulting from volume expansion^[18]. For
13 instance, FeP/C nanocubes that consist of FeP nanoparticles distributed in a carbon
14 scaffold have been fabricated^[21]. The carbon matrix enhances the conductivity of the
15 electrode and enables fast electron/ion transportation. The unique structure provides
16 abundant reactive sites that are evenly distributed in the carbon nanocubes. As a result,
17 improved electrochemical performance is achieved. Similarly, carbon-coated FeP
18 nanoplates were reported, in which the two-dimensional (2D) nanostructure releases
19 the mechanical strain and buffers the drastic volume expansion to achieve stable cycling
20 performance^[20]. Even though improvement of the electrochemical performance has
21 been achieved by introducing conductive carbonaceous materials into FeP, the structural
22 integrity of the electrode during the cycling process is still a challenge that needs to be

1 addressed. Therefore, developing a novel FeP based hybrid by introducing particles
2 with a void space and an integrated carbon shell to control the volume changes, shorten
3 the electron/ion diffusion paths, and improve the whole conductivity could be a
4 potential strategy to further promote its electrochemical performance.

5 Herein, yolk-shell structured FeP@carbon nanoboxes (FeP@CNBs) have been
6 synthesized through a novel phosphidation-in-nanobox strategy. By confining FeP
7 particles in hollow carbon cubes, this unique architectural design offers multiple
8 advantages for addressing the problems associated with FeP during electrochemical
9 processes. The complete and robust carbon shell can not only facilitate efficient electron
10 transfer and enhance the electrical conductivity of the composite, but also prevents the
11 agglomeration of the active materials. More importantly, the extra void space of the
12 yolk-shell structure can accommodate the large volume variation of FeP and maintain
13 the integrity of the electrode microstructure. Furthermore, the nanoboxes are expected
14 to have higher tap density than other nanostructures, which is a significant parameter
15 for electrode materials with high volumetric energy density. The as-synthesized
16 FeP@CNBs electrode has demonstrated a high reversible capacity of 609 and 205 mAh
17 g^{-1} at 100 mA g^{-1} for LIBs and PIBs, respectively. Remarkable rate performance (380
18 mAh g^{-1} at 2 A g^{-1}) and ultra-long cycling life (476 mAh g^{-1} after 400 cycles at 500 mA
19 g^{-1}) in LIBs have also been achieved.

20 2. Experimental section

21 2.1. Material synthesis

22 Synthesis of Fe_2O_3 nanocubes: Fe_2O_3 nanocubes were prepared using the hydrothermal

1 method^[24]. In the typical synthesis process, 16.22 g FeCl_3 was added into 50 mL
2 deionized water to produce a brown solution. Then, 50 mL of 5.4 M NaOH solution
3 was added into the brown solution under magnetic stirring at 75 °C. The resultant
4 solution was then transferred to an autoclave, which was kept at 100 °C for 4 days. After
5 the autoclave was cooled down to room temperature, the product was harvested by
6 centrifugation and washed several times in de-ionized water. The resultant composite
7 was then dried in a 70 °C vacuum oven for 12 h.

8 Synthesis of Fe_2O_3 @polydopamine (PDA) core-shell nanocubes^[25]: 400 mg as-
9 prepared Fe_2O_3 nanocubes were first dispersed into 500 mL of 10 mM Tris-buffer
10 solution by ultrasonication for 30 min. Then, 200 mg of dopamine hydrochloride was
11 added into the above solution, which was kept stirring for 10 hours. The resultant
12 product was collected via centrifugation and washed three times with deionized water
13 and ethanol, respectively, and dried at 70 °C overnight.

14 Synthesis of yolk-shell Fe_2O_3 @CNBs^[26]: the as-prepared core-shell Fe_2O_3 @PDA
15 nanocubes were annealed at 550 °C for 2 h in Ar with a heating rate of 3 °C min⁻¹ to
16 yield the core-shell Fe_2O_3 @C nanocubes. Then, the as-obtained core-shell Fe_2O_3 @C
17 nanocubes was dispersed in 4 M HCl solution with stable stirring for 1 h to partially
18 etch the Fe_2O_3 core to yield the yolk-shell Fe_2O_3 @C nanoboxes. After rinsing,
19 centrifugation, and drying at 70 °C overnight, the yolk-shell Fe_2O_3 @C was harvested.
20 The carbon nanoboxes were prepared by increasing the etching time to 12 h.

21 Synthesis of yolk-shell FeP@CNBs^[27]: Yolk-shell FeP@CNBs were synthesized in a
22 two-zone furnace. Typically, 1 g NaH_2PO_2 was loaded into an alumina boat which was

put at the center of the upstream zone, while another alumina boat containing 50 mg yolk-shell $\text{Fe}_2\text{O}_3@\text{C}$ was put in the center of the downstream zone. Flowing Ar gas was initially passed through the tube for 2 h to remove the air. Subsequently, the temperature of the upstream zone was raised to 300 °C and held for 1.5 h with a heating rate of 2 °C min^{-1} , meanwhile, the temperature of the downstream zone was raised to 550 °C and held for 2 h with a heating rate of 5 °C min^{-1} . After the furnace was cooled down, the yolk-shell $\text{FeP}@\text{C}$ nanoboxes were obtained. For comparison, FeP nanocubes were synthesized by using the Fe_2O_3 nanocubes as the precursor, The phosphidation process was the same to that for yolk-shell $\text{FeP}@\text{C}$ nanoboxes.

2.2. Materials characterization:

The crystal structures of the as-obtained material were measured using X-ray diffraction (XRD, GBC MMA diffractometer, Cu $K\alpha$ lines, $\lambda = 1.54056 \text{ \AA}$) with a scanning rate of 1° min^{-1} . Raman spectra were collected on a JobinYvon HR800 Raman spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were carried out using a VG multilab 2000 (VG Inc.), and all the binding energy data were calibrated using the C 1s peak at 284.8 eV of the surface adventitious carbon. The photoelectron spectrometer used monochromatic Al $K\alpha$ radiation under vacuum of $2 \times 10^{-6} \text{ Pa}$. The morphology and particle sizes of the as-synthesized samples were characterized on a JEOL JSM-7500FA field-emission scanning electron microscope (FESEM). The details of the crystal structure and EDS mapping were further examined by scanning transmission electron microscope (STEM, JEOL JEM-ARM200F), which was conducted at 200 kV. Thermogravimetric analysis (TGA; TA Instruments 2000) was conducted under air

from 25 to 700°C with a heating rate of 5 °C min⁻¹.

2.3. Electrochemical measurements

The working electrodes were prepared by a slurry-coating method. Typically, the prepared materials were ground carefully with Super P and carboxymethyl cellulose (CMC) in a weight ratio of 8:1:1 in deionized water to form a slurry. Then, the as-prepared slurry was spread out on copper foil using a doctor blade, and the foil was dried at 80 °C under vacuum conditions overnight. The electrochemical tests were conducted with CR 2032 coin type cells, which were assembled in an argon-filled glove box. In the lithium ion batteries (LIBs), the counter electrode was a disk of lithium metal, and Celgard 2400 were used as separator. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1:1 by volume). In the case of the potassium ion batteries (PIBs), the electrolyte consisted of a solution of 0.8 M KPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume). The counter and reference electrodes were potassium metal, and the separator was glass fiber. Cyclic voltammetry was carried out on a VMP-3 electrochemical workstation at a scan rate of 0.1 mV s⁻¹. The charge-discharge tests were conducted on a Land CT2001A battery tester over the voltage range of 0.01-2.5V at different constant current densities. All the specific capacities were based on the weight of the composites.

If no special

2.4. Hydrogen evolution reaction characterization and performance test

All electrochemical characterization and performance tests were carried out in a three-electrode configuration in an electrolyte of 0.5 M H₂SO₄ solution on a VMP3 Biologic

1 potentiostat. The counter and reference electrodes were platinum wire and Ag/AgCl in
2 saturated KCl electrode, respectively. To prepare the working electrodes, 4 mg active
3 materials was first added into 1 mL of a solution consisting of a 9:1 (v/v) ratio of
4 absolute ethanol to Nafion (5 wt%). Then, the as-prepared suspension was sonicated
5 for 2 h to produce a homogeneous ink. After that, 10 μ l of the ink was then drop-casted
6 onto a glassy carbon electrode as working electrode. Linear sweep voltammetry (LSV)
7 was conducted with a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy
8 (EIS) was performed in frequencies ranging from 100 kHz to 0.1 Hz. Potentials were
9 converted from Ag/AgCl to reversible hydrogen electrode (RHE) via + (0.197 + 0.0592
10 pH) V.

11 3. Results and discussion

12 [Figure 1a](#) illustrates the detailed synthesis procedure for the FeP@CNBs, which
13 consists of hydrothermal reaction, carbon-coating, Fe₂O₃ etching, and the
14 phosphidation process. First, monodisperse Fe₂O₃ nanocubes were facilely synthesized
15 by hydrothermal reaction and used as the starting materials. Subsequently, a layer of
16 carbon was uniformly and firmly coated on the surfaces of the Fe₂O₃ nanocubes by
17 polydopamine-coating and a high temperature annealing treatment^[28]. As shown in
18 [Figure 1b and c](#), the as-synthesized Fe₂O₃@C nanocubes maintain the morphology of
19 the Fe₂O₃ nanocube precursor with a smooth carbon shell. The thickness of the carbon
20 layer was around 30 nm, which can be identified from the TEM image ([Figure 1c](#)). In
21 order to form the yolk-shell structure, core-shell Fe₂O₃@C nanocubes were dispersed
22 into hydrochloric acid solution (HCl) for Fe₂O₃ etching. In this step, the Fe₂O₃ core was

1 partially removed, and a void space between the Fe_2O_3 and the carbon shell was formed
2 (Figure 1d and e). It is notable that the void space can be controlled by the HCl etching
3 time. When the etching time was extended to 12 h, the Fe_2O_3 core was totally removed,
4 and the hollow carbon nanocubes were harvested (Figure S1). The above yolk-shell
5 $\text{Fe}_2\text{O}_3@\text{C}$ nanoboxes were then subjected to a phosphidation process, during which the
6 Fe_2O_3 yolk was chemically transformed to FeP, and thus, uniform yolk-shell
7 FeP@CNBs were obtained (Figure 1f and g). As shown in the XRD patterns (Figure
8 1h), during the synthesis process for the FeP@CNBs, the starting materials, $\alpha\text{-Fe}_2\text{O}_3$
9 nanocubes, with correspondingly indexed XRD patterns (JCPDS 33-0664), were
10 transformed to $\gamma\text{-Fe}_2\text{O}_3@\text{C}$ nanocubes (JCPDS 33-0664) after the high temperature
11 annealing. All the XRD peaks of the FeP@CNBs can be indexed to orthorhombic FeP
12 (JCPDS: 89-2746) without any obvious impurities, indicating that the $\gamma\text{-Fe}_2\text{O}_3$
13 nanoparticles inside the carbon nanoboxes were successfully transformed to pure-phase
14 FeP crystals during the phosphidation process. Similarly, FeP nanocubes were also
15 synthesized through the same phosphidation procedure, except that $\alpha\text{-Fe}_2\text{O}_3$ nanocubes
16 were used as the precursors (Figure S2). All the XRD peaks of the FeP nanocubes
17 obtained from the phosphidation of $\alpha\text{-Fe}_2\text{O}_3$ nanocubes also can be indexed to
18 orthorhombic FeP (JCPDS: 89-2746) (Figure S3).

19 The scanning electron microscope (SEM) images of the FeP@CNBs (Figure 2a and b),
20 show that the as-obtained FeP@CNBs were highly uniform with an average particle
21 size of ~ 400 nm, consistent with the $\text{Fe}_2\text{O}_3@\text{C}$ nanobox precursor. The yolk-shell structure
22 is confirmed in the TEM images (Figure 2d and e). In the high-resolution TEM

1 (HRTEM) image (Figure 2c), the lattice of (200) and (103) crystal planes with a *d*-
 2 spacing of 0.256 and 0.182 nm, respectively, is observed. Alongside the magnified TEM
 3 image, the fast Fourier transform (FFT) pattern is consistent with the XRD result.
 4 Furthermore, the energy-dispersive X-ray spectroscopy (EDX) elemental mapping
 5 results (Figure 2f, g, h, and i) show that the distribution of Fe and P is concentrated
 6 around the central cores, verifying the existence of the FeP cores in the carbon
 7 nanoboxes. The yolk-shell structure is believed to be important for the electrochemical
 8 performance of the composite. With the advantages of FeP cores to deliver high
 9 reversible capacity, the carbon shell to improve the electronic conductivity of the
 10 composite, and void space to accommodate the volume variation, satisfactory
 11 electrochemical performance of the FeP@CNBs can be anticipated. Further evidence
 12 for the formation of the FeP@CNBs was obtained from the X-ray photoelectron
 13 spectroscopy (XPS) analysis (Figure 2k, l, and m). The XPS survey scan spectrum
 14 revealed the presence of Fe, P, C, and O on the surface of the FeP@CNBs. In the high-
 15 resolution Fe 2p XPS spectrum, two peaks with binding energy of 711.2 and 724.5 eV
 16 were observed, which can be assigned to the Fe 2p_{3/2} and Fe 2p_{1/2} peaks, respectively^[29].
 17 In the high resolution P 2p XPS spectrum, the two peaks centered at 129.3 and 130.2
 18 eV corresponded to the binding energy of P 2p_{3/2} and P 2p_{1/2}, respectively^[16].
 19 Furthermore, the peak located at 133.6 eV is attributed to PO₄³⁻ or P₂O₅, which is caused
 20 by the oxidation of P species because of contact with air^{[30][31]}. In the Raman spectra the
 21 intensity ratios of the D to the G band (*I_D/I_G*) for the FeP@CNBs and γ-Fe₂O₃@C
 22 nanocubes were calculated to be 0.90 (Figure S5), suggesting the presence of a

1 disordered and amorphous carbon component in both composites, which would be
 2 favorable to improve the diffusion rate of Li^+/K^+ ions and electrons^[32]. In order to
 3 determine the FeP content of the FeP@CNBs, thermal analysis was performed on the
 4 FeP nanocubes and FeP@CNBs (Figure S4). In the case of FeP@CNBs, a weight
 5 increase was observed between 450-600 °C in the TGA curve, which was due to the
 6 oxidation of FeP to Fe_2O_3 and P_2O_5 in the air^[23]. In the case of the FeP@CNBs, a small
 7 weight loss of about 2 wt% first occurred below 100 °C because of the removal of
 8 adsorbed water on the surface of the FeP@CNBs. After that, another weight loss took
 9 place between 420-500 °C before the weight increased between 500-600 °C. It is believe
 10 that both carbon burning and FeP oxidation occurred between the 420-600 °C. The
 11 carbon burning was the dominant process between 420-500 °C, however, and thus, a
 12 weight loss was observed. Whereas, the FeP oxidation caused the weight increase from
 13 500 to 600 °C. Based on the TGA results for FeP@CNBs and FeP nanocubes, the weight
 14 contents of FeP and carbon were calculated to be 81wt% and 19wt%, respectively.
 15 The lithium storage behavior of the FeP@CNBs was first investigated by cyclic
 16 voltammetry (CV) at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.01-2.5 V. Figure
 17 3a shows the representative CV curves from the first to the fourth cycles. In the first
 18 cathodic scan, two cathodic peaks located at 1.2 and 1.0 V are observed. The 1.2V peak
 19 can be explained by the intercalation of Li^+ into the FeP to form Li_xFeP ($\text{FeP} + x\text{Li}^+ +$
 20 $x\text{e}^- \rightarrow \text{Li}_x\text{FeP}$ ($x = 0-3$))^[33]. Whereas, the 1.0 V peak is associated with the formation of
 21 solid-electrolyte interphase (SEI) film and the reduction of Li_xFeP to Fe and Li_3P
 22 ($\text{Li}_x\text{FeP} + (3-x)\text{Li}^+ + (3-x)\text{e}^- \rightarrow \text{Fe} + \text{Li}_3\text{P}$)^[34]. During the following anodic scan, only

one broad peak centered at 1.1 V was observed, which is related to the oxidation of Fe to FeP. It is noteworthy that there is an obvious difference between the first and the following cycles, that is, the cathodic peak shifted to 0.6 V after the first cycle. Nevertheless, both the cathodic and anodic peaks in the CV curves overlap from the second cycle onward, suggesting the excellent reversibility and stability of the electrode. A similar phenomenon is also observed in the CV curves of the FeP nanocubes (Figure S6).

The lithium storage performance was also investigated by galvanostatic discharge-charge measurements. The FeP@CNBs delivered a high discharge capacity of 1125.5 mAh g⁻¹ and a charge capacity of 762.8 mAh g⁻¹ in the first cycle, giving an initial coulombic efficiency of 67.8%. The 32.2 % irreversible capacity loss of the initial cycle can be attributed to the formation of the SEI layer on the surface of the FeP@CNBs and electrolyte decomposition. Unexpectedly, as shown in the charge-discharge profile (Figure 2b), there were no obvious plateaus, but sloping lines are observed at 0.6 and 1.1 V in discharge and charge curves, respectively, which can be explained by insufficiently active reactions in the lithiation of FeP to Li_xFeP ($x = 0-3$) and the reverse delithiation of Li_xFeP ($x = 0-3$) to FeP^{[16][32]}. Figure 3c presents the cycling performance of the FeP@CNBs at a current density of 100 mAh g⁻¹. As expected, the FeP@CNBs electrode manages to maintain a high reversible capacity of 609 mAh g⁻¹ after 70 cycles without any distinct decay, indicating remarkable cycling stability. Based on the content of FeP (81%) in the FeP@CNBs and the reversible capacity (250 mAh g⁻¹) contributed by the carbon hollow spheres (Figure S8), the utilization rate of the FeP was calculated

1 to be 75%. In contrast, the FeP nanocubes show a relatively low reversible capacity of
2 477.5 mAh g⁻¹ in the first cycle, and it decreases to 250 mAh g⁻¹ after 70 cycles at 100
3 mA g⁻¹. To further evaluate the cycling stability of the FeP@CNBs, a long-term cycling
4 test was conducted. The results show that the FeP@CNBs achieved a high initial
5 reversible capacity of 545 mAh g⁻¹ and retained a charge capacity of 476 mAh g⁻¹ after
6 400 cycles at 500 mAh g⁻¹ (Figure 3e). Apart from its remarkable cycling performance,
7 FeP@CNBs demonstrated excellent rate capability at varied current rates. As shown in
8 Figure 3d, FeP@CNBs delivered high specific capacities of 608, 563, 490, 441, and
9 380 mAh g⁻¹ at 0.1, 0.2, 0.5, 1, and 2 A g⁻¹, respectively, which is much higher than for
10 the FeP nanocubes, revealing the excellent kinetics of the FeP@CNBs. The effects of
11 the yolk-shell structure towards improving the lithium storage performance of the
12 composite were further investigated by the EIS analysis comparing the FeP@CNBs and
13 FeP nanocubes electrodes (Figure 3f). The results show that the interfacial resistance of
14 the FeP@CNBs is smaller than that of the FeP nanocubes electrode, which can be
15 explained by the presence of the highly conductive carbon shell^[16]. Furthermore, the
16 morphology of the FeP@CNBs electrode after 70 cycles at 100 mA g⁻¹ was
17 characterized by TEM (Figure 3g). It is clear that the yolk-shell structure of the
18 FeP@CNBs was retained, with a layer of SEI also present on the surface of the carbon
19 shell. Void space can still observed in the TEM image, indicating that the void space in
20 the FeP@CNBs is large enough to accommodate the volume changes during the
21 repeated charge-discharge processes. *Ex situ* XRD was also performed to identify the
22 composition of the FeP@CNBs (Figure S 9). Cells were disassembled after charged in

the 70th cycle to 2.5V and the working electrodes were washed with propylene carbonate to remove the residual LiPF_6 , the XRD patterns of the cycled working electrode consist of FeP and Cu signals due to the use of Cu as current collector. Apart from the Cu and FeP peaks, no other peaks are observed in the XRD results, indicating that the composition of the working electrode turned back to FeP after 70 cycles in Lithium ion batteries.

Potassium storage properties were also examined. In the CV curves of both the FeP@CNBs (Figure 4a) and the FeP nanocubes (Figure S10) electrodes, only two peaks located at 0.8 and 2.0 V were observed in the cathodic and anodic scans after the first cycle, respectively, associated with the potassiation and de potassiation of FeP. The profiles of the charge-discharge curves are consistent with the CV results, with sloping plateaus at 0.8 and 2.0 V appearing in the discharge and charge curves, respectively (Figure 4b). Similar to the LIBs voltage profiles, the voltage profiles of KIBs are also sloping and no obvious plateaus observed, which can be ascribed to the insufficient activity of the potassiation/depotassiation reactions. The cycling performance of the FeP@CNBs at 100 mA g^{-1} within a voltage range of 0.01-2.5 V is shown in Figure 4c. Similar to the LIB performance, the PIBs exhibited high reversible capacity of 264 mAh g^{-1} in the first cycle with an initial coulombic efficiency of 47% and remarkable cycling stability. The loss the first reversible capacities is mainly ascribed to the decomposition of electrolyte to form a surface passivation SEI layer. Apart from this, another reason is that irreversible K ion trapped into the porous structure of the carbon layer and lattice of the FeP.^[35,36] TEM is performed to identify the morphology and structure of the

1 FeP@CNBs after the first potassiation. It is clearly that yolk-shell structure is
2 maintained after the first potassiation (Figure S 11). No obvious capacity loss was
3 observed over 300 cycles and a capacity as high as 205 mA g⁻¹ was obtained.
4 Considering that the reversible capacity contributed from the carbon hollow spheres is
5 negligible after 50 cycles (Figure S12), most of the reversible capacity must have come
6 from the active materials. In order to confirm the importance of the yolk-shell structure
7 for the electrochemical performance, the cycling performance of FeP nanocubes were
8 evaluated for comparison under the same conditions. The FeP nanocubes, however,
9 only offered a low reversible capacity of 189 mA g⁻¹ in the first cycle and showed
10 gradual capacity fading in the subsequent cycles. The relatively low reversible capacity
11 of the FeP nanocubes is ascribed to low utilization of the bare FeP nanocubes resulting
12 from the relatively low conductivity of the FeP.

13 Figure 4d shows the rate capacity performances of both FeP@CNBs and FeP nanocubes
14 under different current densities ranging from 0.1 to 2 A g⁻¹. In the case of the
15 FeP@CNBs, reversible capacities of 201, 156, 101, 65 and 37 mAh g⁻¹ are obtained at
16 0.1, 0.2, 0.5, 1 and 2 A g⁻¹, respectively. Furthermore, the capacity of the FeP@CNBs
17 could be restored back to 200 mAh g⁻¹ when the current density was set back to 0.1 A
18 g⁻¹, indicating the outstanding potassium storage performance of FeP@CNBs.

19 Comparisons between our work and the state-of-the-art results reported for previous
20 research on FeP based anode materials are also provided in Table S1. The cycling and
21 rate performances of FeP@CNBs in LIBs are comparable to those for most reported
22 anodes. The remarkable electrochemical performance of the FeP@CNBs can be

1 ascribed to the advantages of the yolk-shell structure. First, the carbon shell, which
2 serves as a self-supporting framework, can prevent the aggregation of FeP particles.
3 This carbon shell is well maintained even when the FeP expands during the
4 lithiation/potassiation processes, thanks to the sufficient void space of the yolk-shell
5 structure. What is more, the growth of a stable SEI layer on the surface of the carbon
6 shell, in turn, prevents the continual rupturing and reformation of the SEI, which occurs
7 commonly in all alloy-based anode materials. Second, the highly electronically and
8 ionically conducting carbon shell greatly enhances the transport kinetics. Third, the
9 electrode microstructure can be well preserved due to the void space, which allows the
10 FeP to expand without deforming the electrode microstructure, so that pulverization is
11 prevented. It is also notable that FeP@CNBs has also been demonstrated as a promising
12 option for the hydrogen evolution reaction ([Figure S13](#)), due to its advantages.

13 4. Conclusions

14 In summary, yolk-shell structured FeP carbon nanoboxes (FeP@CNBs) consisting of
15 FeP nanoparticles surrounded and protected by a carbon shell, have been developed and
16 proved to be a promising materials for rechargeable batteries and the hydrogen
17 evolution reaction. Benefiting from its unique structural features, the FeP@CNBs
18 electrode achieved remarkable electrochemical performance. Notably, the existence of
19 the carbon shell can prevent the aggregation of the FeP nanoparticles and enhance the
20 conductivity of the composite, while the void space between the carbon shell and the
21 FeP accommodates the volume expansion of the FeP during charge-discharge without
22 destroying the electrode microstructure. As a result, the FeP@CNBs electrode has

1 achieved high reversible capacity, superior rate performance, and an extremely stable
2 cycling life.

3 4 5 **Acknowledgements**

6 F. Y. and H. G. contributed equally to this work. The authors would like to thank the
7 Australian National Fabrication Facility – Materials node. The authors would also like
8 to thank the Electron Microscopy Centre (EMC) at the University of Wollongong for
9 the electron microscopy characterizations and Dr. Tania Silver for critical reading of the
10 manuscript and valuable remarks. F.Y. acknowledges the China Scholarship Council for
11 his scholarship support.

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Figure 1. Schematic illustration of the yolk-shell structured $\text{FeP}@\text{C}$ nanobox design and characterization of the intermediate materials

(a) Schematic illustration of the synthesis process for the $\text{FeP}@\text{CNBs}$; (b, d, and f) SEM and (c, e, and g) TEM images of $\text{Fe}_2\text{O}_3@\text{C}$ nanocubes (b and c), $\text{Fe}_2\text{O}_3@\text{CNBs}$ (d and e), and $\text{FeP}@\text{CNBs}$ (f and g); (h) XRD patterns of the intermediate materials.

Figure 2. Characterization of the FeP@CNBs

(a and b) SEM images, (c) HRTEM image with the corresponding FFT pattern in the inset, (d) dark-field and (e) bright-field TEM images, and (f, g, h, and i) elemental mapping analysis of FeP@CNBs; (j, k and l) XPS spectra of FeP@CNBs: survey spectrum (k), Fe 2p (l), and P 2p (m).

Figure 3. Lithium storage properties of FeP@CNBs.

(a) CV curves of the FeP@CNBs in the first four cycles. (b) Charge/discharge curves of FeP@CNBs electrode at 0.1 A g^{-1} in the 1st, 2nd, and 70th cycles. (c) Cycling performance of the FeP@CNBs and the FeP nanocubes at 0.1 A g^{-1} . (d) Rate performance of the FeP@CNBs and FeP nanocube electrodes at varied current densities. (e) Long-term cycling of the FeP@CNBs electrode at 500 mA g^{-1} . (f) Nyquist plots of the FeP@CNBs and FeP nanocubes, with the inset showing the equivalent circuit. (g) TEM image of FeP@CNBs after 70 cycles at 0.1 A g^{-1} . The capacities here are charge

capacity.

Figure 4. Potassium storage properties of FeP@CNBs.

(a) CV curves of the FeP@CNBs in the first four cycles. (b) Charge/discharge curves of FeP@CNBs electrode at 0.1 A g⁻¹ in the 1st, 2nd, and 300th cycles. (c) Cycling performance of FeP@CNBs and FeP nanocubes at 0.1 A g⁻¹. (d) Rate performance of the FeP@CNBs and the FeP nanocubes electrodes at varied current densities. The capacities here are charge capacity.

Table of content:

A unique yolk-shell structured FeP@C nanobox is developed as effective nanostructured anode materials for rechargeable batteries. The complete and robust carbon shell can not only facilitate efficient electron transfer and enhance the electrical conductivity of the composite, but also prevents the agglomeration of the active materials. More importantly, the extra void space of the yolk-shell structure can accommodate the large volume variation of FeP and maintain the integrity of the electrode microstructure. Thus, high reversible capacity and long cycling life are achieved in lithium/potassium ion batteries.

Keywords: Iron phosphide, anode materials, yolk-shell structure, Lithium-ion battery, Potassium-ion battery

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Title: Yolk-shell structured FeP@C nanoboxes as advanced anode materials for rechargeable lithium/potassium ion batteries