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Hierarchical Design of Mn₂P Nanoparticles Embedded in N, P-Codoped Porous Carbon Nanosheets Enables Highly Durable Lithium Storage

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ABSTRACT

Although transition metal phosphides anodes possess high theoretical capacities, their inferior electronic conductivities and drastic volume variations during cycling lead to poor rate capability and rapid capacity fading. To simultaneously overcome these issues, we report a hierarchical heterostructure consisting of isolated Mn₂P nanoparticles embedded into nitrogen and phosphorus co-doped porous carbon nanosheets (denoted as Mn₂P@NPC) as a viable anode for lithium-ion batteries (LIBs). The resulting Mn₂P@NPC design manifests outstanding electrochemical performances, namely, high reversible capacity (774 mAh g⁻¹ at 0.1 A g⁻¹), exceptional rate capability (347 mAh g⁻¹ at 4 A g⁻¹) and excellent cycling stability (99 % capacity retention at 4A g⁻¹ after 2000 cycles). The robust structure stability of Mn₂P@NPC electrode during cycling has been revealed by the *in-situ* and *ex-situ* transmission electron microscopy (TEM) characterizations, giving rise to long-term cyclability. Using *in-situ* selected area electron diffraction (SAED) and ex-situ high-resolution TEM studies, we have unraveled the dominant lithium storage mechanism and confirmed that the superior lithium storage performance of Mn₂P@NPC originated from the reversible conversion reaction. Furthermore, the Mn₂P@NPC||LiFePO₄ full cell exhibits impressive rate capability and cycling stability. This work introduces the potential for engineering highperformance anodes for next-generation high energy density LIBs.

KEYWORDS: Mn₂P nanoparticles; carbon nanosheets; *in-situ* TEM; anode materials; Li ion batteries

1. INTRODUCTION

To meet the rapidly increasing energy demand in electric vehicles and grid-scale energy storage systems, lithium-ion batteries (LIBs) with higher energy densities and longer lifespans have recently sparked an immense interest.¹⁻¹⁵ The development of high-performance LIBs relies on the availability of highly efficient electrode materials.¹⁶⁻²⁰ For LIB anode materials, transition metal phosphides (TMPs) based on the conversion reaction for Li storage has emerged as a promising alternative material that may potentially replace graphite-based anodes.²¹⁻²⁶ TMPs have favorable low intercalation potentials vs Li/Li⁺, low polarization and high theoretical capacities originating from multiple electron transfer per redox center.^{21,27-29} Unfortunately, poor rate performance and severe capacity decay induced by their inferior electronic conductivity and inevitable volume changes during cycling hinder their application as commercial anodes.^{23,27}

Tremendous efforts have been devoted to mitigate these issues; prime examples include structural nano-engineering of TMPs³⁰⁻³¹ and incorporating nanostructured TMPs with a conductive carbon host or substrate.^{21,24,27,29,32-33} Although enhanced properties have been demonstrated in both of these systems, they still exhibit unsatisfactory cycling and rate capabilities, especially at high rates. During cycling, there is free movement, easy aggregation and pulverization of nanostructured TMPs which may occur upon repetitive mechanical stress resulting from large volume variation when nanostructured TMPs are randomly distribution and lose attachment in the composite material.²⁹ On the other hand, recent studies have pointed out that electrodes with hierarchical porous

heterostructures have proven effective for preventing aggregation and pulverization of electroactive materials while also providing excellent electronic and ionic conductivity, electrochemical activity and mechanical stability for enhanced Li ion storage.³⁴⁻³⁷ The performance enhancement of hierarchically heterostructured electrodes with porous features benefits from the faster kinetics of redox reactions and accessible pathways for quick Li⁺-diffusion along the boundaries of coupled nanostructured active materials. These pathways also offer abundant electrode and electrolyte contact-points and free space for accommodating the volume variation during cycling.³⁴ Therefore, it is important, yet quite challenging, to carefully exploit and develop nanostructured TMPs that are well dispersed and robustly immobilized within a porous carbon frame to form hierarchical heterostructures via a facile synthesis approach. The benefits of this design would alleviate the volume changes, prevent agglomeration and facilitate efficient electron and ion transfer for markedly enhanced lithium storage performance. In addition, introduction of heteroatoms, such as nitrogen (N), phosphorus (P), sulfur (S), and boron (B), into carbonaceous materials has been proven to be a feasible strategy to improve the battery's electrochemical performance.³⁸⁻⁴¹ For instance, the incorporation of N into carbonaceous materials can induce many defects or disorders and enhance electronic conductivity, improving the capacity and the rate capability.⁴² Another attractive heteroatom is P, which possesses high electron-donating ability and expands the interlayer spacing, as well as boost electronic conductivity, enhancing the electrochemical performance.^{21,43} Previous studies have demonstrated that carbonaceous materials with P and N dual doping show better electrochemical Page 5 of 35

performance than their counterparts with solo N or P doping.⁴⁴⁻⁴⁵ These results indicate there is a synergistic effect from multiple heteroatom doping that significantly enhances their electrochemical performance.^{21,45}

Here, we present a suitable and viable strategy for fabricating a hierarchical porous heterostructure constructed by 2D ultrathin N and P co-doped porous interconnected carbon nanosheets (NPC) that contain confined and isolated Mn₂P nanoparticles (denoted as Mn₂P@NPC) as a robust anode to enable high performance LIBs. This intriguing architecture integrates nanostructural and microstructural features and offers multiple advantages for achieving enhanced lithium storage. (1) Embedding isolated nanoscale Mn₂P in 2D NPC prevents them from intermediate contact and the interaction of electrolyte with nanoscale Mn₂P allows for fast electron/ion transport, giving rise to exceptional rate performance.^{21,29} (2) The hierarchical porous NPC provides highly efficient pathways for electrons and ions and a structural scaffold prevents the aggregation of embedded active Mn₂P nanoparticles.^{21,46} These benefits are revealed by *in-situ* and *ex-situ* TEM observations and enable the $Mn_2P@NPC$ to exhibit high rate performance together with excellent stability. (3) The porous features of NPC offer extra free space for alleviating the structural strain and accommodating the large volume variation for Mn₂P nanoparticles during cycling, which is confirmed by our *in*situ and ex-situ TEM characterizations, thus alleviating the pulverization issue and leading to long-life cyclability. With these merits, the obtained Mn₂P@NPC anodes present extraordinary electrochemical performance, namely, high reversible capacity, outstanding rate capability and exceptional cycling stability. Furthermore, a full cell with the prelithiated $Mn_2P@NPC$ anode and commercial LiFePO₄ cathode with desirable cycling stability and rate capability is demonstrated. Overall, our work fundamentally and experimentally illustrates the importance and success of engineering hierarchically porous heterostructured electrodes for advanced LIBs anodes.

2. EXPERIMENTAL SECTION

Materials Synthesis. $Mn_2P@NPC$ composites are prepared as follows: 1.260 g melamine (MA) is added into 10 ml Mn(CH₃COO)₂·4H₂O (0.245 g) ethanol solution under magnetic stirring for 30 minutes. Afterwards, the reactor is moved into an ultrasonic bath, and 2 mL of phytic acid (PA) is added dropwise to form a white slurry at room temperature. The slurry is then dried completely in an 80°C drying box and calcinated at 980°C for 3h under nitrogen atmosphere to achieve final product $Mn_2P@NPC$. Pure Mn_2P and NPC can be obtained by a similar process by withholding MA and $Mn(CH_3COO)_2\cdot4H_2O$, respectively.

Materials Characterization. Powder X-ray diffraction (XRD) (PANalytical X'pert PRO X-ray diffractometer) patterns are recorded with Cu K₁ irradiation ($\lambda = 1.5406$ Å). The morphology and structure of the samples are studied by FEI Talos-F200s TEM and a Zeiss SUPRA 55 scanning electron microscope (SEM). Raman spectra are measured on a Raman spectrometer (HORIBA Lab RAM HR Evolution) The N₂ adsorption/desorption curves are determined by BET measurements using a BK112T-B analyzer in a temperature range of 120 °C-200 °C. X-ray photoelectron spectroscopy (XPS) (Physical Electronics' Quantum 2000 Scanning ESCA Microprobe System) is

carried out using Al anode source. All XPS measurements are collected with a 300 mm \times 700 mm spot size using a charge neutralizer during acquisition. Survey scans are collected with a 1.0 eV step size, and are followed by high resolution scans with a step size of 0.05 eV for C 1s, N 1s, Mn 2p and P 2p regions. All the peaks are fitted based on the reference C-C bond at 284.7 eV. The *in- situ* TEM experiment during the electrochemical process of theMn₂P@NPC hybrid are done inside TEM (FEI Talos 200s) using a Nanofactory TEM-STM specimen holder , where the Mn₂P@NPC sample is mounted to an Au wire and a small piece of Li with a solid electrolyte of naturally-grown Li₂O is coated onto a piezo-driven W tip. A bias voltage of -3 V is applied to the Au end to start the lithiation process of Mn₂P@NPC composite.

Electrochemical Testing. The anodes are prepared by homogeneously mixing of asobtained materials ($Mn_2P@NPC$), acetylene black (Super-P), and carboxyl methyl cellulose (CMC) (8:1:1 by weight), then the slurry is casted on the Cu foil followed by drying at 80 °C for 12 under vacuum. The dried Cu foil is punched into discs with a diameter of 12 mm which are then assembled into CR2025 coin cells. Li foil, Celgard 2300, and .1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate membrane (DEC)/dimethyl carbonate (DMC) (1:1:1 by volume) (Samsung Chemical Corporation) are used as counter electrode, separator and electrolyte, respectively. The active material mass loading is measured to be 1 mg cm⁻². All the specific capacity values in this paper are based on the total mass of the Mn_2P @NPC. The measured cells are assembled in an argon-filled glovebox with concentrations of oxygen and moisture below 0.1 ppm. The galvanostatic charge–discharge tests are measured using a NEWARE CT-4008 system (Shenzhen, China) within a voltage window of 0.01–3.00 V (vs Li/Li⁺) under various current densities of 0.1–4 A g⁻¹ at 25 °C. Cyclic voltammetry (CV) is measured from 0.1 to 2 mV s⁻¹ and electrochemical impedance spectrometry (EIS) is performed by employing an AC voltage of 10 mV amplitude over the frequency range from 10 MHz to 0.01 Hz on an electrochemical workstation (CHI660E) at room temperature. With regard to the full cell fabrication, the detail information can be referred to our previous work.⁴⁷ An N/P ratio of 1: 1.2 is designed for the full cell and its capacity is determined by the weight of positive electrode material.

3. RESULTS AND DISCUSSION

Figure 1a schematically illustrates the synthesis protocol of the Mn₂P@NPC. First, stoichiometric amounts of manganese acetate and MA are thoroughly mixed in ethanol solution to form a homogeneous mixture by magnetic stirring. Then, the designed amount of PA is added dropwise into the above mixture until it turns to a white slurry under magnetic stirring. Finally, the Mn₂P@NPC is obtained by subsequent annealing at 980 °C for 3h in a nitrogen atmosphere. **Figure 1b-d** displays the typical FESEM images of as-synthesized Mn₂P@NPC. We can clearly see that the obtained Mn₂P@NPC demonstrates hierarchical porous heterostructure with micro- and nanostructures through the use of microsized porous NPC that contain numerous confined and isolated Mn₂P@NPC clearly demonstrate that Mn₂P NPs are uniformly

embedded into the wrinkled and porous structural feature of NPC. Remarkably, isolated Mn₂P nanoparticles are encompassed by void space, which is highly beneficial in buffering the volume variations during cycling ²¹. Energy dispersive X-ray (EDX) analysis (Figure S1) displays the peaks of Mn, P, N, C and O elements with an atomic ratio of P/Mn of 0.72/1 (Figure 2h) that is higher than the stoichiometric value 0.5/1 for the pure-phased Mn₂P. The ratio of P/Mn is also confirmed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Supplementary Table S1). The excess of P can be attributed to the doping of P in the NPC, which is thereafter verified by XPS results in Figure 1(h-i). The phase purity and crystal structure of Mn₂P@NPC is displayed in Figure 1e. All the identified peaks are consistent with the Mn₂P (JCPDS no. 89-4842). A broadened peak around 26° relates to NPC. For comparison, pure Mn₂P and NPC are also prepared (Figure S2) under the same synthesis conditions without adding MA and manganese acetate, respectively. In addition, the Mn₂P nanoparticles embedded in P-doped porous interconnected carbon nanosheets (denoted as $Mn_2P(a)PC$) are synthesized by a similar synthesis process but replacing MA with glucose. The related material characterizations are shown in Figure S3a-h.

The chemical composition of $Mn_2P@NPC$ is investigated by XPS and displays the existence of Mn, P, N, O and C (Figure 1f), which is consistent with the EDX results. The high-resolution Mn2p spectrum yields two peaks located at 641.5 and 653.8 eV, which correspond to Mn ($2P_{3/2}$) and Mn ($2P_{1/2}$) of Mn in the Mn-P bond.⁴⁸ Figure 1h shows the high-resolution P2p spectrum, in which two small peaks at 129.6 eV and 128.8 eV both correspond to Mn-P and one dominant peak at 133.0 eV corresponds to

P-C.²¹ **Figure 1i** shows the high-resolution C1s spectrum, which can be fitted with four peaks located at 284.5, 285.7, 288.1, and 290.0 eV, corresponding to C-C, C–N/C– O/C-P, C=N/C=O and O=C-O.^{21,45,49} The carbon component is further confirmed by Raman spectrum (**Figure S4a**) with broad peaks centered at ~1339 and 1588 cm⁻¹ that can be recognized as D (disordered) and G (graphite) bands of the carbon materials. The I_D/I_G ratio for Mn₂P@NPC is calculated to be 1.11, which is higher than the reported results of double-carbon network modification anode materials,⁵⁰⁻⁵² revealing the existence of plentiful defects in NPC after N and P dual doping.²¹ The carbon content in the Mn₂P @NPC is estimated to be 18.8 % according to TGA and XRD results (**Figure S5**, more details are given in supporting information). The highresolution N1s spectrum is shown in **Figure 1j**, the peaks located at 399.7, 400.9 and 402.7 eV are related to pyridinic N, pyrrolic N and graphitic N.^{21,28,45}





Figure 1. (a) Schematic illustration the formation of $Mn_2P@NPC$ composite, (b-d) SEM images of $Mn_2P@NPC$ composite, (e) XRD patterns of $Mn_2P@NPC$ composite, Survey (f) and high-resolution scans of Mn 2p (g), P 2p (h), C 1s (i) and N 1s (j) XPS spectrum of $Mn_2P@NPC$ composite.

The detailed microstructures and morphologies of the Mn₂P@NPC are further elucidated by TEM. The low-magnification TEM image shown in Figure 2a unambiguously confirms the porous structure of the microsized NPC with embedded sphere-like Mn_2P nanoparticles featuring diameters from several nanometers to ~100 nm and empty space among these nanoparticles, conforming to SEM results. More interestingly, these Mn₂P nanoparticles present no direct-contact between each other, which is highly important in preventing the agglomeration during electrochemical cycling.²⁹ A closer TEM image in Figure 2b reveals that the individual nanoparticle is uniformly coated by a thin carbon layer with void space around it, embedded in the NPC matrix. The HRTEM and corresponding fast-Fourier transformation (FFT) in the Figure 2c clearly demonstrate the high crystallinity of Mn₂P nanoparticles, in which the clear lattice fringes with interplanar distances of 0.19, 0.2 and 0.28 nm correspond to the $(\overline{2} \ \overline{10})$, $(\overline{201})$ and $(0\overline{1} \ \overline{1})$ lattice planes of hexagonal Mn₂P, respectively. The high-angle annular dark-field (HAADF)-STEM images in Figure 2d further confirm that the isolated Mn_2P nanoparticles are pinned into the porous NPC with good uniformity. The porous nature of NPC is ascertained by the N₂ adsorption/desorption method (Figure S4b). Additionally, the elemental mappings (Figure 2e-j) of the Mn, P, C, N distribution within the Mn₂P@NPC composite unambiguously reveal that isolated Mn₂P nanoparticles are homogeneously immobilized into the microsized porous NPC matrix, confirming the successful formation of Mn₂P@NPC hybrid structure.



Figure 2. (a-b) TEM and (c) HRTEM image of Mn₂P@NPC composite (the inset in Fig. 2c shows the corresponding FFT image), (d-j) STEM image (d) and corresponding EDS mappings of (e) C, (f) N, (g) Mn, (h) P, (i)overlap of Mn, P, and (j) overlap of C, N, Mn, P elements.

The electrochemical performances of as-fabricated $Mn_2P@NPC$ as a LIB anode are conducted using the coin cells. The CV curves of $Mn_2P@NPC$ electrode are recorded at 0.1 mV s⁻¹ between 0.01 and 3 V (vs. Li/Li⁺). As shown in **Figure 3a**, during the first cathodic scan, the broad peak at around 1.20 V is attributed to the formation of a solid electrolyte interphase (SEI) layer, while the subsequent evident cathodic peak located at about 0.43 V associated with a small peak at 0.67 V is related to the conversion reaction of Mn_2P to metallic Mn and Li₃P.^{48,53} During the first anodic scan, two oxidation peaks at 0.69 and 1.08 V can be attributed to the stepwise oxidation of Mn and dealloying reaction of Li₃P to regenerate Mn₂P. From the second scan onward, the cathodic peaks shift slightly to 0.46 and 0.69 V, respectively, while the position of the anodic peaks remain almost unchanged. Moreover, the CV curves approximately overlap, indicating good reversibility of electrochemical reactions during charge/discharge process. The CV curves of NPC and bulk Mn₂P electrode are shown in **Figure S6**. From **Figure S6a**, it can be seen that the NPC electrode displays one broad peak at around 0.94 V during the first cathodic scan due to the irreversible decomposition of electrolyte leading to the formation of SEI, which disappears in the subsequent scans. As shown in **Figure S6b**, the bulk Mn₂P electrode presents similar peaks in the CV curves as Mn₂P@NPC electrode, indicating the typical conversion reaction.

Figures 3b and 3c show the typical discharge–charge profiles of the Mn₂P@NPC electrode during different cycles and their corresponding cycling performance under 0.1 A g⁻¹, respectively. The Mn₂P@NPC electrode delivers an initial discharge and charge specific capacities of 1003 and 601 mA h g⁻¹, respectively, corresponding to a coulombic efficiency of 60 %. The initial large capacity loss is mainly caused by the inevitable formation of the SEI layer and electrode pre-activation,⁵⁴⁻⁵⁶ which can be solved via pre-lithiation through well-developed industrial approach.⁵⁷ Then, the coulombic efficiency increases fast to 94 % at the 2nd cycle and levels off at 97–99 % in subsequent cycles. After slightly dropping in the initial 14 cycles, the capacity gradually rises in the subsequent 150 cycles and then tends to be stable, reaching a

specific capacity of 598 mA h g⁻¹ after 300 cycles with the capacity retention of 99 %, suggesting excellent cycling stability. The *ex-situ* SEM and TEM images illustrated in **Figure S7a-f** confirm that the electrode structure of Mn₂P@NPC is well maintained after 300 cycles without visible structural collapse or loss of Mn₂P particles, suggesting that the carbon sheets are robust enough to buffer the volume variation while preventing pulverization of Mn₂P during cycling and therefore guaranteeing excellent structural stability. The elemental mapping analysis in **Figure S7g-m** clearly reveals the uniform distributions of Mn and P elements in the reacted Mn₂P nanoparticles region and C, N and P element in the NPC region, proving that the hybrid structure of the Mn₂P@NPC is preserved.

Figure 3d shows the rate capabilities of bare Mn₂P, NPC and Mn₂P@NPC electrodes at various current densities while their corresponding discharge–charge voltage profiles of the first cycle is given in **Figure S8a-c**. As shown in **Figure 3d**, the Mn₂P@NPC electrode demonstrates improvement on the rate performance as compared to those of the bare NPC and bulk Mn₂P electrodes. It delivers the reversible capacities of ~774, 618, 534, 472, 412 mA h g⁻¹ at current densities of 0.1, 0.2, 0.5, 1, 2 A g⁻¹, respectively. Even at a high current density of 4 A g⁻¹, a capacity of 347 mA h g⁻¹ is obtained, which is much higher than those of bare NPC (114 mA h g⁻¹) and bulk Mn₂P (34 mA h g⁻¹) electrodes. As the current density is finally returned back to 0.1 A g⁻¹ after 200 cycles, the specific capacity of Mn₂P@NPC electrode is recovered to 725 mA h g⁻¹ (93.7% of the initial capacity), while a capacity of 562 mA h g⁻¹ (85 % of the initial capacity) and 204 mA h g⁻¹ (67 % of the initial capacity) of bare NPC and bulk Mn₂P electrodes after

100 cycles remain, respectively.

In addition, the $Mn_2P@PC$ shows the reversible capacities of 575,470, 376, 317, 271, 227 mA h g⁻¹ with current densities increasing from 0.1 to 0.2, 0.5, 1, 2, 4 A g⁻¹ (Figure S3i), which is lower than that of the $Mn_2P@NPC$ electrode. The enhancement of rate performance is studied by EIS of $Mn_2P@NPC$ and bare Mn_2P electrodes before and after the stability test (Figure S9), where the $Mn_2P@NPC$ electrode demonstrates the smallest charge transfer resistance both before and after cycling. The low resistance is attributed to the collective beneficial effects promoted by the $Mn_2P@NPC$ hybrid with rapid transfer of electrons and ions.

Figure 3e compares the cycling performance of bare Mn₂P, NPC and Mn₂P@NPC electrodes at a current density of 1 A g⁻¹. Clearly, the Mn₂P@NPC electrode exhibits the best cycling performance in comparison with that of bare NPC and bulk Mn₂P electrodes. After 500 cycles, a specific capacity of 564 mA h g⁻¹ is maintained for Mn₂P@NPC electrode. In contrast, only a specific capacity of 181 mA h g⁻¹ can be retained for bare NPC electrode after 500 cycles. The bulk Mn₂P electrode demonstrates fast capacity degradation, reaching a very low capacity of 80 mA h g⁻¹. Additionally, the Mn₂P@NPC electrode also shows better cycling performance than that of the Mn₂P@PC electrode (**Figure S3j**). More strikingly, when the current density is raised to 4 A g⁻¹, a reversible capacity can still be retained at about 365 mA h g⁻¹ even after 2000 cycles with high capacity retention of 99 % and an average CE above 99 %, suggesting excellent long-term cycling stability. It is worthwhile to note that after the initial capacity loss during the first 70 cycles, the trend of capacity as a function of cycle

number displays three stages involving apparent capacity reactivation (from cycle 71 to 622), stabilization (from cycle 623 to 1407), and degradation (from cycle 1408 to 2000) as shown in Figure 3f. The capacity fading during the first 70 cycles is believed to primarily result from the SEI formation and structural reorganization ⁵⁸⁻⁵⁹. The gradual capacity rising in the reactivation stage that is also commonly observed in various nanostructured transition metal compounds electrodes may be attributed to lithiation-induced structural optimization and the reversible formation of organic polymeric/gel-like layer caused by electrolyte decomposition.^{17,22,60-62} This can offer a large fraction of electrochemical reaction interface for hosting excess Li⁺ ions through a "pseudo-capacitance-type behavior".⁶³⁻⁶⁴ This phenomenon is also verified by the capacity plateau variations (Figure S8d) and kinetic analysis in Figure 3g-i. These results emphasize the merits of incorporating NPC and the synergetic effects between Mn₂P and NPC in promoting high capacity, rate capability and ultra-long cycling durability of the electrodes, which are thereafter verified through in-situ TEM observations. Moreover, the electrochemical performance of Mn₂P@NPC electrode outperform the several transition metal-based anodes in previously reported work (Supplementary Table S2).

To reveal the fundamental reasons for the superior rate capability of $Mn_2P@NPC$ electrode, CV tests under different sweep rates from 0.1 to 2 mV s⁻¹ are performed to investigate its electrochemical kinetics.^{47,65} As can be seen in **Figure 3g**, the CV curves keep similar shapes and simultaneously the corresponding current peak values increase with increasing sweep rates. Generally, the peak current value (*i*) in CV profiles is

dependent on the sweep rate (v) on the basis of the following equations:^{33,66-67}

$$i = av^b \tag{1}$$

$$i = k_1 v + k_2 v^{1/2} \tag{2}$$

Where *i* is the current, *v* refers to the sweep rate, a and b are variable parameters, and k1 and k2 are constants, where the b-value varies from 0.5 to 1.0, indicating the diffusion controlled contribution and capacitive contribution.⁶⁵ By plotting the linear relationship between $\log i$ and $\log v$, the b-values are determined by the anodic and cathodic slopes (Figure S10) are 0.76, 0.77, 0.86 and 0.97, respectively, revealing the capacity of the Mn₂P@NPC electrode is dominated by the capacitive contribution.⁶⁵ According to Equation (2), the proportion of capacitive contribution is calculated by separating the current *i* from the diffusion and capacitance. The Mn₂P@NPC affords a 52.0 % capacitive contribution (red region) at 0.1 mV s⁻¹ (Figure 3i). By raising the scan rate from 0.1 to 2 mV s⁻¹, the capacitive contribution increases from 52.0 % to 83.0 % (Figure 3i). A significantly high capacitive contribution of 83.0 % can be obtained at scan rate of 2 mV s⁻¹ (Figure 3h). This enhancement can be mainly ascribed to the advantageous structural features of Mn₂P@NPC, which can provide more electroactive sites and facilitate the rapid Li⁺ diffusion, thus leading to the pseudocapacitive effect especially at ultrahigh rates.²⁸





Figure 3. (a) CV curves of $Mn_2P@NPC$ electrode for the three initial cycles, (b) discharge–charge voltage profiles and (c) corresponding cycling performance of $Mn_2P@NPC$ electrode at 0.1 A g⁻¹, (d) rate performances of bulk Mn_2P , NPC and $Mn_2P@NPC$ electrodes at different current densities, (e) cycling performances of bulk Mn_2P , NPC and $Mn_2P@NPC$ electrodes at 1 A g⁻¹, (f) long-term stability of $Mn_2P@NPC$ electrode at 4 A g⁻¹. (g) CV curves with sweep rates increasing from 0.1 to 2.0 mV s⁻¹, (h) capacitive contribution (represented by the red shaded region) at 2.0

mV s⁻¹ and (i) the ratio of capacitive contribution at various scan rates of the $Mn_2P@NPC$ electrode.

To further reveal the excellent structural stability of Mn₂P@NPC electrode, the morphology and microstructure evolution of Mn₂P@NPC during electrochemical cycling are studied by in-situ TEM through a nano-battery configuration (Figure 4a).^{57,68-69} The morphological and structural evolutions of the Mn₂P@NPC electrode during a lithiation and delithiation process are illustrated by time-resolved TEM images (captured in Supplementary Movie S1) in Figure 4b-g. Before lithiation, it can be clearly seen that numerous isolated Mn₂P nanoparticles are uniformly pinned into the porous NPC. When a potential of -3 V is applied to the Mn₂P@NPC with respect to lithium, lithium ions began to quickly diffuse into Mn₂P@NPC that is in contact with the Li/Li₂O layer as evidenced by volume expansion of Mn₂P nanoparticles after a few seconds. With the lithiation propagating progressively, the diameter of four neighboring nanoparticles (marked as 1, 2, 3 and 4 in Figure 4b) increase accordingly. After 665 s of lithiation, the measured particles expand from 260.7 (particle 1), 183.4 (particle 2), 142.8 (particle 3) and 118.5 (particle 4) nm to 289.6, 206.7, 155.9 and 137.5 nm in diameter, respectively, corresponding to a total volume expansion of 10~16 %. Reversely, a positive potential of 3 V is applied to extract lithium ions from the lithiated Mn₂P@NPC and the diameters of the corresponding lithiated particles gradually shrink to 280.1, 201.9, 152.0 and 127.1 nm after 1036 s of delithation, respectively, accounting for a total volume contraction of 3~8 % compared to the lithiated state. The small volume expansion (~10-16%) upon lithiation and contraction (~3-8%) upon delithation

render a very stable electrode. Impressively, there are no visible cracks or fractures observed in the whole lithiation and delithiation process, indicating high structural integrity, which accounts for the superior cycling performance. Robust structural stability of Mn₂P@NPC is ascertained upon repeated cycling. As clearly observed in **Figure. 4i-p and Figure S11 (captured in Supplementary Movies S2 and S3)**, the Mn₂P@NPC composite can keep its structural integrity well over multiple lithiation/delithiation cycles, without any structural cracking or fracture, suggesting that the 2D porous NPC framework can effectively confine volume change and prevent pulverization/aggregation of Mn₂P and thus give rise to excellent structural integrity.



Figure 4. (a) Schematic of *in-situ* TEM observations, (b–g) Time-lapse TEM images for Mn₂P@NPC electrode during first lithiation process, (h) the relative expansion

schematic of four Mn₂P nanoparticles with respect to different lithiation/delithation times, (i) TEM images of Mn₂P@NPC electrode before cycling, (j) after first lithiation, (k) after first delithiation, (l) after second delithiation, (m) after third delithiation, (n) after fourth delithiation, (o) after fifth delithiation, and (p) after sixth delithiation.

To gain further insights into the reaction mechanism of Mn₂P@NPC during the lithiation/delithiation process, in-situ selected area electron diffraction (SAED) and exsitu TEM observations are performed. Figure 5b-e shows the time-resolved snapshots of SAED patterns of Mn₂P@NPC from the discharged state to the charged state (see Supplementary Movie S4), revealing the conversion reaction mechanism of Mn₂P, which is verified from radial intensity profiles as a function of reaction time produced from real-time SAED patterns (Figure 5a). Figure 5a is produced from in situ diffraction video (Supplementary Movie S4). Movie S4 is recorded every 0.5 s and integrates the intensity values determined by the center distance of diffraction rings into radially averaged intensity profiles⁷⁰. The final intensity profile is obtained after removing the background by employing the power-law model installed in Digital Micrograph and drawing in Origin Software. When lithium ions are inserted/deserted into Mn₂P, the peak changes (peak movement, emergence or disappearance) show phase transitions in Figure 5a, which demonstrate the typical three steps of lithiation/delithiation processes of Mn₂P: intercalation (0-549 s), conversion (549~2106 s), and phase retransformation (2106s to end).⁷⁰ Before lithiation, the SAED pattern in Figure 5b can be well indexed to the corresponding planes of Mn₂P, in

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accordance with the XRD results. Upon lithiation, LiMnP is initially formed due to Li ions insert into the Mn₂P lattice (Figure 5c). After a full lithiation (2106 s) (Figure 5d), diffraction spots of the LiMnP intermediate and Mn₂P phase disappear and diffraction rings from Li₃P and Mn emerge, which is characteristic of the conversion reaction. This result is confirmed by the ex-situ TEM observations of Mn₂P@NPC electrode after initial discharge to 0.01 V as shown in Figure 5f-h. As illustrated in Figure 5f, the Mn₂P@NPC electrode maintains an intact morphology after initial discharge without pulverization. A closer TEM image (Figure 5g) reveals the formation of nanograins in lithiated Mn₂P nanoparticle. HRTEM images (Figure 5h) clearly certify the high crystallinity of nanograins. The measured lattice fringes in Figure 5h of 0.185 and 0.208 nm are the (200) and (103) planes of Li₃P, and 0.210, 0.199 and 0.238 nm correspond to the $(\overline{4}1\overline{1})$, $(2\overline{4}0)$, and $(\overline{2}\ \overline{3}\ \overline{1})$ planes of Mn, respectively. After delithiation for 2297 s (Figure 5e), considerable amounts of Li₃P and Mn are found to be converted back to Mn_2P , while a certain amount of LiP₅ is detected in the delithiated electrode. The existence of LiP₅ is likely due to the difficulty of full conversion of Li₃P using *in-situ* TEM dry cell approach.⁴⁷ Figure 5i-k presents the ex-situ TEM images of the Mn₂P@NPC electrode after initial charge to 3V. The HRTEM image (Figure 5k) reveals the regeneration of Mn₂P electroactive particles and the measured lattice fringes of 0.209 and 0.199 nm match the (201) and (210) planes of Mn₂P, indicating a highly reversible conversion reaction.



 Figure 5. *In-situ* selected area electron diffraction (SAED) and *ex-situ* TEM observations of $Mn_2P@NPC$ electrode. (a) SAED intensity profile as a function of reaction time of $Mn_2P@NPC$ electrode during lithiation/delithation process, (b-e) Time-lapse SAED patterns of $Mn_2P@NPC$ electrode before and after lithium extraction, (f-g) TEM and (h) HRTEM image of $Mn_2P@NPC$ electrode after discharging to 0.01 V at 0.1 A g⁻¹, (i-j) TEM and (k) HRTEM image of $Mn_2P@NPC$ electrode after discharging to 3 V at 0.1 A g⁻¹.

To further evaluate the potential for practical applications of $Mn_2P@NPC$ anodes in LIBs, a full cell comprising of prelithiated $Mn_2P@NPC$ anode and commercial LiFePO₄ cathode is assembled. **Figure 6a** shows the discharge/charge profiles of the full cell at a rate of 0.5 C (1C = 0.13 A g⁻¹) between 1.0 and 3.9 V. The full cell is cycled at 0.2 C for two times and then at 0.5 C for the following cycles, delivering a first cycle coulombic efficiency of 86.8 %. At 0.5 C rate, the full cell delivers a reversible capacity of 122.9 mA h g⁻¹ at the 80th cycle, namely, its capacity retention over the course of 80 cycles is 84.4 % (**Figure 6c**). **Figure 6d** shows the performance of the full cell at various current rates and its galvanostatic charge–discharge voltage profiles are displayed in **Figure 6b**. As can be observed, at rates of 0.2 C, 0.5 C, 1 C and 2 C, the full cell can deliver capacities of ~131, 114, 100, 86 mA h g⁻¹, respectively. Even at 4 C, a stable capacity of 118 mA h g⁻¹ (90 % of initial capacity) is recovered. Moreover, the cell shows good capacity retention of 80 % after 100 cycles at 1C (**Figure**

6d). The full cell can easily light a Xiamen University (XMU) logo that is composed with 32 LEDs in parallel (inset of **Figure 6c**), highlighting the potential of $Mn_2P@NPC$ anodes for practical applications.



Figure 6. (a) voltage curves at 0.5 C rate, (b) voltage curves at various rate of 0.2 C,

0.5 C, 1 C, 2 C and 4 C, (c) cycling performance at 0.5 C, the inset digital photo is a LED XMU logo powered by the full cell and (d) rate performances at various C rate of $Mn_2P@NPC||LiFePO_4$ full cell.

4. CONCLUSIONS

In summary, a unique hierarchically porous heterostructured Mn₂P@NPC hybrid consisting of homogeneous and isolated Mn₂P nanoparticles tightly embedded in hierarchical porous NPC, has been successfully synthesized via a simple and viable strategy. The obtained $Mn_2P@NPC$ hybrid combines the advantages of nanostructure (Mn₂P nanoparticles) and microstructure (microsized NPC) to trigger fast ion and electron transportation, robust structure integrity, and effective accommodation of volume variation of Mn₂P nanoparticles without agglomeration during cycling. Consequently, the resultant Mn₂P@NPC electrodes demonstrate prominent electrochemical performance, namely, outstanding rate performance and superior longlife durability In-situ TEM and ex-situ TEM results show strong evidence that the exceptional long-term durability is attributed to the tight embedding of isolated Mn₂P into hierarchical porous NPC that provide a buffer matrix for effectively accommodating volume change and preventing the aggregation of Mn₂P nanoparticles during cycling. In-situ SAED and ex-situ HRTEM results reveal that the Mn₂P@NPC undergoes a conversion reaction mechanism for lithium storage and the high capacity of Mn₂P@NPC originates from the reversible conversion reaction. The full cell assembled from the prelithiated Mn₂P@NPC anode and commercial LiFePO₄ cathode retains a discharge capacity of 122.9 mA h g⁻¹ after 80 cycles at 0.5 C with desirable

rate performance. This work represents a significant progress in rational design of novel hybrid structures as advanced negative electrodes in LIBs

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

The EDX spectrum, Raman spectrum, BET N₂ adsorption-desorption isotherm, TGA spectrum of Mn₂P@NPC composite; XRD patterns and SEM images of the NPC and bulk Mn₂P, XRD patterns, CV curves of the NPC and bulk Mn₂P, TEM images and electrochemical performance of Mn₂P@PC composite; SEM and TEM images of Mn₂P@NPC electrode after cycles, galvanostatic charge–discharge profiles of Mn₂P@NPC electrode, NPC electrode and bulk Mn₂P electrode at various current densities, EIS curves of Mn₂P@NPC and bulk Mn₂P electrode before and after the cycling test, the fitted linear relationship between log (i) and log (v) of the Mn₂P@NPC electrode, *In-situ* TEM images of another Mn₂P@NPC electrode before and after and after mages of another Mn₂P@NPC electrode before and after and after mages of another Mn₂P@NPC electrode before and after and after mages of another Mn₂P@NPC electrode before and after mages of mages of another Mn₂P@NPC electrode before and after mages of another Mn₂P@NPC electrode before mages of Mn₂P@NPC electrode before mages of mages

Video·S1: Lithiation/delithiation cycle of the Mn₂P@NPC electrode (mp4).

Video·S2: Six lithiation/delithiation cycles of the Mn₂P@NPC electrode (mp4).

Video·S3: Three lithiation/delithiation cycles of the Mn₂P@NPC electrode (mp4).

Video·S4: *In-situ* SAED observation of lithiation/delithiation of the Mn₂P@NPC electrode (mp4).

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Song, M.-K.; Park, S.; Alamgir, F. M.; Cho, J.; Liu, M. Nanostructured Electrodes for Lithium-Ion and Lithium-Air Batteries: The Latest Developments, Challenges, and Perspectives. *Mat. Sci. Eng. R.* **2011**, *72*, 203-252.

(2) Liu, Z.; Yu, Q.; Zhao, Y.; He, R.; Xu, M.; Feng, S.; Li, S.; Zhou, L.; Mai, L. Silicon Oxides: A Promising Family of Anode Materials for Lithium-Ion Batteries. *Chem. Soc. Rev.* **2019**, *48*, 285-309.

(3) Leng, J.; Wang, Z.; Wang, J.; Wu, H. H.; Yan, G.; Li, X.; Guo, H.; Liu, Y.; Zhang, Q.; Guo, Z. Advances in Nanostructures Fabricated Via Spray Pyrolysis and Their Applications in Energy Storage and Conversion. *Chem. Soc. Rev.* 2019, *48*, 3015-3072.
(4) He, H.; Fu, W.; Wang, H.; Wang, H.; Jin, C.; Fan, H. J.; Liu, Z. Silica-Modified SnO₂ -Graphene "Slime" for Self-Enhanced Li-Ion Battery Anode. *Nano Energy* 2017, *34*, 449-455.

(5) Xu, Q.; Sun, J. K.; Yu, Z. L.; Yin, Y. X.; Xin, S.; Yu, S. H.; Guo, Y. G. SiO_x Encapsulated in Graphene Bubble Film: An Ultrastable Li-Ion Battery Anode. *Adv. Mater.* **2018**, *30*, 1707430.

(6) Wang, D.; Liu, H.; Li, M.; Wang, X.; Bai, S.; Shi, Y.; Tian, J.; Shan, Z.; Meng, Y.

S.; Liu, P.; Chen, Z. Nanosheet-Assembled Hierarchical Li₄Ti₅O₁₂ Microspheres for High-Volumetric-Density and High-Rate Li-Ion Battery Anode. *Energy Storage Mater.* **2019**, *21*, 361-371.

(7) Wang, D. Y.; Si, Y.; Guo, W.; Fu, Y. Long Cycle Life Organic Polysulfide Catholyte for Rechargeable Lithium Batteries. *Adv. Sci.* **2020**, *7*, 1902646.

(8) Yang, T.; Guo, B.; Du, W.; Aslam, M. K.; Tao, M.; Zhong, W.; Chen, Y.; Bao, S. J.; Zhang, X.; Xu, M. Design and Construction of Sodium Polysulfides Defense System for Room-Temperature Na-S Battery. *Adv. Sci.* **2019**, *6*, 1901557.

(9) Luan, J.; Zhang, Q.; Yuan, H.; Sun, D.; Peng, Z.; Tang, Y.; Ji, X.; Wang, H. Plasma-Strengthened Lithiophilicity of Copper Oxide Nanosheet-Decorated Cu Foil for Stable Lithium Metal Anode. *Adv. Sci.* **2019**, *6*, 1901433.

(10) Wang, Y.; Han, J.; Gu, X.; Dimitrijev, S.; Hou, Y.; Zhang, S. Ultrathin Fe₂O₃ Nanoflakes Using Smart Chemical Stripping for High Performance Lithium Storage. *J. Mater. Chem. A* **2017**, *5*, 18737-18743.

(11) Gao, H.; Yang, F.; Zheng, Y.; Zhang, Q.; Hao, J.; Zhang, S.; Zheng, H.; Chen, J.; Liu, H.; Guo, Z. Three-Dimensional Porous Cobalt Phosphide Nanocubes Encapsulated in a Graphene Aerogel as an Advanced Anode with High Coulombic Efficiency for High-Energy Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5373-5379. (12) Yang, T.; Liu, J.; Zhang, M.; Yang, D.; Zheng, J.; Ju, Z.; Cheng, J.; Zhuang, J.; Liu, Y.; Zhong, J.; Liu, H.; Wang, G.; Zheng, R.; Guo, Z. Encapsulating MnSe Nanoparticles inside 3D Hierarchical Carbon Frameworks with Lithium Storage Boosted by In Situ Electrochemical Phase Transformation. *ACS Appl. Mater. Interfaces* **2019**, *11*, 33022-33032.

(13) Zheng, F.; Yang, C.; Xiong, X.; Xiong, J.; Hu, R.; Chen, Y.; Liu, M. Nanoscale Surface Modification of Lithium-Rich Layered-Oxide Composite Cathodes for Suppressing Voltage Fade. *Angew. Chem., Int. Ed.* **2015**, *54*, 13058-62.

(14) Zheng, F.; Ou, X.; Pan, Q.; Xiong, X.; Yang, C.; Fu, Z.; Liu, M. Nanoscale Gadolinium Doped Ceria (GDC) Surface Modification of Li-Rich Layered Oxide as a High Performance Cathode Material for Lithium Ion Batteries. *Chem. Eng. J.* **2018**, *334*, 497-507.

(15) Yang, C.; Ou, X.; Xiong, X.; Zheng, F.; Hu, R.; Chen, Y.; Liu, M.; Huang, K. V₅S₈–Graphite Hybrid Nanosheets as a High Rate-Capacity and Stable Anode Material for Sodium-Ion Batteries. *Energy Environ. Sci.* **2017**, *10*, 107-113.

(16) Lu, J.; Wu, T.; Amine, K. State-of-the-Art Characterization Techniques for Advanced Lithium-Ion Batteries. *Nat. Energy* **2017**, *2*, 17011.

(17) Cuan, J.; Zhou, Y.; Zhang, J.; Zhou, T.; Liang, G.; Li, S.; Yu, X.; Pang, W. K.; Guo, Z. Multiple Anionic Transition-Metal Oxycarbide for Better Lithium Storage and Facilitated Multielectron Reactions. *ACS Nano* **2019**, *13*, 11665–11675.

(18) Li, Q.; Zhao, Y.; Liu, H.; Xu, P.; Yang, L.; Pei, K.; Zeng, Q.; Feng, Y.; Wang, P.; Che, R. Dandelion-Like Mn/Ni Co-Doped CoO/C Hollow Microspheres with Oxygen Vacancies for Advanced Lithium Storage. *ACS Nano* **2019**, *13*, 11921–11934

(19) Liu, H.; Zhu, Z.; Huang, J.; He, X.; Chen, Y.; Zhang, R.; Lin, R.; Li, Y.; Yu, S.; Xing, X., Yan, Q.; Li, X.; Frost, M. J.; An, K.; Feng, J.; Kostecki, R.; Xin, H.; Ong, S. P.; Liu, P. Elucidating the Limit of Li Insertion into the Spinel Li₄Ti₅O₁₂. ACS Mater.

Lett. 2019, 1, 96-102.

(20) Luo, Y.; Xu, X.; Zhang, Y.; Chen, C. Y.; Zhou, L.; Yan, M.; Wei, Q.; Tian, X.; Mai, L. Graphene Oxide Templated Growth and Superior Lithium Storage Performance of Novel Hierarchical Co₂V₂O₇ Nanosheets. *ACS Appl. Mater. Interfaces* **2016**, *8*, 2812-2818.

(21) Bai, J.; Xi, B.; Mao, H.; Lin, Y.; Ma, X.; Feng, J.; Xiong, S. One-Step Construction of N, P-Codoped Porous Carbon Sheets/CoP Hybrids with Enhanced Lithium and Potassium Storage. *Adv. Mater.* **2018**, *30*, 1802310.

(22) Wu, C.; Kopold, P.; van Aken, P. A.; Maier, J.; Yu, Y. High Performance Graphene/Ni₂P Hybrid Anodes for Lithium and Sodium Storage through 3D Yolk-Shell-Like Nanostructural Design. *Adv. Mater.* **2017**, *29*,1604015.

(23) Yang, F.; Gao, H.; Hao, J.; Zhang, S.; Li, P.; Liu, Y.; Chen, J.; Guo, Z. Yolk–Shell Structured FeP@C Nanoboxes as Advanced Anode Materials for Rechargeable Lithium-/Potassium-Ion Batteries. *Adv. Funct. Mater.* **2019**, *29*, 1808291.

(24) Li, W.; Yu, J.; Wen, J.; Liao, J.; Ye, Z.; Zhao, B.; Li, X.; Zhang, H.; Liu, M.; Guo, Z. An Amorphous Zn–P/Graphite Composite with Chemical Bonding for Ultra-Reversible Lithium Storage. *J. Mater. Chem. A* **2019**, *7*, 16785-16792.

(25) Li, W.; Ke, L.; Wei, Y.; Guo, S.; Gan, L.; Li, H.; Zhai, T.; Zhou, H. Highly Reversible Sodium Storage in a GeP₅/C Composite Anode with Large Capacity and Low Voltage. *J. Mater. Chem. A* **2017**, *5*, 4413-4420.

(26) Zhou, D.; Fan, L.-Z. Co₂P Nanoparticles Encapsulated in 3D Porous N-Doped Carbon Nanosheet Networks as an Anode for High-Performance Sodium-Ion Batteries. *J. Mater. Chem. A* **2018**, *6*, 2139-2147.

(27) Dong, C.; Guo, L.; He, Y.; Chen, C.; Qian, Y.; Chen, Y.; Xu, L. Sandwich-Like Ni₂P Nanoarray/Nitrogen-Doped Graphene Nanoarchitecture as a High-Performance Anode for Sodium and Lithium Ion Batteries. *Energy Storage Mater.* **2018**, *15*, 234-241.

(28) Yuan, H.; Wu, M.; Zheng, J.; Chen, Z. G.; Zhang, W.; Luo, J.; Jin, C.; Sheng, O.; Liang, C.; Gan, Y; Xia, Y.; Zhang, J.; Huang, H.; Liu, Y.; Nai, J.; Tao, X. Empowering Metal Phosphides Anode with Catalytic Attribute toward Superior Cyclability for Lithium-Ion Storage. *Adv. Funct. Mater.* **2019**, *29*, 1809051.

(29) Shi, S.; Li, Z.; Sun, Y.; Wang, B.; Liu, Q.; Hou, Y.; Huang, S.; Huang, J.; Zhao, Y. A Covalent Heterostructure of Monodisperse Ni₂P Immobilized on N, P-Co-Doped Carbon Nanosheets for High Performance Sodium/Lithium Storage. *Nano Energy* **2018**, *48*, 510-517.

(30) Chen, Y.; Zhang, W.; Zhou, D.; Tian, H.; Su, D.; Wang, C.; Stockdale, D.; Kang, F.; Li, B.; Wang, G. Co-Fe Mixed Metal Phosphide Nanocubes with Highly Interconnected-Pore Architecture as an Efficient Polysulfide Mediator for Lithium-Sulfur Batteries. *ACS Nano* **2019**, *13*, 4731-4741.

(31) Liu, W.; Zhi, H.; Yu, X. Recent Progress in Phosphorus Based Anode Materials for Lithium/Sodium Ion Batteries. *Energy Storage Mater.* **2019**, *16*, 290-322.

(32) Li, Z.; Yin, L. Efficient Gel Route to Embed Phosphorus into MOF-Derived Porous FeP_x as Anodes for High Performance Lithium-Ion Batteries. *Energy Storage Mater.* **2018**, *14*, 367-375.

(33) Hou, B. H.; Wang, Y. Y.; Ning, Q. L.; Fan, C. Y.; Xi, X. T.; Yang, X.; Wang, J.; Zhang, J. P.; Wang, X.; Wu, X. L. An FeP@C Nanoarray Vertically Grown on Graphene Nanosheets: An Ultrastable Li-Ion Battery Anode with Pseudocapacitance-Boosted Electrochemical Kinetics. *Nanoscale* **2019**, *11*, 1304-1312.

(34) Yuan, C.; Wu, H. B.; Xie, Y.; Lou, X. W. Mixed Transition-Metal Oxides: Design, Synthesis, and Energy-Related Applications. *Angew. Chem., Int. Ed.* **2014**, *53*, 1488-1504.

(35) Chen, J.; Pan, A.; Wang, Y.; Cao, X.; Zhang, W.; Kong, X.; Su, Q.; Lin, J.; Cao, G.; Liang, S. Hierarchical Mesoporous MoSe₂@CoSe/N-Doped Carbon Nanocomposite for Sodium Ion Batteries and Hydrogen Evolution Reaction Applications. *Energy Storage Mater.* **2019**, *21*, 97-106.

(36) Li, B.; Xi, B.; Feng, Z.; Lin, Y.; Liu, J.; Feng, J.; Qian, Y.; Xiong, S. Hierarchical Porous Nanosheets Constructed by Graphene-Coated, Interconnected TiO₂ Nanoparticles for Ultrafast Sodium Storage. *Adv. Mater.* **2018**, *30*, 1705788

(37) Wang, Z.; Zhang, S.; Zeng, H.; Zhao, H.; Sun, W.; Jiang, M.; Feng, C.; Liu, J.; Zhou, T.; Zheng, Y.; Guo, Z. Hierarchical Porous NiO/β-NiMOO₄ Heterostructure as Superior Anode Material for Lithium Storage. *ChemPlusChem* **2018**, *83*, 915-923.

(38) Li, Y.; Xu, P.; Chen, G.; Mou, J.; Xue, S.; Li, K.; Zheng, F.; Dong, Q.; Hu, J.; Yang, C.; Liu, M. Enhancing Li-S Redox Kinetics by Fabrication of a Three Dimensional Co/CoP@Nitrogen-Doped Carbon Electrocatalyst. *Chem. Eng. J.* **2020**, *380*, 122595.

(39) Hou, H.; Shao, L.; Zhang, Y.; Zou, G.; Chen, J.; Ji, X. Large-Area Carbon Nanosheets Doped with Phosphorus: A High-Performance Anode Material for Sodium-Ion Batteries. *Adv. Sci.* **2017**, *4*, 1600243.

(40) Yun, Y. S.; Le, V.-D.; Kim, H.; Chang, S.-J.; Baek, S. J.; Park, S.; Kim, B. H.; Kim, Y.-H.; Kang, K.; Jin, H.-J. Effects of Sulfur Doping on Graphene-Based Nanosheets for Use as Anode Materials in Lithium-Ion Batteries. *J. Power Sources* **2014**, *262*, 79-85.

(41) Wu, Z. S.; Ren, W.; Xu, L.; Li, F.; Cheng, H. M. Doped Graphene Sheets as Anode Materials with Superhigh Rate and Large Capacity for Lithium Ion Batteries. *ACS Nano* **2011**, *5*, 5467-5471.

(42) Qie, L.; Chen, W. M.; Wang, Z. H.; Shao, Q. G.; Li, X.; Yuan, L. X.; Hu, X. L.; Zhang, W. X.; Huang, Y. H. Nitrogen-Doped Porous Carbon Nanofiber Webs as Anodes for Lithium Ion Batteries with a Superhigh Capacity and Rate Capability. *Adv. Mater.* **2012**, *24*, 2047-2050.

(43) Wang, Y.; Fu, Q.; Li, C.; Li, H.; Tang, H. Nitrogen and Phosphorus Dual-Doped Graphene Aerogel Confined Monodisperse Iron Phosphide Nanodots as an Ultrafast and Long-Term Cycling Anode Material for Sodium-Ion Batteries. *ACS Sustainable Chem. Eng.* **2018**, *6*, 15083-15091.

(44) Ma, C.; Deng, C.; Liao, X.; He, Y.; Ma, Z.; Xiong, H. Nitrogen and Phosphorus Codoped Porous Carbon Framework as Anode Material for High Rate Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 36969-36975.

(45) Niu, F.; Yang, J.; Wang, N.; Zhang, D.; Fan, W.; Yang, J.; Qian, Y. MoSe₂-Covered N,P-Doped Carbon Nanosheets as a Long-Life and High-Rate Anode Material

for Sodium-Ion Batteries. Adv. Funct. Mater. 2017, 27, 1700522.

(46) Wu, F.; Srot, V.; Chen, S.; Lorger, S.; van Aken, P. A.; Maier, J.; Yu, Y. 3D Honeycomb Architecture Enables a High-Rate and Long-Life Iron (III) Fluoride-Lithium Battery. *Adv. Mater.* **2019**, *31*, 1905146.

(47) Zheng, Z.; Li, P.; Huang, J.; Liu, H.; Zao, Y.; Hu, Z.; Zhang, L.; Chen, H.; Wang, M.-S.; Peng, D.-L.; Zhang, Q. High Performance Columnar-Like Fe₂O₃@Carbon Composite Anode Via Yolk@Shell Structural Design. *J. Energy Chem.* **2020**, *41*, 126-134.

(48) Mei, P.; Lee, J.; Pramanik, M.; Alshehri, A.; Kim, J.; Henzie, J.; Kim, J. H.; Yamauchi, Y. Mesoporous Manganese Phosphonate Nanorods as a Prospective Anode for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 19739-19745.

(49) Pu, Z.; Amiinu, I. S.; Zhang, C.; Wang, M.; Kou, Z.; Mu, S. Phytic Acid-Derivative Transition Metal Phosphides Encapsulated in N, P-Codoped Carbon: An Efficient and Durable Hydrogen Evolution Electrocatalyst in a Wide PH Range. *Nanoscale* **2017**, *9*, 3555-3560.

(50) Wang, X.; Chen, K.; Wang, G.; Liu, X.; Wang, H. Rational Design of Three-Dimensional Graphene Encapsulated with Hollow FeP@Carbon Nanocomposite as Outstanding Anode Material for Lithium Ion and Sodium Ion Batteries. *ACS Nano* 2017, *11*, 11602-11616.

(51) Shen, L.; Zhang, X.; Li, H.; Yuan, C.; Cao, G. Design and Tailoring of a Three-Dimensional TiO₂–Graphene–Carbon Nanotube Nanocomposite for Fast Lithium Storage. *J. Phys. Chem. Lett.* **2011**, *2*, 3096-3101.

(52) Li, Z.; Zhang, L.; Ge, X.; Li, C.; Dong, S.; Wang, C.; Yin, L. Core-Shell Structured CoP/FeP Porous Microcubes Interconnected by Reduced Graphene Oxide as High Performance Anodes for Sodium Ion Batteries. *Nano Energy* **2017**, *32*, 494-502.

(53) Gao, X.; Wang, B.; Zhang, Y.; Liu, H.; Liu, H.; Wu, H.; Dou, S. Graphene-Scroll-Sheathed α-MnS Coaxial Nanocables Embedded in N, S Co-Doped Graphene Foam as 3D Hierarchically Ordered Electrodes for Enhanced Lithium Storage. *Energy Storage Mater.* **2019**, *16*, 46-55.

(54) Chen, M.; Liu, J.; Chao, D.; Wang, J.; Yin, J.; Lin, J.; Jin Fan, H.; Xiang Shen, Z. Porous α -Fe₂O₃ Nanorods Supported on Carbon Nanotubes-Graphene Foam as Superior Anode for Lithium Ion Batteries. *Nano Energy* **2014**, *9*, 364-372.

(55) Zhang, Q.; Wang, J.; Dong, J.; Ding, F.; Li, X.; Zhang, B.; Yang, S.; Zhang, K. Facile General Strategy toward Hierarchical Mesoporous Transition Metal Oxides Arrays on Three-Dimensional Macroporous Foam with Superior Lithium Storage Properties. *Nano Energy* **2015**, *13*, 77-91.

(56) Jia, S.; Wang, Y.; Liu, X.; Zhao, S.; Zhao, W.; Huang, Y.; Li, Z.; Lin, Z. Hierarchically Porous CuO Nano-Labyrinths as Binder-Free Anodes for Long-Life and High-Rate Lithium Ion Batteries. *Nano Energy* **2019**, *59*, 229-236.

(57) Zhang, Q.; Chen, H.; Luo, L.; Zhao, B.; Luo, H.; Han, X.; Wang, J.; Wang, C.; Yang, Y.; Zhu, T.; Liu, M. Harnessing the Concurrent Reaction Dynamics in Active Si and Ge to Achieve High Performance Lithium-Ion Batteries. *Energy Environ. Sci.* **2018**, *11*, 669-681.

(58) Li, T.; Wang, B.; Ning, J.; Li, W.; Guo, G.; Han, D.; Xue, B.; Zou, J.; Wu, G.;

Yang, Y.; Dong, A.; Zhao, D. Self-Assembled Nanoparticle Supertubes as Robust Platform for Revealing Long-Term, Multiscale Lithiation Evolution. *Matter* 2019, 1, 976-987. (59) Sun, H.; Xin, G.; Hu, T.; Yu, M.; Shao, D.; Sun, X.; Lian, J. High-Rate Lithiation-Induced Reactivation of Mesoporous Hollow Spheres for Long-Lived Lithium-Ion Batteries. Nat. Commun. 2014, 5, 4526. (60) Zhang, J.; Wang, K.; Xu, Q.; Zhou, Y.; Cheng, F.; Guo, S. Beyond Yolk-Shell Nanoparticles:Fe₃O₄@Fe₃C Core@Shell Nanoparticles as Yolks and Carbon Nanospindles as Shells for Efficient Lithium Ion Storage. ACS Nano 2015, 9, 3369-3376. (61) Zhao, K.; Liu, F.; Niu, C.; Xu, W.; Dong, Y.; Zhang, L.; Xie, S.; Yan, M.; Wei, Q.; Zhao, D.; Mai, L. Graphene Oxide Wrapped Amorphous Copper Vanadium Oxide with Enhanced Capacitive Behavior for High-Rate and Long-Life Lithium-Ion Battery Anodes. Adv. Sci. 2015, 2, 1500154. (62) Cao, K.; Jiao, L.; Liu, H.; Liu, Y.; Wang, Y.; Guo, Z.; Yuan, H. 3D Hierarchical Porous α-Fe₂O₃ Nanosheets for High-Performance Lithium-Ion Batteries. Adv. Energy Mater. 2015, 5, 1401421. (63) Li, Y.; Huang, Y.; Zheng, Y.; Huang, R.; Yao, J. Facile and Efficient Synthesis of α-Fe₂O₃ Nanocrystals by Glucose-Assisted Thermal Decomposition Method and Its Application in Lithium Ion Batteries. J. Power Sources 2019, 416, 62-71. (64) Lian, Q.; Zhou, G.; Liu, J.; Wu, C.; Wei, W.; Chen, L.; Li, C. Extrinsic Pseudocapacitve Li-Ion Storage of SnS Anode Via Lithiation-Induced Structural Optimization on Cycling. J. Power Sources 2017, 366, 1-8. (65) Wang, Q.; Wang, B.; Zhang, Z.; Zhang, Y.; Peng, J.; Zhang, Y.; Wu, H. Tailoring Yolk-Shell FeP@Carbon Nanoboxes with Engineered Void Space for Pseudocapacitance-Boosted Lithium Storage. Inorg. Chem. Front. 2018, 5, 2605-2614. (66) Yu, J.; Wang, Y.; Kong, L.; Chen, S.; Zhang, S. Neuron-Mimic Smart Electrode: A Two-Dimensional Multiscale Synergistic Strategy for Densely Packed and High-Rate Lithium Storage. ACS Nano 2019, 13, 9148-9160. (67) Chen, C.; Wen, Y.; Hu, X.; Ji, X.; Yan, M.; Mai, L.; Hu, P.; Shan, B.; Huang, Y. Na⁺ Intercalation Pseudocapacitance in Graphene-Coupled Titanium Oxide Enabling Ultra-Fast Sodium Storage and Long-Term Cycling. Nat. Commun. 2015, 6, 6929. (68) An, W.; Gao, B.; Mei, S.; Xiang, B.; Fu, J.; Wang, L.; Zhang, Q.; Chu, P. K.; Huo, K. Scalable Synthesis of Ant-Nest-Like Bulk Porous Silicon for High-Performance Lithium-Ion Battery Anodes. Nat. Commun. 2019, 10, 1447. (69) Zhao, L.; Wu, H. H.; Yang, C.; Zhang, Q.; Zhong, G.; Zheng, Z.; Chen, H.; Wang, J.; He, K.; Wang, B., Zhu, T.; Zeng, X. C.; Liu, M.; Wang, M. S. Mechanistic Origin of the High Performance of Yolk@Shell Bi₂S₃@N-Doped Carbon Nanowire Electrodes. ACS Nano 2018, 12, 12597-12611. (70) Hwang, S.; Yao, Z.; Zhang, L.; Fu, M.; He, K.; Mai, L.; Wolverton, C.; Su, D. Multistep Lithiation of Tin Sulfide: An Investigation Using In Situ Electron Microscopy. ACS Nano 2018, 12, 3638-3645.

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