Two-dimensional black phosphorus for rechargeable batteries

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TWO-DIMENSIONAL BLACK PHOSPHORUS FOR RECHARGEABLE BATTERIES

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

The increasing demand of clean and sustainable energy drives the development of energy storage devices. Rechargeable batteries, including lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), have been considered as one of the most promising energy storage systems. However, it is still desirable to develop LIBs and SIBs with high energy storage, fast rate capability and long stability to meet their potential applications in portable electronic devices, electric vehicles (EVs) and hybrid electric vehicles (HEVs). Phosphorene, mono- or few-layer black phosphorus (BP), has attracted much attention as a promising anode for rechargeable batteries, due to its high theoretical specific capacity (2596 mAh g^{-1}) and ultrafast Li/Na ions diffusion along the zigzag direction. However, it faces major challenges of low-yield preparation of phosphorene and the poor air-stability. In addition, phosphorene exhibits low initial reversible capacities and fast capacity fading when tested as anodes for LIBs and SIBs, due to the sluggish reaction kinetics and large volume change ($\sim 300\%$). Therefore, large-scale preparation methods, effective passivation approaches and advanced strategies towards improved electrochemical performance are necessary before the direct application of phosphorene into these areas. In our studies, we aim to address the problems aforementioned.

Firstly, we identify formamide as an appropriate solvent to produce high-yield phosphorene with good crystallinity and tunable size distributions via liquid-phase sonication of bulk BP, which largely outperforms the commonly used ones (e.g., NMP, DMF, IPA) in previous reports. In addition, phosphorene obtained in formamide can be stable for further processing and applications.

Furthermore, a densely-packed graphene-phosphorene composite (PG-SPS) is designed and prepared via a facile spark plasma sintering (SPS) method, during which densification and reduction process take place simultaneously. As a result, the PG-SPS sample exhibits much improved air-stability due to effectively suppressing the permeation of water or oxygen molecules into the sample.

Abstract

Importantly, the densely packed PG-SPS sample shows improved volumetric capacities due to its high packing density (0.6 g cm^{-3}) without scarifying its electrochemical performance.

In addition, to enhance the charge transfer kinetics and surface wettability with electrolyte, nanoscale surface engineering of exfoliated few-layer BP is performed by homogeneous deposition of horizontally aligned PEDOT nanofibers on surface-modified BP nanosheets. The as-obtained BP/PEDOT composites exhibit much improved wettability towards the electrolyte compared to that of the pure BP nanosheets. Accordingly, the purposely engineered E-BP/PEDOT architecture exhibits significantly enhanced reversible specific capacities compared to that of the pure few-layer BP electrode. Importantly, due to the high mass percentage of the BP in the sample, the Na storage properties of E-BP/PEDOT outperform that of the E-BP/graphene composites based on the overall mass of whole electrodes.

Furthermore, a 0D-2D heterostructure of Ni_2P nanocrystals (NCs)-BP nanosheets (denoted as $\text{Ni}_2\text{P}@\text{BP}$) was also constructed via a facile strategy. In such a heterostructure, the 2D morphology of BP nanosheets is well maintained and Ni_2P NCs display an average diameter of $\sim 5 \text{ nm}$. As a demonstration of its viability, the $\text{Ni}_2\text{P}@\text{BP}$ shows much improved Li storage properties versus the bare BP when evaluated as electrode materials for LIBs.

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Abbreviations

Abbreviations

LIBs	Lithium-ion Batteries
SIBs	Sodium-ion Batteries
TMDs	Transition Metal Dichalcogenides
TMPs	Transition Metal Phosphides
NMP	N-Methyl-2-pyrrolidone
DMF	Dimethylformamide
CHP	N-cyclohexyl-2-pyrrolidone
DMSO	Dimethyl Sulf-oxide
THF	Tetrahydrofuran
IPA	Isopropyl Alcohol
EtOH	Ethanol
MeOH	Methanol
CE	Coulombic Efficiency
BP	Black Phosphorus
SPS	Spark Plasma Sintering
PG-SPS	Densely Packed Phosphorene-Graphene composite
PGO	Phosphorene-graphene Oxide Composite
GO	Graphene Oxide
RGO	Reduced Graphene Oxide
PEDOT	Poly(3,4-ethylenedioxythiophene)
EDOT	3,4-Ethylenedioxythiophene
2D	Two-dimensional
0D	Zero-dimensional
BPQDs	Black Phosphorus Quantum Dots
FETs	Field Effect Transistors
AM	Armchair
ZZ	Zigzag
CVT	Chemical Vapor Transport
CVD	Chemical Vapor Deposition

Abbreviations

DI	Distilled
ICP-CVD	Inductively Coupled Plasma Chemical Vapor
h-BN	Hexagonal Boron Nitride
XRD	X-ray Diffraction
AES	Auger electron spectroscopy
HRTEM	High-Resolution Transmission Electron Microscopy
FESEM	Field-emission Scanning Electron Microscopy
HEMM	High Energy Mechanical Milling
STEM-HAADF	High-angle Annular Dark-field Scanning Transmission
Electron Microscopy	
DFEC	Transdifluoroethylene Carbonate
VC	Vinylene Carbonate
FEC	Fluoroethylene Carbonate
ES	Ethylene Sulfite
SEI	Solid-electrolyte Interphase
XPS	X-ray Photoelectron Spectroscopy
PVdF	Polyvinylidene Fluoride
EIS	Electrochemical Impedance Spectroscopy
UV-vis-NIR	Ultraviolet-visible-near Infrared
AFM	Atomic Force Microscopic
R _{ct}	Charge Transfer Resistance
W _o	Warburg Resistance
TGA	Thermogravimetric Analysis
SWCNT	Single-walled Carbon Nanotubes
PC	Propylene Carbonate
FFT	Fast Fourier Transform
FTIR	Fourier Transform Infrared Spectroscopy
CA	Contact Angles
CV	Cyclic Voltammetry
GITT	Galvanostatic Intermittent Titration Technique

Abbreviations

NCs	Nanocrystals
SAED	Selective Area Electron Diffraction
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda

Abbreviations

Chapter 1 Introduction

The increasing demand of clean and sustainable energy drives the development of energy storage devices (e.g., LIBs, SIBs). In this chapter, the research background of energy storage including the current research progress of LIBs and SIBs and their main bottlenecks will be firstly presented. Then, based on the background, the motivation and objectives of the project will be proposed. Finally, the thesis organization will be provided.

1.1 Background

With the rapid development of the economy and increasing environmental pollution in the world, there is an urgent and increasing demand for environmentally friendly energy supply. Among numerous energy storage and conversion technologies, hydrogen fuel cell seems to be the ultimate strategy to EVs due to its highest energy density. However, the great challenges of the developing efficient electro-catalysis as well as the safety issues significantly hinder its practical application. Currently, Pb-acid batteries, nickel–metal hydride batteries (Ni-MH batteries), Ni-Cd batteries, and lithium-ion batteries (LIBs) have been widely used. Compared with the other three energy storage systems, rechargeable LIBs with high energy densities and long cycling life have been proved to be the most efficient energy storage system in portable devices (e.g., phones, laptops, digital electronics, etc.), as shown in Figure 1.1.¹ However, when it comes to the employment of LIBs in pure EVs and HEVs and plug in

hybrid electric vehicles (PHEVs), three to six times energy density of the present lithium batteries technology is required.

Figure 1.1 Comparison of the different batteries in terms of volumetric and gravimetric energy density.

In addition, LIBs suffer from increasingly growing cost due to the finite resources of lithium, which will ultimately fail to satisfy industrial demand especially for electric vehicles and other large-scale system like grid storage devices. Sodium-ion batteries (SIBs) become promising alternatives to LIBs due to its abundant resources, resulting in potentially lower cost than LIBs. It is known that sodium shares the similar chemical and physical properties with lithium in many aspects. Therefore, the development of Na battery technologies

could learn from the accumulated experience of LIBs. Considering that the study of SIBs is still in its infancy, effective strategies towards both advanced LIBs and SIBs are necessary.

In order to address the market demands of high energy density, much active research attention has been paid on developing high capacity anode materials. Graphite has made LIBs dominate the energy-supply market for more than 20 years due to its low cost and abundant availability, and is still the anode of choice. However, its limited theoretical specific capacity of $\sim 370 \text{ mAh g}^{-1}$ cannot meet with high energy needs. In addition, it has been reported as an unsuitable anode for the SIBs system due to that it is difficult to form compounds with Na. Recently, alloying anodes, including Sn, Sb, Ge, P, have attracted much attention due to their much high specific capacity and safe characteristics, demonstrating great potential for high-energy LIBs and SIBs. Of all alloying materials, phosphorus, a nonmetallic element of the group 15, has attracted much attention due to its abundance ($\sim 0.1\%$ of the earth's crust). It mainly exists in three allotropes: white, red and black phosphorus. Among them, white phosphorus is toxic and highly reactive with air and thus unsuitable as electrode materials. Red phosphorus has poor electrical conductivity, resulting in a modest cycle life and rate performance. Very recently, black phosphorus (BP) with high electrical conductivity and layer structure has been rediscovered and triggered intensive exploration for rechargeable batteries with a high theoretical capacity of 2596 mA h g^{-1} , assuming $\text{Li}_3\text{P}/\text{Na}_3\text{P}$ is formed after full lithiation/sodiation process.

It is known that thin nanosheets with sufficient active sites are beneficial for building effective transport pathways for charge transfer and diffusion. Delamination of BP crystals into monolayer or few-layer, dubbed phosphorene, has been mainly realized by scotch tape technique or liquid phase exfoliation process. However, it faces major challenges of low-yield preparation of phosphorene as well as its poor air-stability. In addition, as anodes for LIBs and SIBs, phosphorene is faced with the challenges of large volume change ($\sim 300\%$) as well as sluggish reaction kinetics as a typical alloying anode, leading to low initial reversible specific capacity and fast capacity fading.

1.2 Motivation

Large-scale synthesis of well-designed anode materials is necessary for their practical application. Although liquid-phase exfoliation via sonication or shear mixing has been proved fruitful to delaminate graphene and 2D transition metal dichalcogenides (TMDs), the stronger interlayer interaction of BP poses a great challenge to the exfoliation process. Besides most of the commonly used exfoliation solvents, such as N-Methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), efforts have to be made on exploring suitable solvents with matched surface energies to that of phosphorene.

Moreover, the ready degradation of phosphorene in ambient conditions leads to the deterioration of its physical and electric properties. Currently, various passivation approaches, including both depositing protective layers and covalent surface modification on the surface of phosphorene, are demonstrated on one

piece of mechanically cleaved phosphorene. So far, limited studies have been presented on passivating large amount of phosphorene simultaneously, which is critical for volume applications of phosphorene in some fields, such as sensors, energy storage and conversion. Therefore, it is of great interest to develop effective passivation methods on large amounts of phosphorene.

In addition, nano-structuring inevitably induces some side effects on exfoliated phosphorene. Although confined thickness and large lateral dimension of phosphorene are beneficial for circumventing the pulverization of the electrodes, its high specific surface area may give rise to a lower first-cycle Coulombic efficiency (CE) due to parasitic reactions with the electrolyte as well as a reduced volumetric capacity caused by the low packing efficiency of nanostructures. Therefore, an improved first-cycle CE and enhanced volumetric capacity for phosphorene as anodes for LIBs and SIBs are highly desirable.

Furthermore, the architecture of electrode materials and the interfacial reactions between electrodes and electrolytes is very important for the electrochemical performances of rechargeable batteries. The good wettability of electrodes with electrolytes has a pronounced impact on providing easy access of electrolyte and facilitating the diffusion of electrons/ions in the electrode. In contrast, inferior wetting property is detrimental to electrolyte permeation and hence limits the reversible reaction kinetics, resulting in unsatisfactory reversible capacity. Therefore, well-designed nanostructures with good wettability with electrolyte could be an effective strategy towards enhanced electrochemical performance.

Lastly, developing BP-carbon composites has been demonstrated as effective strategies towards overcoming the challenges of sluggish reaction kinetics and large volume change of BP as anodes for LIBs. However, high portion of conductive carbon materials possibly lead to reduced specific capacity based on the overall mass of the whole electrode, considering that carbon materials exhibit relatively low specific capacities compared to the bare phosphorene. Constructing controllable and well-designed heterostructures based on ultrathin 2D nanosheets are fundamentally and technologically attractive in batteries or electronic devices. Therefore, hybridization of phosphorene with other electrochemical active materials, such as transition metal oxides, metal chalcogenides, and metal phosphides, has been identified as an intriguing route to engineer their properties through taking advantages of different building blocks.

1.3 Objectives and Scope

The goal of this thesis is to develop effective strategies towards high-performance BP-based anodes for LIBs and SIBs. Specifically, the objectives mainly include the following categories:

(1) High-yield synthesis of size-controllable BP nanosheets via liquid-phase exfoliation.

- Search appropriate molecules for high-yield synthesis of BP nanosheets.
- Investigate the role of various molecules in the BP liquid-phase

exfoliation.

- Control the size of the as-obtained BP nanosheets.
- Characterize the as-obtained BP nanosheets.

(2) Preparation of an air-stable densely packed phosphorene-graphene composite towards advanced lithium storage properties

- Design and prepare the densely packed phosphorene-graphene composite (PG-SPS) via spark plasma sintering (SPS) process.
- Characterize the as-obtained PG-SPS sample.
- Investigate the air stability of the as-obtained PG-SPS sample.
- Evaluate the lithium storage properties of the PG-SPS sample before and after exposure to ambient conditions.

(3) Preparation of functionalized few-layer black phosphorus with super-wettability towards enhanced reaction kinetics for rechargeable batteries

- Nanoscale surface engineering of few-layer BP performed by homogeneously depositing horizontally aligned Poly(3,4-ethylenedioxythiophene) (PEDOT) nanofibers on specially surface-modified BP nanosheets.
- Characterize the as-obtained E-BP/PEDOT.
- Investigate the wettability of E-BP/PEDOT with electrolyte.
- Evaluate the sodium and lithium storage properties of the E-BP/PEDOT sample.

(4) Preparation of 0D–2D Ni₂P nanocrystals–black phosphorus heterostructure.

- Synthesize a 0D-2D heterostructure, Ni₂P NCs–BP nanosheets (denoted as Ni₂P@BP) via a facile hydrothermal method.
- Characterize the as-obtained Ni₂P@BP.
- Study the electrical property of Ni₂P@BP.
- Evaluate the lithium storage properties of the Ni₂P@BP sample.

1.4 Dissertation Overview

The thesis organization can be divided into several sections.

Chapter 1 introduces the important role of LIBs and SIBs in recent energy storage and conversion systems and points out their challenges due to increasing demand of clean energy. According to the research background, the motivation and objectives were established.

Chapter 2 gives an overview of the recent progress of currently available methods of producing BP bulk and phosphorene. The effective passivation approaches towards improving the air-stability of phosphorene are also discussed. Then, the research efforts on the phosphorene and phosphorene-based materials for potential applications in LIBs and SIBs are discussed, including the working mechanism, various composites (e.g., BP-carbon and BP-noncarbon composites) reported currently.

Chapter 3 includes high-yield synthesis of BP nanosheets via liquid-phase sonication in formamide. Further, the application of a densely-packed

phosphorene-graphene composite in LIBs is presented. Its high packing density provides excellent air stability due to effectively suppressing the permeation of water or oxygen molecules into the sample. In addition, much improved volumetric capacity as anodes of LIBs was also achieved.

Chapter 4 proposed the effective nanoscale surface engineering of few-layer BP with by homogeneously depositing horizontally aligned Poly(3,4-ethylenedioxythiophene) (PEDOT) nanofibers on specially surface-modified BP nanosheets. Such material design could achieve simultaneously: (1) enhanced charge transfer kinetics and (2) super surface wettability with electrolyte. Benefiting from the unique functionalization, the reaction kinetics are greatly enhanced accordingly for both sodium and lithium storage.

Chapter 5 presents the design and synthesis of 0D–2D Ni_2P nanocrystals–black phosphorus heterostructure. Compared with the bare BP, the specially designed $\text{Ni}_2\text{P}@BP$ architecture shows much enhanced electrical conductivity. As a result, The $\text{Ni}_2\text{P}@BP$ shows improved Li diffusion kinetics and excellent Li storage properties.

Chapter 6 gives a summary of my thesis work and some recommendation for future work.

Chapter 2 Literature Review

In this chapter, the introduction to black phosphorus is presented firstly. Then, the currently available methods of producing BP bulk and phosphorene are provided. The effective passivation approaches towards improving the air-stability of phosphorene are also discussed. After that, the research efforts on the phosphorene and phosphorene-based materials for potential applications in lithium ion batteries (LIBs), and sodium ion batteries (SIBs) are overviewed.

2.1 Introduction to Black Phosphorus

The successful exfoliation of black phosphorus (BP) into monolayer or few-layer BP, dubbed phosphorene, has attracted tremendous research interest since 2014.²⁻⁵ It is known that the discovery of graphene in 2004 has inspired considerable efforts devoted to the active exploration of two-dimensional (2D) crystals and their potential applications.⁶⁻⁹ For example, transition metal dichalcogenides (TMDs) (MoS_2 ,¹⁰⁻¹⁴ TiS_2 ,¹⁵⁻¹⁷ MoSe_2 ,¹⁸⁻²¹ WSe_2 ,²²⁻²⁴ etc.), layered metal oxides/hydroxides,²⁵⁻²⁸ graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)²⁹⁻³¹ and MXenes³²⁻³⁴ have been intensively studied and tested in numerous applications, such as catalysis, batteries, light harvesting devices and as lubricants. Recently, phosphorene, as another elementary 2D material after graphene, has triggered numerous theoretical and experimental investigations in many fields owing to its unique structure and intriguing anisotropic properties,³⁵⁻⁴⁴ which are rarely found in other 2D materials. In addition, BP quantum dots (BPQDs),⁴⁵⁻⁴⁹ phosphorene nanoribbons,⁵⁰⁻⁵² phosphorene nanotubes⁵³⁻⁵⁵ have also attracted much research

interest. Being chemically and electronically active, phosphorene shows vast potential for photodetectors,⁵⁶⁻⁵⁹ field effect transistors (FETs),⁶⁰⁻⁶⁴ rechargeable batteries,⁶⁵⁻⁶⁶ thermoelectric devices⁶⁷⁻⁶⁸ and other applications.⁶⁹

The discovery of BP crystals can be traced back to 100 years ago. It was noticed as the most stable one compared to other phosphorus allotropes (e.g., white, red and violet phosphorus). BP crystal is composed of puckered-honeycomb layers stacked by weak van der Waals interactions, giving the possibility of preparing phosphorene via mechanical or sonication exfoliation methods.⁷⁰⁻⁷² Different from other 2D materials, the unique structure arrangement of BP with different bond angles and bond lengths along the armchair (AM) and zigzag (ZZ) directions respectively can provide the answers to its appealing anisotropic physical, thermal conductivity, optical and electrical properties.⁷³⁻⁷⁶ Apart from its anisotropy structure and fascinating properties, BP shows a layer-dependent bandgap, which can be tuned from 0.3 to 2 eV with the decreased thickness from bulk to single layer.⁷⁷⁻⁷⁸ The tunable bandgap of BP can keep direct in a wide range of thickness, which is a great challenge to TMDs.⁷⁹⁻⁸⁰ Therefore, the widely tunable direct bandgap makes BP hold great potential bridging the gap between zero-gap graphene and large-gap TMDs (1-2 eV).^{46, 71} Moreover, the bandgap of phosphorene and its nanoribbons has also been predicted theoretically that can be engineered by the plane strain and edge structures.⁸¹⁻⁸² Recently, phosphorene has attracted much attention as promising anodes for rechargeable batteries including lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) due to its high theoretical specific capacity (2596

mAh g⁻¹)^{65, 83} and ultrafast Li/Na ions diffusion along the zigzag direction.⁸⁴⁻⁸⁶

Despite the recent progress of phosphorene in (opto)electrical or electrochemical devices, it faces major challenges of low-yield preparation of phosphorene⁸⁷ as well as its poor air-stability.⁸⁸⁻⁸⁹ Therefore, large-scale preparation methods and effective passivation strategies are still necessary before the direct application of phosphorene into these areas.

2.2 Synthesis of Black Phosphorus Crystals and Phosphorene

BP crystals have been prepared by several methods, such as high pressure synthesis,⁹⁰⁻⁹³ high-energy ball milling technique,⁹⁴⁻⁹⁸ and chemical vapor transport (CVT) deposition process.⁹⁹⁻¹⁰² For the synthesis of phosphorene, a top-down method of exfoliating BP bulk has been largely used, which is realized by weakening the interaction of adjacent layers of BP.¹⁰³⁻¹⁰⁴ However, very limited bottom-up methods, such as chemical vapor deposition (CVD) or wet-chemical process, have been reported due to the complicated chemistry of phosphorene.

2.2.1 Synthesis of Black Phosphorus Crystals

In 1914, Bridgman reported an accidental discovery of BP crystals for the first time during converting white phosphorus to red phosphorus under the high pressure of 1.2 GPa at 200 °C.¹⁰⁵ Subsequently, a few methods were used in an attempt to synthesize BP single crystals with large size, such as modified Bridgeman's method,¹⁰⁶⁻¹⁰⁷ mercury catalysis,¹⁰⁸ and liquid bismuth.¹⁰⁹⁻¹¹⁰ However, highly flammable white phosphorus was often used as the precursor

and the as-obtained BP crystals were not large enough (e.g., needle-like BP single crystal with the size of $5 \times 0.1 \times 0.07 \text{ mm}^3$).^{109, 111} Until 1982, BP single crystals larger than $5 \times 5 \times 10 \text{ mm}^3$ (**Figure 2.1a**) were prepared by Endo *via* converting red P into melting black P at 900 °C and then slowly cooling down through a high isobaric pressure of 1 GPa.⁹³ This method solved the deficiency of big-size and high-quality BP crystals, but still largely limited by high-pressure apparatus in terms of the large-scale applications. Recently, high-energy mechanical ball-milling of commercial red phosphorus has also been demonstrated as a viable method of synthesizing BP bulk (**Figure 2.1b**), but it produces small BP crystals.¹¹² Therefore, a nontoxic and effective preparation method is still desired for industrial applications.

Very recently, Land *et al* prepared high-quality BP crystals by simply using Au, Sn, and SnI₄ as mineralizers in evacuated silica ampoules.¹¹³ This method, named as CVT process, endows the synthesis of BP free from using toxic agents (e.g., mercury and liquid bismuth) and complicated apparatus. It was further modified by Köpf in 2014 only using Sn/SnI₄ as the mineralizer, resulting in a short reaction and large, high-quality BP crystals.⁹⁹ In the method, red phosphorus together with Sn and SnI₄ as the starting materials was set to a temperature of 650 °C and then slowly cooled to 550 °C after 7.5 h. A representative silica glass ampoule after the synthesis of black phosphorus is shown in Figure 1c. SnI₄ (orange) and red phosphorus (red) from the gas phase are condensed at the right hand side of the ampoule. BP is formed in large bunches. Excessive Sn reacted to form Sn-Phosphides, which are present in small

round spheres. Compared to the Lang's method, byproducts like Au_3SnP_7 , AuSn , or Au_2P_3 were successfully avoided by removing Au as the mineration additive. This method provides easy access to high-quality BP crystals with facile fabricating process. Actually, Sn and I from SnI_4 are still the possible candidates to form side phases. In addition, the yield of BP crystals is still not high enough. Generally, 500 mg of red phosphorus are used as precursor in this method, indicating the maximum yield of BP is 500 mg considering the complete phase transformation. Therefore, growing BP crystals with improved purity as well as high yield is still challenging and needs further investigation.

2.2.2 Synthesis of Phosphorene

Reliable methods for preparing high-quality phosphorene are critical for practical applications. Two categories, e.g. the top-down and bottom-up approaches, are generally utilized for the preparation of ultrathin layered materials.¹¹⁴⁻¹¹⁵ The top-down methods mainly rely on exfoliation of bulk crystals into mono- or few-layer nanosheets by weakening the interlayer interaction chemically or mechanically, while the bottom-up methods are based on the chemical synthesis, such as chemical vapor deposition (CVD), wet-chemical synthesis and epitaxial process. Currently, intensive studies are reported on the phosphorene preparation via the top-down methods, such as mechanical exfoliation (scotch-tape technique) and liquid-phase exfoliation in various solvents.¹¹⁶

It is known that scotch-tape technique resulted in the discovery of graphene by repeatedly peeling off layers from the bulk material. Currently, this method has been widely used for the preparation of graphene analogues nanosheets (e.g., MoS₂,¹¹⁷⁻¹¹⁹ BN,¹²⁰⁻¹²² mica,¹²³⁻¹²⁵ etc.). Phosphorene is also prepared using the scotch-tape technique from BP crystals. The method can be optimized to produce high-quality phosphorene with the thickness of 1.6 ~10 nm and the lateral size of several micrometer (Figure 2.1c).¹²⁶ Although mechanical exfoliation of BP crystals is widely used, it is limited due to its extremely low yield. Large-scale synthesis of phosphorene in processable dispersions is still necessary for applications such as batteries, supercapacitors, solar cells etc.

Alternatively, liquid-phase exfoliation and shear mixing^{77, 127} or their combination⁷⁵ are viable options as promising large-scale production techniques. The size selection of as-exfoliated phosphorene can be realized by controlling different centrifuge speeds.¹²⁸ Up to date, numerous efforts have been made on exploring efficient organic/inorganic molecules used in the liquid-phase exfoliation of BP crystals. Recently, high-quality phosphorene with controllable sizes was prepared by liquid phase sonication in N-cyclohexyl-2-pyrrolidone (CHP).¹²⁹ The low-magnification transmission electron microscopic (TEM) images of phosphorene obtained in CHP was shown in **Figure 2.1c**. Dimethylformamide (DMF) and dimethyl sulf-oxide (DMSO) are also demonstrated as suitable solvents for preparing stable dispersions of ultrathin phosphorene.¹³⁰ However, the appropriate solvents for exfoliating BP bulk with high yield tend to be those with high boiling points. Therefore, the difficulty in

removal of the liquid from the as-exfoliated phosphorene limits their practical implement. Recently, ultrathin phosphorene (the thickness of ca. 2nm) with clean surface was prepared by exfoliating BP bulks in the distilled (DI) water.¹³¹⁻¹³² However, the yield of exfoliating BP in DI water is still not high enough. Therefore, it is necessary to explore proper solvents with low boiling points and high exfoliation efficiency or developing other effective synthesis methods.

Figure 2.1. The synthesis of BP crystals and phosphorene. a) Large BP single crystal (size: larger than $5 \times 5 \times 10 \text{ nm}^3$) prepared via high-pressure process. Reproduced with permission from Ref. [93]. Copyright 1982, The Japan Society of Applied Physics. b) Scanning electron microscopy (SEM) image of BP crystals prepared using high-energy mechanical ball-milling method. Reproduced with permission from Ref. [112]. Copyright 2012, American Chemical Society. c) Representative low-resolution transmission electron microscopic (TEM) images of phosphorene obtained in CHP. The inset is the corresponding Butterworth filtered high-angle annular dark field (HAADF) STEM image. Reproduced with permission from Ref. [129]. Copyright 2015, Nature Publishing Group.

Wet-chemical synthesis has been largely used in the preparation of various 2D layered materials due to its low cost and easy scalability.¹³³⁻¹³⁴ Recently, wet-chemical synthesis of phosphorene has also been explored as one of the bottom-up methods. Few-layer P-based nanosheets (the thickness of $< 5 \text{ nm}$) were for the first time prepared via the phase transformation from commercial red phosphorus

under a wet-chemical solvothermal reaction.¹¹⁷ During the synthesizing process, the bottom-up assembly of phosphorus nanodomains was driven by continuous vaporization-condensation process at the temperature of 400 °C under 50 bar. However, those nanosheets composited of amorphous P and black P show insufficient purity and relatively high degree of oxidation. As deduced by Zhao *et al.*, transformation from red phosphorus to BP is a spontaneous process ($\Delta G = -16.37 \text{ kJ mol}^{-1} < 0$).¹³⁵ Based on the phase transformation of phosphorus and Gibbs free energy theory, they prepared phosphorene (the thickness of ca. 3 nm) by a hydrothermal reaction using red phosphorus microspheres as raw materials and NH_4F as an effective agent to reduce the activation energy of red phosphorus. However, similar to the previous report, these as-obtained BP nanosheets also show polycrystalline and plenty of structural distortion. Those methods might shed light on further development of wet-chemical synthesis strategies.

2.3 Air-Instability of Phosphorene and Passivation Approaches

Although BP bulk stands out as the most thermodynamically stable allotrope of phosphorus, the atomically phosphorene gradually degrades in the presence of air.¹³⁶⁻¹³⁸ It is found that unprotected phosphorene possesses strong affinity for oxygen or water molecules upon exposure to ambient conditions, which presents a fundamental obstacle hindering the potential adoption of phosphorene in (photo) electronics and electrochemical devices. This has been largely reported since the successful preparation of phosphorene. Island *et al.* demonstrated an increase of

over 200% in volume of phosphorene during the continuous exposure (122 h) to ambient conditions.¹³⁸ The large volume increase of exposed phosphorene could be ascribed to the irreversible reaction between phosphorene and the ambient species, particularly O_2/H_2O , promote the formation of PO_x (e.g., phosphoric acid).

The ready degradation of phosphorene in ambient conditions leads to the deterioration of its physical and electric properties. Recently, a few works have proposed effective passivation approaches by protecting phosphorene from ambient atmosphere, including implementing protective layers to encapsulate phosphorene or covalent surface modification of phosphorene. Several studies have deposited capping overlayers to provide enhanced environmental stability of phosphorene and phosphorene-based devices.¹²¹ Atomic layer deposition (ALD) of a AlO_x capping layer on phosphorene has been demonstrated as an effective and scalable approach as shown in **Figure 2.2a**.¹³⁹ Similarly, the SiO_2 layer deposited on bare phosphorene by the inductively coupled plasma chemical vapor (ICP-CVD) was reported with an extended lifetime of phosphorene.¹⁴⁰ A fully encapsulated phosphorene was also realized by contacting phosphorene with monolayer graphene and then fully encapsulated the device with hexagonal boron nitride (h-BN) in a layer-by-layer configuration.¹⁴¹ Compared to those passivation composites such as deposited AlO_x and SiO_2 , h-BN is chemically inert and pinhole free, minimizing the possible reaction of phosphorene with air. However, recent studies by Kim *et al* reveal that even a thick Al_2O_3 layer is inadequate to provide long-term stability of phosphorene, which may be due to

the slow diffusion of adsorbents through the capping layers and causing eventual breakdown.¹⁴² Therefore, they developed a double-layer capping strategy by further coating a hydrophobic fluoropolymer film on top of the Al_2O_3 capping layer. The hydrophobic layer is critical for preventing the adsorption of moisture from air and diffusion into the device, giving much enhanced air-stability during months-long observation.

Except for depositing capping layers on the surface of phosphorene, covalent surface modification of phosphorene has also been reported as a helpful passivation approach towards air-stable phosphorene. Recently, a titanium sulfonate ligand was coordinated with phosphorene, resulting in good air-stability of phosphorene dispersion in water and exposure to air.¹⁴³ The successful passivation was demonstrated due to surface coordination occupying the long pair electrons of phosphorus, suppressing the oxidative reaction of phosphorene with oxygen and water molecules effectively. Very recently, covalent functionalization of phosphorene (**Figure 2.2b**) was further realized by simply immersing phosphorene in aryl diazonium salt solutions (4-nitrobenzene-diazonium: 4-NBD and 4-methoxybenzenediazonium: 4-MBD tetrafluoroborate salts) for a series of reaction times (0 ~ 180 mins).¹⁴⁴ During the soaking process, the modification proceeds spontaneously. The P-C bonds form after phosphorene reacting with 4-NBD and 4-MBD for 30 mins. This spectral feature for both molecules was further enhanced after increasing reaction time to 180 mins. With a formation of covalent P-C bonds, the morphology of the chemically modified BP remains constant within 10 days of

Figure 2.2. a) Micrographic images of unencapsulated and AlO_x encapsulated BP. Reproduced with permission from Ref. [139]. Copyright 2014, American Chemical Society. b) Reaction scheme of benzene-diazonium tetrafluoroborate derivatives and mechanically exfoliated few-layer BP (light blue) on a Si (grey)/SiO₂ (purple) substrate. Reproduced with permission from Ref. [144]. Copyright 2016, Nature Publishing Group.

exposure to ambient conditions. On the contrary, the unprotected phosphorene appears with large protrusions, indicating its severe oxidation. Therefore, those covalent functionalization strategies may provide insight into feasible and easy protection of phosphorene.

Actually, those passivation approaches discussed above, including both depositing protective layers and covalent surface modification on the surface of phosphorene, are demonstrated on one piece of mechanically cleaved phosphorene. So far, limited studies have been presented on passivating large

amount of phosphorene simultaneously, which is critical for volume applications of phosphorene in some fields, such as sensors, energy storage and conversion.

2.4 Black Phosphorus for Lithium-Ion Batteries

The theoretical specific capacity of BP as anodes for LIBs is as high as 2596 mAh g⁻¹ based on the formation of Li₃P.¹⁴⁵⁻¹⁴⁶ This value is almost ten times that of commercially used graphite (372 mAh g⁻¹),¹⁴⁷⁻¹⁴⁸ which renders BP a promising anode of LIBs with high gravimetric and volumetric energy density. However, BP is faced with the challenges of large volume change (~ 300%) as well as sluggish reaction kinetics as a typical alloying anode, leading to low initial reversible specific capacity and fast capacity fading.¹¹⁷ During past decade, extensive studies have been focused on the electrochemical mechanism,¹⁴⁹ first-principles calculations,¹⁵⁰⁻¹⁵¹ and developing BP-carbon composites.⁶⁵

2.4.1 Electrochemical Activities

The puckered layer structure of BP provides 2D interstitial space for Li insertion and extraction. Owing to the unique properties of phosphorene, numbers of theoretical calculations have been carried out related to the diffusion of Li ions in phosphorene.^{84, 152-153} It is found that stronger interaction between Li and phosphorene than that in graphene could potentially provide high open circuit voltage and enhance the electrochemical performance accordingly.⁸⁴ In addition, the ultrafast diffusion of Li ions along the zigzag directions of phosphorene due to the low shallow energy barrier (0.08 eV) is almost 10⁴ and

10^2 times faster than that in graphene and MoS_2 , respectively, indicating that phosphorene possesses potentially excellent Li storage properties.¹⁵³ Good reversibility has been also reported due to the self-recovery of phosphorene monolayer when it is distorted during the intercalation of Li ions at high Li/P ratio.^{152, 154} Therefore, favorable features of phosphorene as anodes of LIBs including ultrafast diffusivity, good reversibility and high open circuit voltage have been demonstrated theoretically as a promising candidate as anodes towards high-performance LIBs.

Recently, the electrochemical behavior of BP with high purity and crystallinity has also been experimentally studied by controlling different discharge termination voltages.¹⁵⁵ As shown in **Figure 2.3a-b**, *ex situ* X-ray diffraction (XRD) patterns were conducted at the different discharging and charging potential. When the potential is lowered from 2 to 0.78 V, various Li_xP phases (e.g., LiP_7 , LiP_5 , Li_3P_7 in sequence) are formed. The LiP phase produced is analyzed by high-resolution TEM (Figure 3c) when the potential is held at about 0.78 V. At the potential of 0.63 V, the molar ratio of Li and P is determined to be 1.93:1 characterized by Auger electron spectroscopy (AES), assumed to be the theoretical phase of Li_2P . When the discharge termination voltage is further lowered to 0 V, the main product becomes Li_3P . Upon charging process, the Li_3P phase disappeared and Li_2P reappeared at the potential of 1.12 V. Finally, amorphous phosphorus was believed to form with

Figure 1.3. The black phosphorus–carbon composite for the first cycle. a) Differential capacity plot. b) X-ray diffraction patterns (numbers correspond to the voltage point indicated in Figure a). c) TEM image and corresponding lattice spacing of LiP phase formed at 0.78 V during the first discharge. Reproduced with permission from Ref. [155]. Copyright 2007, John Wiley & Sons, Inc.

no obvious diffraction peaks at fully charged state. Therefore, the reactions of BP involved as anodes of LIBs could be as follows:

However, BP bulk or micro-sized particles suffer from rapid capacity fading due to its large volume change as well as sluggish reaction kinetics.¹⁵⁶ Isolating BP bulk into ultrathin phosphorene has been demonstrated as an answer to prolonging its cycling life. As evidenced by *in situ* TEM, phosphorene exhibit excellent structural integrity even after several lithiation/dethiation cycles.¹²⁷ Nevertheless, they exhibit poor initial reversible capacity of 210 mAh g⁻¹

accompanied by the low first-cycle Coloumbic efficiency (11.5 %), which is far from its theoretical capacity (2596 mAh g^{-1}).¹²⁸ Therefore, improvement of initial reversible capacity of BP nanosheets is still challenging before practical applications.

2.4.2 BP-Carbon Composites

Coupling conductive carbon with BP has been demonstrated theoretically and experimentally as an effective strategy to boost the electrochemical performance of BP as anodes for LIBs due to improved electrical conductivity as well as enhanced accommodation ability of large volume change.⁹⁴ During the past years, different carbon materials have been used to combine with BP, such as carbon black (super P), carbon nanotube, and graphene etc. Recently, BP-carbon (super P) composites with an optimum ratio of 7:3 were synthesized by high energy mechanical milling (HEMM) technique with red phosphorus and super P as the starting materials.¹⁵⁵ As a result, a high initial reversible capacity of 1814 mAh g^{-1} with an improved 1st- cycle Coloumbic efficiency (CE) of about 90% could be achieved compared to that of pure BP (1279 mAh g^{-1} , CE of 57 %). In addition, the cycling performance was further increased by controlling the voltage range. When the BP-carbon composite is cycled within the potential of 0-2.0 V versus Li^+/Li , the capacity degrades fast with about 10% retention during 30 cycles due to the large volume change originating from generating Li_3P phase. For the potential range of 0.78-2.0 V, good cycling performance with no obvious fading over 100 cycles was observed by avoiding the formation of the Li_3P phase.

However, the reversible reaction between P and LiP only exhibits a specific capacity of 600 mAh g^{-1} . Stable cycling performance has not been achieved with a specific capacity close to the full capacity of BP (2596 mAh g^{-1}). Very recently, robust phosphorus-carbon (P-C) bonds in BP-carbon composites (the ratio of P and C = 1:3) prepared via HEMM are demonstrated to be critical to improve the high capacity retention.¹⁵⁷ The stable P-C bonds are a key factor to maintain good electrical connection between BP and the conductive carbon matrix, affording a high initial charge specific capacity of 2382 mAh g^{-1} and a good cycling life with a specific capacity retention of 1849 mAh g^{-1} over 100 cycles. Furthermore, the BP/graphite composite shows highest reversible capacity as well as the most stable cycling performance among the various composites, including BP/carbon black, BP/graphene oxide and BP/C₆₀. Therefore, it is found that carbon structures also play a critical role in boosting the BP anodes for LIBs. Although good performance of BP as anodes for LIBs is achieved *via* those effective strategies, the BP used above is still the bulk/microsized BP crystals. Thin nanosheets with sufficient active sites may be beneficial to provide effective transport pathways for charge transfer and diffusion, which may show better rate performance.

Theoretically, phosphorene/graphene heterostructure (P/G) has been investigated as a good candidate for LIBs based on first-principles calculations due to improved binding energy and high diffusion mobility of Li ions in the P/G anodes.¹⁵⁸ Very recently, a paper-like flexible LIB electrode was experimentally prepared by combining exfoliated phosphorene (80 wt%) with conductive

graphene sheets (20 wt%).¹³² The characterizations including its photograph, SEM images, STEM-HAADF image and the corresponding EDS elemental mappings are shown in **Figure 2.4a-f**, respectively. The as-prepared porous phosphorene-G paper possesses mechanical robustness benefiting from the flexible two-dimensional structure of both graphene and phosphorene. On the contrary, a BP nanoparticle-G hybrid paper prepared via the same procedure with phosphorene-G paper is very brittle due to the intimate contact between phosphorene and graphene. This demonstrates that phosphorene exhibit favorable features for flexible electrochemical energy storage applications. In addition, high specific capacities (920 mAh g^{-1} at 100 mA g^{-1} , **Figure 2.4g**), good rate capability (141 mAh g^{-1} at 2500 mA g^{-1} , **Figure 2.4h**) and prolonged cycle performance (402 mAh g^{-1} over 500 cycles at 500 mA g^{-1} , **Figure 2.4i**)

Figure 2.4. a) Photograph of a BP-G hybrid paper. b) Top-view, and c) cross-sectional-view SEM images of the BP-G hybrid paper. d) STEM-HAADF image, and the corresponding EDS elemental mappings of e) the C-K line, and f) P-K line, of a region of the BP-G hybrid paper. g) The second galvanostatic charge/discharge profiles of the BP nanosheet, G paper, and BP-G hybrid paper electrodes at a current density of 100 mA g^{-1} within a potential window of $0.001\text{--}3 \text{ V (vs. Li}^+/\text{Li}^0)$. h) Rate performance of the BP nanosheet, graphene paper, and BP-G hybrid paper electrodes at different current densities. i) Cycling stability and Coulombic efficiency of the BP-G hybrid paper electrode at 500 mA g^{-1} for 500 cycles after the rate capability test. Reproduced with permission from Ref. [132]. Copyright 2017, John Wiley & Sons, Inc.

could be achieved for the free-standing phosphorene-G paper electrode based on its total mass.

The oxidation of BP nanosheets in ambient conditions tends to degrade the electrochemical performance. Therefore, air-stable BP-based electrodes are highly desired. However, so far there have been limited reports on applicable strategies towards passivating phosphorene and phosphorene-based as anode materials for LIBs.

2.4.3 BP-Noncarbon Composites

As discussed above, developing BP-carbon composites has been demonstrated as effective strategies towards overcoming the challenges of sluggish reaction kinetics and large volume change of BP as anodes for LIBs. However, high portion of conductive carbon materials possibly lead to reduced specific capacity based on the overall mass of the whole electrode, considering that carbon materials exhibit relatively low specific capacities compared to the bare phosphorene. Constructing controllable and well-designed heterostructures based on ultrathin 2D nanosheets (e.g., MoS₂/WS₂,^{39, 40} Fe₃O₄/MoS₂,⁴¹ WSe/MoSe,¹⁵⁹ GaSe/MoSe₂,¹⁶⁰ PANI/MoS₂¹⁵⁹) are fundamentally and technologically attractive in batteries or electronic devices. Therefore, hybridization of phosphorene with other electrochemical active materials, such as transition metal oxides, metal chalcogenides, and metal phosphides, has been identified as an intriguing route to engineer their properties through taking advantages of different building blocks.

Currently, the investigation of BP-noncarbon composites, especially for LIBs applications, is still in its infancy. The absence of dangling bonds on BP basal plane presents a difficulty to further modify phosphorene. Therefore, efforts could be devoted to conjugate functional groups (e.g., -OH, -COOH, thiol ligands) on the surface of phosphorene for further hybridization. However, considering the sensitive property of phosphorene to oxidizing and aqueous conditions, careful processing under inert atmosphere to construct phosphorene-based heterostructures would be necessary and also challenging in order to minimize the phosphorene oxidation.

2.5 Black Phosphorus for Sodium-Ion Batteries

Sodium shares similar chemical properties with lithium in many aspects. Therefore, the development of Na battery technologies could learn from the accumulated experience of LIBs.⁹⁵ Recent studies on cathode materials for SIBs have demonstrated comparable performance to the LIBs counterparts.¹⁶¹ However, identifying viable anodes is the major scientific challenge for competitive SIBs technology.¹⁶² The development of anodes for SIBs has been largely based on hard-carbon materials, which provides a relatively low specific capacity, especially a low volumetric capacity.¹⁶³⁻¹⁶⁵ Recently, BP has been considered as one of the most promising anodes due to its high sodium storage capacity, layered structure and suitable operating potential (~ 0.45 V vs Na/Na⁺).¹⁶⁶⁻¹⁶⁷ Numerous theoretical investigations have been focused on the monolayer phosphorene as anodes for SIBs using a first-principle calculation.¹⁶⁸⁻

¹⁷⁰ It is found that Na diffusion on phosphorene is ultrafast and anisotropic, potentially endowing phosphorene with excellent electrochemical response.^{86,}
¹⁶⁹⁻¹⁷¹ Therefore, phosphorene is also demonstrated as a promising anode for SIBs.

The sodiation of phosphorene proceeds according to two steps including both intercalation (1.5–0.54 V vs Na/Na⁺) and alloying (0.54–0.0 V vs Na/Na⁺), finally forming the Na₃P phase recognized by *ex situ* X-ray diffraction (XRD) techniques.¹⁷² Upon alloying, an anisotropic volumetric expansion with a 92 % expansion along y axis and 0 % along x axis was observed using *in situ* TEM. However, the complete sodiation of BP leads to a large volume expansion (~500 %) and thus fast capacity fading during cycling. To achieve stable cyclability, these authors fabricated a layer-by-layer phosphorene-graphene hybrid as anodes of SIBs for the first time as illustrated in **Figure 2.5a-b**. Graphene in such a sandwich structure plays a critical role in buffering the anisotropic expansion as well as facilitating the electron transport. With increasing content of graphene in the composite, excellent sodium storage performance in terms of cyclability was achieved benefiting from these advantages as shown in Figure 6c. In addition, the phosphorene-graphene hybrid with 48.3% of phosphorus exhibited a high reversible capacity (2440 mA h g⁻¹ at 0.02 C) and good capacity retention (2080 mAh g⁻¹ after 100 cycles) based on the mass of phosphorus (Figure 6d). Therefore, phosphorene-graphene hybrids and other phosphorene-carbon based materials could be suitable anodes for SIBs in the future. Actually, considering the electrochemically inactive property of graphite/graphene and low specific capacities of other carbon materials,

phosphorene for SIBs also face the similar challenge to LIBs. That is, high percent of carbon materials would lead to reduced specific capacities based on the whole mass of the composite electrodes. Therefore, developing phosphorene-based hybrid heterostructures with high-capacity nanomaterials could be an effective strategy, as discussed above in the part (2.4.3) of BP-carbon composites for LIBs.

Figure 2.5. a) Digital photographs of NMP dispersions of graphene and phosphorene and their mixture prepared by mixing at a volume ratio of 6:1. Red light beams were incident from the side to demonstrate the Tyndall effect. b) Structural evolution of the sandwiched phosphorene–graphene structure during sodiation. c) Reversible desodiation capacities for the first 100 galvanostatic cycles of various phosphorene–graphene electrodes with different carbon–phosphorus mole ratios (C/P) of 1.39, 2.07, 2.78 and 3.46, between 0.02 and 1.5 V at a current density of 0.05 A g⁻¹. d) Reversible desodiation capacity and Coulombic efficiency for the first 100 galvanostatic cycles of the phosphorene/graphene (48.3 wt% P) anode tested under different currents. Reproduced with permission from Ref. [172]. Copyright 2015, Nature Publishing Group.

Furthermore, electrolyte additives have been considered as an indispensable role for the improvement of SIBs. Na_3P , as an electrochemically reduced product of BP during sodiation process, has much shorter inter-sodium distances (2.98-3.22 Å) due to covalent character of Na-P bonds than metallic sodium (3.71 Å).¹⁷³⁻¹⁷⁴ This favorable feature endows BP with higher volumetric energy densities than other Na alloys (e.g., Sn, Sb). However, the highly reactive surface of Na_3P induces severe electrolyte decomposition, leading to large irreversible capacity.¹⁷⁵ Electrolyte additives with no more than 5% either by weight or by volume have been largely studied in LIBs as one of the most economic and effective methods for the improvement of LIBs performance.¹⁷⁶⁻¹⁷⁸ Therefore, the successful experience of LIBs could be learnt by SIBs due to the similar electrochemical properties. Actually, among those additives (transdifluoroethylene carbonate (DFEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC) and ethylene sulfite (ES)) used for LIBs, FEC has been demonstrated as the efficient one for SIBs to stabilize the solid-electrolyte interphase (SEI) and thus suppress the electrolyte decomposition.¹⁷⁹⁻¹⁸¹ For example, enhanced cycling performance (approximately 1000 mAh g⁻¹ after 80 cycles) was achieved for P/C composite by adding FEC in the electrolyte.¹⁴⁶ On the contrary, dramatic capacity degradation happened after 40th cycle due to the unstable SEI film. Currently, the study of the most suitable electrolyte additives for BP-based anode materials for SIBs is still in early stage. Therefore, further systematic exploration and study of optimal electrolyte additives is still necessary.

Chapter 3 An Air-Stable Densely Packed Phosphorene-Graphene Composite towards Advanced Lithium Storage Properties

In this chapter, high-yield synthesis of phosphorene with good crystallinity and tunable size distributions via liquid-phase exfoliation of bulk BP in formamide is presented firstly. Afterwards, a densely packed phosphorene-graphene composite (PG-SPS, a packing density of 0.6 g cm^{-3}) is prepared by a simple and easily up-scalable spark plasma sintering (SPS) process. The excellent air stability of PG-SPS over the 60 days observation in maintaining its high Li storage properties was investigated.

3.1 Introduction

Delamination of black phosphorus (BP) into monolayer or few-layer, dubbed phosphorene, and manipulation of its newly discovered properties that are unattainable by its bulk structure have been a recent scientific breakthrough. Its tunable direct band gap, high carrier mobility, large on/off ratios ($> 10^5$) and in plane anisotropic properties^{4, 60, 182-187} pave the way for a wide range of applications, including field-effect transistors¹⁸⁸⁻¹⁹⁰, thin-film solar cells¹⁹¹, tunable infrared photodetectors⁵⁹⁻⁶⁰, thermoelectric devices¹⁹²⁻¹⁹⁵, and gas sensors.¹⁹⁶ As an elemental analogue of graphene, researchers intended to exploit its structural similarity to substitute graphene as anode for lithium ion batteries (LIBs). In addition, theoretical studies have revealed that Li diffusion along zigzag directions in phosphorene is hundreds times faster than that in MoS_2 or

graphene^{187-188, 197-198}. Nevertheless, bulk/microsized BP particles always suffer from low reversible capacity, fast capacity fading caused by its huge volume change (~ 300 %) as well as sluggish electron kinetics in response to lithium reactions^{96, 199}. With respect to the aforementioned issues, successful thinning of BP into ultrathin 2-dimensional (2D) phosphorene could be the answer to prolonging its cycle life due to effective accommodation of the large volume change and shortening the diffusion length during charge/discharge²⁰⁰⁻²⁰¹.

Very recently, exciting progress has been achieved with a phosphorene-graphene composite working as a high-capacity anode for sodium-ion batteries²⁰². The graphene layers in the hybrid structures can function as a mechanical backbone and an electrical highway considering the inferior electric conductivity of phosphorene. However, there are still some hurdles before phosphorene can be directly put into commercial practice. Although liquid-phase exfoliation via sonication or shear mixing²⁰³⁻²⁰⁷ has been proved fruitful to delaminate graphene and 2D transition metal dichalcogenides (TMDs), the stronger interlayer interaction of BP poses a great challenge to the exfoliation process^{204, 208-209}. Besides most of the commonly used exfoliation solvents, such as N-Methyl-2-pyrrolidone (NMP), dimethylformamide (DMF) and et al., efforts have to be made on exploring suitable solvents with matched surface energies to that of phosphorene. Moreover, air stability of phosphorene has been a long-standing problem that plagues its electrochemical activities, in which exposure of phosphorene to water and oxygen may lead to the deterioration of its electric property^{138, 210-213}. In addition, nanostructuring inevitably induces some side

effects on exfoliated phosphorene. Although confined thickness and large lateral dimension of phosphorene are beneficial for circumventing the pulverization of the electrodes, its high specific surface area may give rise to a lower first-cycle Coulombic efficiency (CE) due to parasitic reactions with the electrolyte as well as a reduced volumetric capacity caused by the low packing efficiency of nanostructures²¹⁴⁻²¹⁶.

To overcome these bottlenecks, we demonstrate the preparation of densely stacked phosphorene-graphene composite (PG-SPS) via spark plasma sintering (SPS)²¹⁷ that applies pulsed direct current through the sample during low temperature sintering process within a short duration. In this study, high concentration (ca. 0.19 mg/mL) few-layer BP can be obtained by sonicating ground BP crystals in formamide, which is higher than using several other common solvents as parallel control experiments. Subsequently, phosphorene-graphene oxide composite (PGO) paper prepared by vacuum filtration was subjected to SPS (denoted by PG-SPS sample) to further densify and reduce the composite. For comparison, conventional annealing process done under H₂/Ar atmosphere was carried out to transform PGO into phosphorene-graphene hybrid (denoted by PG sample). SPS treatment has successfully improved the density of PG-SPS (0.6 g cm⁻³), which is much higher than that of PG (0.16 g cm⁻³). In addition to this advantage, BP in PG-SPS is more resistant to oxidation compared to PG after ambient exposure due to effectively suppressing permeation of water or oxygen molecules into deeper layers of the sample. Furthermore, the effectiveness of SPS treatment in improving the electrochemical performances of

PG-SPS sample can be reflected by its enhanced first-cycle CE, specific capacity ($1306.7 \text{ mAh g}^{-1}$) and volumetric capacity ($256.4 \text{ mAh cm}^{-3}$), rate capabilities (e.g., 415.0 mAh g^{-1} at 10 A g^{-1}), and cycling stability (91.9 % retention after 800 cycles at 10 A g^{-1}) compared to the few-layer BP and the loosely stacked PG. Moreover, the exposed PG-SPS electrode exhibits negligible degradation of Li storage properties after exposure to ambient conditions for 60 days. In contrast, the exposed PG electrode only exhibits 353 mAh g^{-1} after only 10 days ambient exposure compared to the as-prepared ones (620 mAh g^{-1}) after 50 cycles at 100 mA g^{-1} .

3.2 Experimental Section

3.2.1 Materials

Black phosphorus (BP) crystals ($\sim 99.998\%$) were purchased from Smart Element. N-Methyl-2-pyrrolidone (NMP, 99.5%, anhydrous), dimethyl sulfoxide (DMSO, $\geq 99.9\%$), tetrahydrofuran (THF, $\geq 99.9\%$, anhydrous), isopropyl alcohol (IPA, 99.7%), and methanol (99.8 %, anhydrous) were purchased from Sigma Aldrich. Dimethylformamide (DMF, 99.8%, anhydrous), ethanol (99.8 %, anhydrous), formamide (98%, analytic reagent grade), and acetone ($\geq 99.5\%$) were purchased from Fluka. All the materials were used as received without any further purification.

3.2.2 Preparation of few-layer BP in different solvents

$1.00 \pm 0.01 \text{ mg}$ BP crystals were mixed with $300 \mu\text{L}$ of each solvent and were ground with the mortar and pestle for 3 mins. Then the mixture was transferred

to a glass vial containing 3 mL of each solvent. After bubbled with argon for 10 mins and careful sealing with parafilm, the vials were sonicated at 20-25 °C for 4 h at the power of 200W. After settling down for 12 h, the top 2/3 of the solutions were further centrifuged at 2000 or 4000 rpm for 1h. Then the top 1/2 of supernatant was collected (marked as 2000BP and 4000BP, respectively) by centrifugation at 9000 rpm for 30 mins.

3.2.3 Preparation of PGO Paper

Graphene oxide (GO) was synthesized from natural graphite by a modified Hummers method²¹⁸⁻²²⁰. The few-layer BP was obtained using the same method of 2000BP. In brief, 80 mg of BP crystals were ground and bubbled with argon and then sonicated in 240 mL of formamide for 4 h. After settling down for 3 h, the top 2/3 solutions were centrifuged at 2000 rpm for 1h. The top 1/2 of the supernatant was collected via centrifugation at 9000 rpm for 30 mins. The concentration of few-layer BP was determined as 0.16 mg mL⁻¹. Then GO was added into the solution in a mass ratio of (GO/2000BP: 3/1). After further sonication for 1h, the homogeneous suspension was filtered using Polytetrafluoroethylene (PTFE) filter membranes with a pore size of 0.22 µm and subsequently washed with ethanol. The as-obtained paper was peeled off and dried in vacuum overnight at 50 °C.

3.2.4 Preparation of PG

The PGO paper was annealed at 300 °C for 1h with the increasing rate of 5 °C min⁻¹ under H₂/Ar (v/v: 5/95) atmosphere.

3.2.5 Preparation of PG-SPS

The PGO paper was cut into several circular disks with the diameter of 12mm. Then SPS is employed at 300 °C under the pressure of 10 MPa and vacuum condition (0.01 pars) for 3 mins.

3.2.6 Structural Characterizations

UV-Vis-IR was recorded using 200 μ l of mixture dispersed in 2 mL ethanol on a CARY 5000 spectrophotometer (Agilent) at room temperature. SEM images were obtained using a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F). X-ray diffraction (XRD) measurement was performed on a Shimadzu XRD-600 with Cu K α radiation (λ = 0.15404 nm) operated at 40 kV and 30 mA. TEM images were obtained using JEOL-2100F at an acceleration voltage of 200 kV. Raman spectra were measured by using a 488 nm micro-Raman spectrometer (WITec). The Raman band of a silicon wafer at 520 cm^{-1} was used as a reference. AFM images were obtained using Asylum Research Cypher S. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Theta Probe electron spectrometer (VG ESCALAB200i-XL, Thermo Scientific). The binding energies were calibrated using C 1s peak at 284.5 eV as the reference. Spark plasma sintering method is applied using SPS-1050 apparatus (Sumitomo Coal Mining, Japan).

3.2.7 Electrochemical Measurements

The few-layer BP electrode was prepared by mixing 70 wt% 2000BP with 20 wt% super P and 10 wt% polyvinylidene fluoride (PVDF) as the binder to form a slurry. The PG-SPS and PG electrodes were prepared by mixing 90 wt% active materials with 10 wt% PVDF. Then the slurry was coated onto a copper foil and dried at 50 °C for 12 h under vacuum. The coin cells (2032) were assembled in an argon-filled glovebox with concentrations of moisture and oxygen below 0.1 ppm, using lithium metal as the counter/reference electrode, a Celgard 2400 membrane as the separator, and the 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1, v/v). The charge-discharge tests were performed with a NEWARE battery tester in a voltage window of 0.01-3.0 V. Cyclic voltammetry (0.01-3.0V, 0.1 mV s⁻¹) was carried out on Solartron analytical equipment (Model 1470E). Electrochemical impedance spectroscopy (EIS) was performed on a Bio-Logic SP-150 potentiostat in a frequency range of 1 MHz–0.01 Hz with an AC amplitude of 10 mV. Spark plasma sintering (SPS) method is applied using SPS-1050 apparatus (Sumitomo Coal Mining, Japan).

3.3 Results and Discussions

Bulk BP is composed of layered orthorhombic crystal structure with the space group *Cmca* (no. 64), in which weak van der Waals interactions are dominated along the crystal *z* axis (**Figure 3.1a**). The *x* and *y* directions correspond to the zigzag (ZZ) and the armchair (AM) directions, respectively. In a monolayer

phosphorene (Figure 3.1b), each atom is bonded to three neighboring atoms, forming a honeycomb-puckered network by sp^3 hybridization of phosphorous atoms.

Figure 3.1. Crystal structure of black phosphorus (BP). a) Schematic diagram of multilayer BP crystal. b) Front view of a monolayer phosphorene. The Zigzag direction is 'x', the armchair direction is 'y', and the direction normal to the flake is 'z'.

In order to cast light onto the role of molecules in the BP liquid-phase exfoliation, we firstly prepared various dispersions by grinding and subsequently sonicating bulk BP (the SEM image of bulk BP is shown in **Figure 3.2**) in different solvents with varying surface tensions (22.10-58.2 dyne cm^{-1}) (**Table 3.1**). The solvents include N-Methyl-2-pyrrolidone (NMP, labeled as 1), dimethylformamide (DMF, labeled as 2), dimethyl sulfoxide (DMSO, labeled as 3), formamide (labeled as 4), tetrahydrofuran (THF, labeled as 5), isopropyl

alcohol (IPA, labeled as 6), ethanol (EtOH, labeled as 7), methanol (MeOH, labeled as 8), acetone (labeled as 9) and deionized water (DI water, labeled as 10). **Figure 3.3a-b** shows the photographs of the ground BP suspensions before sonication and stored for 12 h after sonication. It is noticed that NMP, DMF, DMSO, formamide, and IPA are effective for BP exfoliation to give the brown dispersions. Their supernatants (top 2/3 of the dispersion after being stored for 12 h) were collected and characterized by ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectroscopy (**Figure 3.3c**).

Figure 3.2. Low-magnification SEM image of bulk BP.

Table 3.1 Summary of BP exfoliation in different solvents.

Solvents	Surface tension (dynes cm ⁻¹)	Boiling point (°C)	Concentration (mg mL ⁻¹)	Yield (%)
N-Methyl-2-pyrrolidone (NMP)	39.3	202	0.07	14

Dimethylformamide (DMF)	37.1	152	0.08	16
Dimethyl sulfoxide (DMSO)	42.78	189	0.12	24
Formamide	58.20	210	0.19	38
Tetrahydrofuran (THF)	26.4	66	~0	~0
Isopropyl alcohol (IPA)	21.7	82	0.08	16
Ethanol (EtOH)	22.1	78	0.02	4
Methanol (MeOH)	22.7	64	0.03	6
Acetone	25.2	56	~0	~0
DI water	40.9	100	~0	~0

According to the Lambert-Beer Law: $A/l = \alpha C$ where A is absorbance intensity, l is the cell length, α is the extinction coefficient and C is the concentration, A scales linearly with C for minor dispersions in ethanol. Therefore, the concentration of few-layer BP in each solvent can be sorted in the following descending order: formamide > DMSO > DMF ~ NMP ~ IPA > ethanol ~ methanol > acetone ~ THF ~ DI water. Their concentrations are further measured by careful filtration, washing and weighing steps, as shown in **Table 3.1**. High concentration (0.19 mg mL^{-1}) few-layer BP can be achieved using formamide as exfoliation solvent, corresponding to a yield of 38%. It is higher than those of dispersions in DMSO (0.12 mg mL^{-1} , 24%), DMF (0.08 mg mL^{-1} , 16%), NMP (0.07 mg mL^{-1} , 14%), and IPA (0.08 mg mL^{-1} , 16%). The plot (Figure 3.3d) of surface tension vs. concentration demonstrates that the yield of few-layer BP

monotonically increases with the increasing surface tension, which is similar to the trend of graphene and TMDs exfoliations²²¹⁻²²². Based on these results, formamide can be regarded as an appropriate molecule that can give rise to higher efficiency in BP exfoliation.

Figure 3.3. Liquid-phase exfoliation of BP via ultrasonication in a range of solvents. a) Photographs of ground BP dispersions in solvents before sonication and b) stored for 12 h after sonication process. c) Optical absorption spectrum of minor dispersions (top 2/3 of the supernatant after being stored for 12 h) in ethanol. d) Plot of surface tension vs. phosphorene concentration in different solvents.

Figure 3.4. Characterization of phosphorene obtained with varying size distributions by different centrifuge speed. a) Representative atomic force microscopic (AFM) image of 2000BP (collected after centrifugation at 2000 rpm). b) Representative dark field scanning TEM image of 2000BP at a holey carbon TEM copper grid. c) HRTEM image of 2000BP. d) Representative AFM image of 4000BP (collected after centrifugation at 4000 rpm). e) TEM image of 4000BP lying on the holey carbon. Insets are the photo (left) and Tyndall effect (right) of the 4000BP dispersions in formamide. f) Raman spectra of 4000BP ($\lambda = 488$ nm).

As the properties of phosphorene are size-dependable, it is crucial to sort out each fraction by size to suit the specifications of different applications. For examples, large nanosheets are preferred to be used in mechanical reinforcement while smaller ones are promising materials for catalysis. Therefore, BP nanosheets dispersed in formamide can be systematically separated by size with a size selection technique that is controlled by centrifuge speed. The supernatant (top 2/3 of the dispersion after being stored for 12 h) was firstly centrifuged at 2000 revolutions per minute (rpm) for 1 h to remove those thicker sheets. Then

the top 1/2 of as-obtained supernatant was further centrifuged at 9000 rpm for 30 mins to collect the as-obtained BP sheets (the product is marked as 2000BP). As shown in the AFM image (**Figure 3.4a**) and corresponding height profiles (**Figure 3.5a**), the average topographic height is about 3.1~4.3 nm, corresponding to about 7 ± 1 layers of BP. The lateral size of these 2000BP ranges from 1 μm to 50 nm. Figure 3.4b shows a dark field scanning TEM image of a representative 2000BP sheet. No bubbles or other signs of degradation are observed, indicating the good chemical stability of the as-obtained BP sheets. The high-resolution transmission electron microscopy (HRTEM) image (**Figure 3.4c**) shows a clear lattice spacing of 0.22 nm corresponding to the (014) plane of BP (JCPDS No.76-1957), indicating the atomic structure and persisted crystallinity. Furthermore, the supernatant (top 2/3 of the dispersion after being stored for 12 h) was also centrifuged at 4000 rpm for 1 h. Then the top 1/2 of as-obtained supernatant was centrifuged at 9000 rpm for 30 mins to collect the as-obtained BP sheets (marked as 4000BP). It is noticed that thinner (1.4~2.1 nm, 3 ± 1 layers) and smaller (50-300nm in lateral dimension) BP sheets can be obtained, as shown in the AFM height image (**Figure 3.4d**) corresponding height profiles (**Figure 3.5b**). A TEM image of a typical 4000BP sheet lying on the carbon film is shown in Figure 3.4e. The Tyndall effect (the right inset of **Figure 3.4e**) was observed by laser irradiation, indicating the well-dispersed colloidal system. The 4000BP sheets dispersion can be stable for hundreds of hours (**Figure 3.6**) with negligible color change, during which only little sediment was observed. Three prominent peaks at 363.6, 441.5 and 468.2

cm^{-1} can be observed in Raman spectroscopy (**Figure 3.4f**), which are ascribed to one out-of-plane phonon mode (A_g^1), and two in-plan modes (B_g^2 and A_g^2), respectively²⁰⁷.

Figure 3.5. AFM height profiles of (a) 2000BP and (b) 4000BP.

Figure 3.6. Photograph of 4000BP after hundreds of hours.

To further demonstrate the advantage of high-yield preparation of few-layer BP, a PGO paper (**Figure 3.7a**) was prepared by vacuum filtration of a

homogeneous mixture of the as-obtained few-layer BP (2000BP) and GO. SPS method (**Figure 3.8**) is subsequently applied on the PGO paper at 300 °C under the pressure of 10 MPa and vacuum condition (0.01 par) to prepare PG-SPS. Upon the SPS process, GO can be reduced to conductive reduced graphene

Figure 3.7. Characterization of PGO paper, PG-SPS, and PG samples. a) Photograph of a phosphorene-graphene oxide layer-by-layer composite (PGO) paper (Diameter: 40 mm). b) Raman spectra of PG-SPS and PG samples. c) Cross-sectional SEM images of PG-SPS and PG samples.

oxides (rGO), which become the mechanical backbone and electron pathway in the PG-SPS composite. In addition, the possible adsorbents (e.g., H₂O, O₂) at the interfaces of few-layer BP and GO can be removed under the vacuum condition to avoid the further degradation of few-layer BP. Moreover, the stacking of phosphorene and rGO can be significantly enhanced during the annealing and simultaneous pressing process, which can effectively inhibit the permeation of oxygen or water. For comparison, PG paper was also obtained by annealing PGO paper at 300 °C under H₂/Ar (v/v: 5/95) atmosphere. The Raman spectra (**Figure 3.7b**) of the PG-SPS and PG samples shows a broad peak between 300-470 cm⁻¹

as well as the D and G bands at 1340 and 1650 cm^{-1} , respectively, indicating the presence of both BP and rGO. As shown in their

Figure 3.8. Schematic diagram of Spark plasma sintering (SPS).

cross-sectional SEM images (**Figure 3.7c**), the PG-SPS sample shows a much more densely packed structure as compared to the loosely stacked PG. With similar mass (controlled by the identical preparation of the PGO paper), the PG-SPS sample shows a thickness of $44\text{ }\mu\text{m}$, which is $< 1/3$ of the PG ($142\text{ }\mu\text{m}$). Therefore, a density of 0.6 g cm^{-3} can be achieved for PG-SPS, much higher than that of PG (0.16 g cm^{-3}). Their electrical conductivity is also investigated using a four-point probe system. As shown in **Figure 3.9**, the conductivity of PG-SPS (18.7 S cm^{-1} , the average value of 9 different points) is about 3.2 times that of PG (5.8 S cm^{-1} , the average value of 9 different points) due to the strong layer-by-layer interaction between P and C atoms in the PG-SPS sample.

Figure 3.9. Electrical conductivity of PG and PG-SPS measured at 9 different positions.

We also investigated the air stability of the as-prepared samples, e.g., few-layer BP, PG and PG-SPS. The as-exfoliated few-layer BP (2000BP or 4000BP) show poor chemical stability when they are exposed to ambient conditions. Their degradations take place gradually via reactions with water and oxygen. As shown in **Figure 3.10**, one typical few-layer BP after exposure to ambient

Figure 3.10. Air stability of black phosphorus sheets. TEM observation of one BP sheet after exposed to the ambient conditions for 4 days in a) 0 s, b) 15 s, and c) 30 s. Scale bar = 100 nm. The yellow arrows indicate the same position.

condition for 4 days exhibits rapid morphology change upon TEM observation. The yellow arrows indicate the same position during the TEM observation. It is noticed that there are bubbles generated, flowed and grew in the degraded sample, indicating the existence of oxidized phosphorus (e.g., phosphoric acid) in the few-layer BP after exposure to ambience. For PG-SPS and PG samples, they were exposed to the identical in-door ambient conditions (temperature 25-

Figure 3.11. XRD analysis of the air stability of PG-SPS versus PG. a) Fresh PG-SPS sample and b) PG-SPS after exposure to the ambience for 60 days. c) Fresh PG sample and d) PG after exposure to the ambience for 10 days.

28 °C, humidity 75-85 %) for several days. In the as-prepared condition, both PG-SPS and PG samples (**Figure 3.11**) show three peaks at $2\theta = 16.9^\circ$, 34.2° and 52.4° , attributed to the diffractions of (002), (004) and (006) planes of BP (JCPDS No. 76-1957), respectively. After exposure to ambience for 60 days, the PG-SPS sample still show clear diffraction peaks from the well crystalline few-layer BP.

The integrity of PG-SPS sample can be also confirmed by the TEM image (**Figure 3.12a**) with the integral sets of selected area diffraction (SAED) patterns from BP and rGO. On the contrary, only one minor peak corresponding to the (002) plane of BP was observed for the PG sample after exposure to ambient conditions for only 10 days. In addition, aggregates appear instead of sheets as shown in the TEM image of the PG sample after exposure (**Figure 3.12b**), indicating its severe degradation.

Figure 3.12. TEM images of (a) PG-SPS after exposure and (b) PG after exposure. The insets are corresponding SAED patterns.

The air stability of PG-SPS and PG is further assessed using X-ray photoelectron spectroscopy (XPS) measurement (**Figure 3.13**). In situ sputtering was conducted for 2 mins to etch ~4-6 nm of the surface layer. The survey spectra (**Figure 3.14**) of PG and PG-SPS show predominant peaks of C, P and O. Figure

3.13a shows that the as-prepared PG sample have the 2p_{3/2} (P1) and 2p_{1/2} (P2) doublet at 129.6 eV and 130.4 eV, respectively,

Figure 3.13. X-ray photoelectron spectroscopy (XPS) analysis of the air stability of PG-SPS versus PG. P 2p core-level spectra for (a) fresh PG, (b) PG after exposure to the ambience for 10 days, (c) fresh PG-SPS and (d) PG-SPS after exposure to the ambience for 60 days. All spectra are taken after 2 mins *in situ* sputtering, which removes about 4-6 nm of the materials on the surface.

which are the characteristics of the phosphorus-phosphorus bonds within BP. A low sub-band is also observed at ~ 133.0 eV, suggesting the presence of oxidized phosphorus (i.e., PO_x , ca. 16 atomic %) due to the unavoidable oxidation during sample processing. After exposure to ambient conditions for 10 days, 95.2 atomic % of phosphorus in PG sample was oxidized (**Figure 3.13b**), indicating severe degradation of BP. On the contrary, 26.1 atomic % of

Figure 3.14. Survey spectrum of (a) PG-SPS after exposure to the ambience for 60 days and (b) PG after exposure for 10 days.

phosphorus in fresh PG-SPS sample was initially oxidized as shown in Figure 3.13c, which exhibits negligible increase (Figure 3.13d) during long-time exposure (60 days in ambience). The little increase of PO_x in as-prepared PG-SPS compared to fresh PG sample might be mainly stemmed from the P-O-C bond that links between the C-OOH or C-OH group of graphene oxide and P atoms during SPS process. The presence of P-O-C bond of PG-SPS can also be confirmed by the peak located at 998 cm^{-1} in the Fourier transform infrared spectroscopy (FTIR) measurement (Figure 3.15).²²³⁻²²⁵

When the PG-SPS sample was made into electrodes on Cu foil, it shows a thickness of $\sim 29.3\text{ }\mu\text{m}$ as shown in Figure 3.16a, which is much thinner than that of PG electrode ($\sim 57.2\text{ }\mu\text{m}$, as shown in Figure 3.16b) with the same mass loading of 0.65 mg cm^{-2} . This high packing efficiency of PG-SPS is expected to improve the volumetric capacity of the battery. Electrochemical behaviors of the as-prepared PG and PG-SPS samples as anode materials of LIBs were then

investigated in the voltage window of 0.005-3 V versus Li⁺/Li. The cyclic voltammetry (CV) curves of PG-SPS (**Figure 3.17a**) and PG (**Figure 3.17b**) during the first 3 cycles were obtained at a scan rate of 0.1 mV s⁻¹. Both PG-SPS and PG electrodes show two sharp peaks at 0.9 and 0.2V and a broad one at 0.75 V during the first cathodic scan, and two peaks at 1.06 and 1.2 V during the anodic scan, indicating the same lithiation/delithiation mechanism. The multistep reactions can be ascribed to the conversion of BP → Li_xP → Li₃P, similar to the previous studies^{96, 199, 226}. Their first galvanostatic charge/discharge measurements at a current density of 100 mA g⁻¹ are shown in **Figure 3.16c**. Here, all the specific capacities were calculated based on the total mass of the composites including both phosphorene and graphene. It is observed that few-layer BP exhibits a low CE (only 11.5 %) in the first cycle, indicating a It is observed that few-layer BP exhibits a low CE (only 11.5 %) in the first cycle, indicating a negligible reversible specific capacity (210 mAh g⁻¹) due to the severe side reactions from the largely exposed surface as well as the large volume expansion of ~ 300% from P to Li₃P. With the introduction of rGO layer as a mechanical backbone and an electrical highway, PG and PG-SPS electrodes show improved initial specific capacities of 2763 mAh g⁻¹ and 2166.6 mAh g⁻¹, with the corresponding CEs of 34.3% and 60.2 %, respectively. It is noticed that, although the initial discharge specific capacity of PG-SPS is lower than that of PG, a much higher CE and an improved reversible specific capacity (1302 mAh g⁻¹) can be obtained for PG-SPS electrode. This can be mainly ascribed to the reduced side reactions with the electrolyte due to the

Figure 3.15. FTIR measurements of as-prepared PG-SPS and PG samples.

Figure 3.16. Electrochemical characterization of as-prepared PG-SPS and PG electrodes. Cross-sectional SEM images of PG-SPS (a) and PG (b) electrodes on Cu foil with the same mass loading of 0.65 mg cm^{-2} . c) The first galvanic charge/discharge measurements of few layered BP, PG and PG-SPS at a current density of 100 mA g^{-1} . d) Rate capabilities of PG and PG-SPS electrodes at various current densities. e) Cycling life of PG and PG-SPS electrodes based on volumetric capacities at a current density of 100 mA g^{-1} . f) Long-term cycle life of PG-SPS electrode at high current densities of 500 mA g^{-1} (200 cycles) and 10 A g^{-1} . Note: all the specific capacities were calculated based on the total mass of the composites; Spec. capacity stands for specific capacity; Vol. capacity stands for volumetric capacity.

Figure 3.17. Cyclic voltammetry (CV) of the (a) PG-SPS and (b) PG electrodes during the first 3 cycles at a scan rate of 0.1 mV s^{-1} .

lower exposed specific surface area (SSA) as well as fast electron kinetics from the good electrical connection between the few-layer BP and rGO of the densely packed PG-SPS.

The rate capability of the as-prepared PG-SPS and PG electrodes (**Figure 3.16d**) was investigated at various current densities. For the PG-SPS electrode, a high reversible capacity of $1013.3 \text{ mAh g}^{-1}$ is obtained at a current density of 100 mA g^{-1} . When the current densities are increased, specific capacities of 909.1 mAh g^{-1} (89.7 %) at 200 mA g^{-1} , 821.4 mAh g^{-1} (73.8 %) at 500 mA g^{-1} , 726.1 mAh g^{-1} (65.2 %) at 1 A g^{-1} , 639.8 mAh g^{-1} (57.5 %) at 2 A g^{-1} , 519.6 mAh g^{-1} (46.7 %) at 5 A g^{-1} , 415.0 mAh g^{-1} (37.3 %) at 10 A g^{-1} can be retained, implying the excellent rate capabilities of the PG-SPS electrode. When the current density returns to 100 mA g^{-1} , a specific capacity of 919.9 mAh g^{-1} can still be achieved. As a comparison, PG electrode shows relatively lower specific capacities of 820 mAh g^{-1} , 685.3 mAh g^{-1} , 578.4 mAh g^{-1} , 497 mAh g^{-1} , 433 mAh g^{-1} , 355.9 mAh g^{-1}

g^{-1} , 287.9 mAh g^{-1} at corresponding current densities, respectively. The cycling performance of the samples at a current density of 100 mA g^{-1}

Figure 3.18. Cycling life of PG and PG-SPS electrodes based on specific capacities at a current density of 100 mA g^{-1} .

mA g^{-1} is shown in **Figure 3.18**. The PG-SPS electrode can deliver a specific capacity of 870 mAh g^{-1} after 50 cycles, while a lower specific capacity of 620 mAh g^{-1} is retained for the PG electrode. When the gravimetric capacities are converted to volumetric capacities (**Figure 3.16e**), the amount delivered by PG-SPS electrode ($170.8 \text{ mAh cm}^{-3}$) was 2.7 times that of the loosely stacked PG electrode (63.5 mAh cm^{-3}) after 50 cycles at 100 mA g^{-1} . In addition, a specific capacity of 725 mAh g^{-1} (82.4 % retention) over 200 cycles at 500 mA g^{-1} and a specific capacity of 432 mAh g^{-1} (91.9 % retention) at a very high current density of 10 A g^{-1} over 800 cycles can be achieved by PG-SPS electrode, as shown in **Figure 3.16f**. The excellent cycling performance of PG-SPS electrode can be

ascribed to the strong C-P-C-P-C atoms bonding among the densely packed architecture, which effectively restrains the few-layer BP from aggregation and ensures the ultrahigh electron pathway during cycling process.

To further investigate the effect of BP degradation on electrochemical activities, both PG-SPS exposed to ambient conditions for 60 days and PG for 10 days were tested as anode materials of LIBs. Their rate capabilities are evaluated at various current densities, as shown in **Figure 3.19a**. Exposed PG-SPS electrode still exhibits high specific capacities of 896.1 mAh g⁻¹ at 100 mA g⁻¹, 812.3 mAh g⁻¹ (90.6 %) at 200 mA g⁻¹, 729.3 mAh g⁻¹ (81.3 %) at 500 mA g⁻¹, 673.0 mAh g⁻¹ (75.1 %) at 1 A g⁻¹, 616.3 mAh g⁻¹ (68.8 %) at 2 A g⁻¹, 537.3 mAh g⁻¹ (59.9 %) at 5 A g⁻¹, 469.8 mAh g⁻¹ (52.4 %) at 10 A g⁻¹ and returns to 823.4 mAh g⁻¹ at 100 mA g⁻¹, respectively. In contrast, exposed PG electrode shows significant reduction in specific capacities, e.g., 472.7 mAh g⁻¹ at 100

Figure 3.19. Electrochemical characterization of exposed PG-SPS and PG electrodes. a) Rate capabilities of PG (exposed) and PG-SPS (exposed) electrodes at various current densities. b) Cycling life of PG after exposure for 10 days and PG-SPS after exposure for 60 days at a current density of 100 mA g⁻¹. c) Electrochemical impedance spectra (EIS) measured at the third fully discharged state and corresponding fitted equivalent circuit model (inset). R_s = bulk resistance, R_{ct} = charge transfer resistance, CPE1 = constant phase element, and W_o = Warburg impedance.

mA g⁻¹, 304.9 mAh g⁻¹ at 500 mA g⁻¹, 122.3 mAh g⁻¹ at 10 A g⁻¹ and returns to 365.0 mAh g⁻¹ at 100 mA g⁻¹. Furthermore, as shown in Figure 3.19b, the specific capacity of PG-SPS electrode drops slightly to 823 mAh g⁻¹ after 50 cycles at 100 mA g⁻¹ compared to that of as-prepared PG-SPS electrode (870 mAh g⁻¹), while only 357mAh g⁻¹ is retained at 100 mA g⁻¹ during the 50th cycle for PG electrode after exposed to the ambience for 10 days. To understand the mechanisms behind different degradation of the activities, electrochemical impedance spectra (EIS) measurements were performed at the third fully discharged state. As shown in Figure 3.19c, the semicircle in the high-middle frequency range represents the charge transfer resistance (R_{ct}) between the electrolyte and the electrodes and the low frequency line stands for the Warburg resistance (W_o) related to the Li ion diffusion in electrode materials. According to the fitted equivalent circuit in the inset of Figure 3.19c, the R_{ct} of the as-prepared PG-SPS (61 Ω), exposed PG-SPS (67 Ω), as-prepared PG (85 Ω) and exposed PG (129 Ω) electrodes can be obtained. It indicates that the as-prepared PG-SPS possesses lower resistance than the as-prepared PG and thus allows for much faster charge transfer, which originates from the conductive graphene matrix as well as stronger interaction between BP and rGO among the PG-SPS sample. After exposure to ambient conditions, the R_{ct} of PG-SPS shows little increase from 61 Ω to 67 Ω , while the R_{ct} of PG samples increases from 85 Ω to 129 Ω . Based on the analyses above, we can conclude that severe degradation of BP significantly affects the electron transfer kinetics, leading to inferior electrochemical properties.

3.4 Conclusion

In this work, phosphorene with a high yield (38 %) can be prepared using an appropriate solvent— formamide, which is higher than several other commonly used molecules, including NMP, DMF, IPA. In addition, the obtained phosphorene shows high quality with good crystallinity as well as tunable size distributions. It can be stabilized in formamide for hundreds of hours without noticeable degradation. Furthermore, a densely packed phosphorene-graphene composite (PG-SPS) was prepared using simple and up-scalable spark plasma sintering (SPS) process. It possesses a high packing density of 0.6 g cm^{-3} , which is beneficial for improve the volumetric capacity when working as anode materials of LIBs. In addition, excellent air stability can be achieved due to effectively suppressing the permeation of water or oxygen molecules into the PG-SPS sample. When it was explored as the anode materials of LIBs, PG-SPS electrode shows a much improved first-cycle CE of 60.2 % due to the reduced exposed surface and good electrical connection between rGO and BP as compared to those of few-layer BP (only 11.5 %) and the loosely stacked PG (34.3 %) electrodes. Moreover, high gravimetric capacity ($1306.7 \text{ mAh g}^{-1}$) and volumetric capacity ($256.4 \text{ mAh cm}^{-3}$), good rate capabilities (e.g., 415.0 mAh g^{-1} at 10 A g^{-1}) and excellent cycling performance (91.9 % retention after 800 cycles at 10 A g^{-1}) were achieved in the PG-SPS electrode. After exposure to ambient conditions for 60 days, the specific capacity of PG-SPS electrode drops slightly to 823 mAh g^{-1} after 50 cycles at 100 mA g^{-1} . In contrast, the PG electrode exhibits severe degradation of specific capacity (353 mAh g^{-1} during the 50th

cycle at 100 mA g^{-1}) after exposure to the ambience for only 10 days compared to that of as-prepared PG (620 mAh g^{-1}). Our findings may open up new strategies towards the development of phosphorene as advanced electrode materials.

Chapter 4 Functionalized Few-layer Black Phosphorus with Super-Wettability towards Enhanced Reaction Kinetics for Rechargeable Batteries

In this chapter, nanoscale surface engineering of few-layer BP is performed by homogeneously depositing horizontally aligned Poly(3,4-ethylenedioxythiophene) (PEDOT) nanofibers on specially surface-modified BP nanosheets. Such material design could achieve simultaneously: (1) enhanced charge transfer kinetics and (2) super surface wettability with electrolyte. Benefiting from the unique functionalization, the reaction kinetics are greatly enhanced accordingly for both sodium and lithium storage.

4.1 Introduction

Sodium-ion batteries (SIBs) as an alternative energy storage system to lithium-ion batteries (LIBs) have prompted extensive research interest due to the global abundance of sodium source.²²⁷⁻²³² Currently, the major challenge for practical applications of SIBs is their low energy storage performance, which can be improved by developing robust electrode materials with high specific capacity and long cycling life.²³³⁻²⁴⁰ The direct adapting of LIBs electrodes, in particular anodes, to SIBs turns out to be unsuccessful. For example, graphite, the commonly used anode for LIBs, has been reported as an unsuitable anode for the SIBs system due to that it is difficult to form compounds with Na.²⁴¹⁻²⁴³ Furthermore, silicon (theoretical capacity of 4200 mAh g⁻¹ for LIBs) is also

electrochemically inactive to Na storage despite the theoretical existence of Si-Na alloys.¹⁷² Therefore, the development of advanced anode materials remains a major issue hindering the practical applications of SIBs. Recently, black phosphorus (BP) has attracted great attention in many fields including field-effect transistors,^{3, 244} photodetectors,^{7, 245} and batteries.^{128, 156, 246} Ever-increasing studies have been focused on few-layer BP working as a promising anode for SIBs, primarily due to: (1) high gravimetric capacity of 2596 mAh g⁻¹,²⁴⁷⁻²⁴⁸ which is currently the highest one among the available anode materials for SIBs; (2) layered orthorhombic crystal structure with a larger interlayer channel size (3.08 Å),¹²⁹ (3) ultrafast Na ions diffusion along the zigzag direction ensuring high rate capability;^{52, 249-250} and (4) the natural abundance of P.^{175, 251}

In reality, there might be concerns on lacking of scalable synthesis approach of BP and their operation safety when considered for high-energy-density batteries. The commonly adapted chemical vapor transport (CVT) deposition process⁹⁹⁻¹⁰² has a maximum yield of BP crystals of only about 0.5 g, which is too low. However, the recently reported high-energy ball-milling process, using commercial red phosphorus as precursor, has been demonstrated to prepare BP powders successfully,⁹⁴⁻⁹⁸ which indicate that BP may be prepared with a simple and potentially scalable process with low cost. For the concern on the operation safety of BP, it is mainly related to the concern on the flammability of phosphorus materials. Actually, only white phosphorus is known for their high flammability in air. Red phosphorus and black phosphorus are much stable. According to our study, the black phosphorus is stable up to 405 °C under N₂ atmosphere without

any detected chemical reaction (**Figure 4.1**). This indicates that the BP could be considered for application of high energy-density-battery with proper package and sealing process.

Figure 4.1. Thermogravimetric analysis (TGA) and the corresponding differential thermal analysis (DTA) of black phosphorus under nitrogen atmosphere.

However, for battery electrode application, BP exhibits large volume change (up to 300% upon cycling) and slow reaction kinetics during sodiation/desodiation process, leading to poor cycling stability and low reversible capacity.^{112, 172} Recently, exciting progress has been made through combining nanostructured BP with carbonaceous materials, which significantly enhances the Na storage properties.^{155, 158, 252} A graphene/phosphorene hybrid with an optimized phosphorene loading of 43.8 wt % exhibits good cycle stability and high rate capability.¹⁷² Another BP/graphite composite prepared through ball

milling of red P and graphite mixture could also deliver a high initial capacity of $\sim 1300 \text{ mAh g}^{-1}$, but rapidly decayed to 200 mAh g^{-1} after only 30 cycles.²⁵³ For such BP/C composite, the delivered capacity calculated based on the overall mass of the whole anodes is still not very competitive because of the large portion of low-capacity carbonaceous materials incorporated. Therefore, other strategies are necessary to be developed to explore the potentials of BP as a high-capacity and durable anode for SIBs.

The architecture of electrode materials and the interfacial reactions between electrodes and electrolytes is very important for the electrochemical performances of rechargeable batteries.²⁵⁴⁻²⁵⁵ Herein, we demonstrate the nanoscale surface engineering of exfoliated few-layer black phosphorus (labelled as E-BP), which is performed by homogeneous deposition of horizontally aligned PEDOT nanofibers on surface-modified BP nanosheets. The PEDOT nanofibers on BP nanosheets ensure a continuous conductive network as well as super-wettability with electrolyte. Accordingly, the purposely engineered E-BP/PEDOT architecture exhibits significantly enhanced reversible specific capacities (1597 mAh g^{-1} for SIBs and 1631 mAh g^{-1} for LIBs) compared to that of E-BP electrode (345 mAh g^{-1} for SIBs and 210 mAh g^{-1} for LIBs). As a result, it largely outperforms the E-BP/graphene composites with a 2.7 times higher specific capacity after 100 cycles. Our results may afford an effective strategy to develop advanced electrode for SIBs.

4.2 Experimental Section

4.2.1 Materials

Black phosphorus (BP) crystals (~99.998%) were purchased from smart-element. Dimethylformamide (DMF, 99.8%, anhydrous), ethanol (99.9 %, anhydrous), 3,4-Ethylenedioxythiophene (EDOT, 97%), D-(+)-Glucose ($\geq 99.5\%$) and ferric chloride (FeCl_3 , $\geq 99.99\%$, anhydrous) were purchased from Sigma. All the materials were used as received without any further purification.

4.2.2 Preparation of E-BP

20 mg of BP crystals were ground with the mortar and pestle in 1.5 ml of DMF for 20 mins. Then the mixture was transferred to a glass vial containing 30 mL of DMF solution. After bubbled with argon for 30 mins and careful sealing with parafilm, the vials were sonicated at in ice bath for 4h with the power of 200 W. After sonication, the mixture was centrifuged at 2000 rpm for 15 mins to remove aggregates. Finally, exfoliated BP (E-BP) nanosheets were collected by centrifugation at 8000 rpm for 30 mins.

4.2.3 Preparation of H/E-BP

The as-obtained E-BP was further dispersed in 20 ml of DMF, following by adding 40 mg of D-(+)-Glucose. Then the solution was bubbled with argon for 30 mins, and then transferred into 23 ml of Teflon lined stainless steel autoclaves and kept in the electric oven at 180 °C for 3 h. After cooling down to room temperature naturally, the product was washed with ethanol for several times.

4.2.4 Preparation of E-BP/PEDOT

The as-obtained H/E-BP was dispersed into 20 ml of 100 % ethanol by sonication. 53.24 mg (40 μ L) of EDOT was added into the above solution, followed by stirring for 15 mins. Then 270 mg of FeCl_3 dissolved into 10 ml ethanol was introduced into it. The final solution was first kept fast stirring (2000 rpm) for 5 mins and then slow stirring (400 rpm) for 40 mins and the products were collected after washing by ethanol for several times.

For preparation of E-BP/PEDOT*, 26.62 mg (20 μ L) of EDOT and 135 mg of FeCl_3 were used and other steps are same with the procedure of preparing E-BP/PEDOT.

For preparation of E-BP/PEDOT**, 106.48 mg (80 μ L) of EDOT and 540 mg of FeCl_3 were used and other steps are same with the procedure of preparing E-BP/PEDOT.

4.2.5 Method of Determining the Mass Percentage of P in E-BP/PEDOT

It is claimed that high portion of conductive carbon materials in the BP-carbon composites will reduce the specific capacities based on the whole mass of the electrode. Therefore, it is necessary to determine the mass percentage of BP in the architecture of E-BP/PEDOT. The method is as follows.

The E-BP/PEDOT sample (weight: W_1) was dispersed into the nitric acid (20ml, 5 mol/L). After stirring for 3h, the solution became almost clear due to the complete dissolval of BP. Then, the residue (supposed to be the mixture of

amorphous carbon and PEDOT) was collected by centrifuging and washing by ethanol at 14000 rpm for several times. After drying process, the weight of residue was determined as W_2 . Therefore, the portion of E-BP in E-BP/PEDOT was calculated as: $(W_1 - W_2)/W_1$.

Using the method above, the mass percentage of E-BP in E-BP/PEDOT*, E-BP/PEDOT and E-BP/PEDOT** was determined as 94%, 90.2% and 83%, respectively.

4.2.6 Preparation of PEDOT

40 μ L of EDOT was added into 20 ml of 100 % ethanol followed by stirring for 15 mins. Then 270 mg FeCl_3 dissolved into 10 ml ethanol was introduced into it. The final solution was first kept fast stirring (2000 rpm) for 5 mins and then kept slow stirring (400 rpm) for 40 mins and the products were collected after washing by ethanol for several times.

4.2.7 Structural Characterizations

SEM images were obtained using a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F). X-ray diffraction (XRD) measurement was performed on a Shimadzu XRD-600 with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15404$ nm) operated at 40 kV and 30 mA. TEM images were obtained using JEOL-2100F at an acceleration voltage of 200 kV. Raman spectra were measured by using a 532 nm micro-Raman spectrometer (Witec CRM200) with 2400 lines/mm grating. The Raman band of a silicon wafer at 520 cm^{-1} was used as a

reference. AFM images were obtained using Asylum Research Cypher S. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Theta Probe electron spectrometer (VG ESCALAB200i-XL, Thermo Scientific).

4.2.8 Electrochemical Measurements

Electrodes was prepared by mixing 70 wt% active materials with 20 wt% single-walled carbon nanotubes (SWCNT) and 10 wt% polyvinylidene fluoride (PVDF) as the binder to form a slurry. Then the slurry was coated onto a copper foil and dried at 50 °C for 12 h under vacuum. The mass loading is about 1mg cm⁻² and the thickness of the electrode without a current collector was ~11.6 μm. The coin cells (2032) were assembled in an argon-filled glovebox with concentrations of moisture and oxygen below 0.1 ppm, using sodium/lithium metal as the counter/reference electrode, a Whatman GF/D microfiber filter paper as the separator, and 1 M NaClO₄ dissolved in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was used as SIBs electrolyte and the 1 M LiPF₆ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1/1 v/v) as LIBs electrolyte. The charge-discharge tests were performed with a LAND battery tester in a voltage window of 0.01-3.0 V. Cyclic voltammetry (0.01-3.0V, 0.1 mV s⁻¹) and Electrochemical impedance spectroscopy (EIS) were performed on a Bio-Logic SP-150 potentiostat in a frequency range of 1 MHz–0.01 Hz with an AC amplitude of 10 mV.

4.3 Results and Discussion

The overall synthetic procedure of E-BP/PEDOT ultrathin nanosheets involves four steps as illustrated in **Scheme 4.1** (for details see the Experimental Section). Briefly, E-BP was prepared *via* sonication of BP single crystals in dimethylformamide (DMF). Subsequently, hydroxyl groups were introduced onto the surface of BP nanosheets by mild hydrothermal carbonization of glucose, during which glucose became amorphous carbon with oxygen containing functional groups and coated onto the surface of BP nanosheets. The

Scheme 4.1. Preparation steps of E-BP/PEDOT architectures. (1) Fabricating few-layer BP nanosheets (E-BP) *via* liquid-phase sonication of bulk BP crystal in dimethylformamide (DMF). (2) Introducing conformal hydroxyl groups on BP nanosheets *via* polymerization of glucose through hydrothermal reaction. (3) Absorbing EDOT molecules on the hydroxyl groups *via* hydrogen bonding. (4) *In-situ* growth of PEDOT fibers on surface modified BP nanosheets at room temperature.

as-obtained product is labelled as H/E-BP. The H/E-BP nanosheets with modified surface were then used to adsorb 3,4-ethylenedioxythiophene (EDOT) molecules *via* hydrogen bonding between the hydroxyl groups and the oxygen in EDOT

molecules. Finally, PEDOT nanofibers were deposited on H/E-BP nanosheets (labelled as E-BP/PEDOT) *via in-situ* polymerization of EDOT in ethanol solution under ambient conditions.

The as-prepared E-BP nanosheets were first examined by atomic force microscopy (AFM) measurement, as shown in Figure 4.2a. The topographic heights (Figure 4.3) are 2.7~6.2 nm, corresponding to 5 ~12 layers of BP. The crystal structure of the E-BP nanosheets was verified by the X-ray diffraction (XRD) pattern (Figure 4.4a). Three diffraction peaks at $2\theta = 16.9^\circ$, 34.2° , and 52.4° can be indexed to the (002), (004), and (006) planes of BP (JCPDS No. 76-1957), respectively. A representative transmission electron microscopy (TEM) image (Figure 4.4b) exhibits transparent feature of the nanosheets, indicating the ultrathin sheet characteristic of the as-obtained E-BP. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Figure 4.2b) and corresponding fast Fourier transform (FFT) pattern (the inset of Figure 4.2b) of E-BP nanosheets present a well-defined structure with lattice fringe spacings of 0.256 and 0.225 nm, which can be assigned to the (111) and (014) planes of orthorhombic black phosphorus, respectively. Three prominent peaks at 363.6 , 441.5 and 468.2 cm^{-1} can be observed in Raman spectroscopy (Figure 4.4c), corresponding to the A_g^1 (out-of-plane), B_g^2 and A_g^2 (in-plane) modes, respectively, which are in good accordance with previous observations for BP nanosheets.¹²⁹

Figure 4.2. Characterizations of E-BP and H/E-BP. a) Representative AFM image of E-BP obtained after exfoliation and centrifugation. b) HADDF-STEM image of E-BP (the insets are corresponding FFT pattern). c-d) TEM and HRTEM images of the H/E-BP.

After surface modification of E-BP, the as-obtained H/E-BP nanosheets exhibit smooth and well-preserved sheet morphology, as revealed in the typical TEM image (**Figure 4.2c**). The high-resolution TEM (HRTEM) image (**Figure 4.2d**) demonstrates the ultrathin amorphous carbon coating (ca. 1.5 nm in thickness) on BP nanosheets, as indicated by the red dash line. The Raman spectrum confirm the existence of amorphous carbon with the signatures of D band (1350 cm^{-1}) and G band (1590 cm^{-1}),¹⁰⁰ as shown in **Figure 4.5**.

Figure 4.3. AFM height profiles of the E-BP.

Figure 4.4. a) XRD pattern, b) typical TEM image, and c) Raman spectrum of the E-BP.

In addition, the peak centered at 693 cm^{-1} could be ascribed to the P-C bond stretching modes, which forms during the hydrothermal carbonization of glucose onto the BP surface. The peak of P-C bond in the raman spectrum is consistent with the previous experimental report⁶⁵ and theoretical calculations.²⁵⁶⁻²⁵⁷ Furthermore, a clear lattice spacing of 0.22 nm shown in the core region corresponds to the (014) planes of BP (JSPDS No. 76-1957), revealing the

persisted crystallinity of H/E-BP. To investigate the surface modification, Fourier transform infrared (FTIR) spectroscopy was carried out on H/E-BP and E-BP. As shown in **Figure 4.6**, the broad peak located at 1050 cm^{-1} can be attributed to the C-O bond stretching as a characteristic one of C-OH, which provides the evidence of successful surface modification with hydroxyl groups.

The H/E-BP functionalized with surface hydroxyl group is demonstrated to be effective to adsorb EDOT *via* hydrogen bonding. Thus, PEDOT nanofibers were successfully grown on the H/E-BP nanosheets by *in situ* polymerization of EDOT (weight: 53.24mg). As revealed in the TEM images (**Figure 4.7a** and the inset), those PEDOT fibers grown on the BP nanosheets

Figure 4.5. Raman spectrum of the H/E-BP. The inset presents the high-resolution Raman spectrum ranging from 1200 to 1700 cm^{-1} .

have diameters of 4-8 nm and an average length of ~ 100 nm. The content of PEDOT can also be controlled by adjusting the ratio between the amount of BP

and the amount of PEDOT molecules (e.g., BP: EDOT = 20mg: 26.62mg; 20mg: 53.24mg; 20mg: 106.48mg) used during the synthesis. As shown in **Figure 4.8a**, a control sample was prepared with less PEDOT fibers grown on

Figure 4.6. Fourier transform infrared (FTIR) spectrum of the H/E-BP and E-BP.

H/E-BP (marked as E-BP/PEDOT*) by using 26.62 mg of EDOT. However, the PEDOT fibers will aggregate if using 106.48mg of EDOT during the synthesis, as marked by the dashed lines (**Figure 4.8b**) and the as-obtained sample was labeled as E-BP/PEDOT**. In addition, the mass percentage of BP for E-BP/PEDOT*, E-BP/PEDOT and E-BP/PEDOT** was determined to be 94%, 90.2% and 83%, respectively (the method can be seen in **4.2.5**). To further confirm the presence of PEDOT, FTIR spectroscopy (**Figure 4.7b**) was carried

Figure 4.7. Characterizations of E-BP/PEDOT architectures. a) TEM images of E-BP/PEDOT architecture. The inset is a high-magnification TEM image. b) FTIR spectroscopy profiles of E-BP/PEDOT architecture and PEDOT products. c) HRTEM images of E-BP/PEDOT. d) Representative dark-field STEM image and corresponding elemental mappings mapping of E-BP/PEDOT (the highlight is lacy carbon support from copper grid).

Figure 4.8. Typical TEM image of the (a) E-BP/PEDOT* and (b) E-BP/PEDOT**. The area marked by dashed line indicates the aggregated PEDOT.

out on the E-BP/PEDOT and pure PEDOT fibers (the TEM shown in **Figure 4.9**). The peaks located at 926.3, 1097, 1356 and 1520 cm^{-1} can be assigned to the C-S, C-O-C, C-C and C=C bond vibrations, respectively,²⁵⁸ which is well consistent with those peaks of the as-prepared pure PEDOT fibers. A clear lattice spacing of 0.22 nm in the HRTEM image (**Figure 4.7c**) corresponds to the (014) plane of BP, confirming the well-preserved crystallinity of BP nanosheets after deposition of PEDOT fibers. It is observed that the PEDOT fibers referred as the amorphous region are solidly anchored on the H/E-BP surface. Furthermore, the corresponding STEM elemental mappings (**Figure 4.7d**) demonstrate the distribution of P, C and S in a typical nanosheet, indicating the uniform distribution of the PEDOT fibers on the BP sheets. It should be noted that the presence of hydroxyl group plays a critical role for

Figure 4.9. TEM image of the pure PEDOT fibers.

uniform growth of PEDOT on the BP nanosheets. Without surface modification, PEDOT fibers will form separately and not be anchored on the BP nanosheets, as shown in **Figure 4.10**.

Figure 4.10. TEM image of the PEDOT fibers formed separately from E-BP.

In addition, X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the as-obtained E-BP/PEDOT. As shown in **Figure 4.11a**, the P2p spectrum exhibits the 2p_{3/2} and 2p_{1/2} doublet at 129.7 eV and 130.4 eV, which are the characteristics of the phosphorus-phosphorus bonds within BP. A peak at ~ 133.1 eV is also observed, suggesting the presence of oxidized phosphorus (i.e., PO_x, ca. 18 atomic %). This may be due to the unavoidable oxidation of BP nanosheets originating from its high sensitivity to water or oxygen.¹³⁶⁻¹³⁸ However, after exposure to ambient conditions (temperature 25 °C, humidity 75-80 %) for 7 days, 92.3 atomic % of phosphorus

in E-BP/PEDOT sample was oxidized (**Figure 4.11b**), indicating that further strategies are necessary to improve its air-stability.

Figure 4.11. P 2p core-level X-ray photoelectron spectroscopy (XPS) spectroscopy of the (a) fresh E-BP/PEDOT and (b) the one exposed in ambient conditions for 7 days.

The good wettability of electrodes with electrolytes has a pronounced impact on providing easy access of electrolyte and facilitating the diffusion of electrons/ions in the electrode. In contrast, inferior wetting property is detrimental to electrolyte permeation and hence limits the reversible reaction kinetics, resulting in unsatisfactory reversible capacity.²⁵⁹ To probe the effect of PEDOT on the wettability of BP nanosheets, the wetting properties of pure E-BP, H/E-BP, E-BP/PEDOT* and E-BP/PEDOT were studied. Their contact angles (CA) with liquid electrolyte (1M NaClO₄ dissolved in propylene carbonate) were measured and shown in **Figure 4.12**. As shown in **Figure 4.12a**, the E-BP electrode has a CA of about 27° with electrolyte after waiting for 1 min to reach the stable status. After surface modification, the CA of

Figure 4.12. Characterization of wetting properties. Optical images of contact angles between electrolyte and a) E-BP, b) H/E-BP, c) E-BP/PEDOT* (less PEDOT grown on BP nanosheets) and d) E-BP/PEDOT electrodes.

H/E-BP (**Figure 4.12b**) with the electrolyte slightly decreases to 22.5°. Importantly, the CA is significantly reduced after depositing PEDOT nanofibers on the H/E-BP nanosheets, suggesting the improved wettability with electrolyte. The CA value of E-BP/PEDOT* is determined to be 12.7° (**Figure 4.12c**). Notably, the electrolyte droplet spreads out completely on E-BP/PEDOT electrode within 3s (**Figure 4.12d**), indicating its super wettability with the electrolyte after reasonably tailoring the content of PEDOT. As described by Wenzel's equation,

$$\cos \theta' = r \cos \theta, \quad (1)$$

where θ' is the apparent CA on a rough surface, θ is the intrinsic CA on the flat surface, and r is the surface roughness, the cooperation between the surface chemical compositions and topographic structures is crucial to construct special wettability.²⁶⁰ Accordingly, the superior wettability of E-BP/PEDOT can be

attributed to the close polarity between hydroxyl groups and electrolyte as well as the properly horizontal arrangement of PEDOT fibers that enhance the surface roughness (r) of the nanosheets. The present results demonstrate that this smart surface engineering approach is very effective to create super-wettability for BP nanosheets and may be extended to modify other electrode materials.

To evaluate the sodium storage capability of the E-BP/PEDOT composite, cyclic voltammetry (CV) measurements were firstly performed on half cells in the potential window of 0.01-3 V versus Na/Na⁺ (**Figure 4.13b**) at a scan rate of 0.1 mV s⁻¹. As can be seen, the CV profile of E-BP/PEDOT composite electrode exhibits similar electrochemical characteristics with that of pristine BP nanosheets electrode (**Figure 4.13a**). Specifically, during the first cathodic process, a wide reduction peak is first observed between 0.9-1.3 V region. This is due to the irreversible process of the solid electrolyte interphase (SEI) formation. The intensity of this broad peak decays in the subsequent cycles. There is another peak located at 0.54 V, which could be associated with sodiation process to form the Na_xP phases. During the reverse anodic process, a small peak at 0.51 V and a well-defined one at 0.7 V are observed, which correspond to the desodiation process from the reduction product. In the following three cycles, three peaks including one at 0.12V during reduction and another two at 0.51 and 0.65V during oxidation remain, indicating the reversible desodiation/sodiation process. These observations are consistent with the previous report.¹⁷⁵ It has been studied that a Na₃P phase will be produced in the full reduction state by *ex situ* XRD for the sodiated electrode, confirming the three-electron reduction reaction

of BP as anodes for SIBs.¹⁸ Note that the E-BP/PEDOT electrode is amorphous after one cycle, as evidenced by *ex situ* XRD (Figure 4.14) with no obvious characteristic peaks from crystalline BP.

Figure 4.13. Electrochemical characterizations. a, b) CVs of the E-BP and E-BP/PEDOT electrodes for the first 4 cycles at a scan rate of 0.1 mV s⁻¹. c) The first galvanic charge/discharge measurements of E-BP, H/E-BP, E-BP/PEDOT* and E-BP/PEDOT electrodes at 100 mA g⁻¹. d) Rate capabilities of E-BP and E-BP/PEDOT electrodes at various current densities.

The first sodiation and desodiation profiles of E-BP, H/E-BP, E-BP/PEDOT* and E-BP/PEDOT electrodes are shown in Figure 4.13c. The initial discharge specific capacities of E-BP, H/E-BP, E-BP/PEDOT*, and E-BP/PEDOT electrodes are 2540, 2723.9, 2909, and 3100 mAh g⁻¹, respectively. During the charging process, E-BP, H/E-BP, E-BP/PEDOT*, and E-BP/PEDOT electrodes

exhibit reversible specific capacities of 342, 310, 1013, and 1597 mAh g⁻¹, respectively. Accordingly, the 1st-cycle coulombic efficiency (CE) is improved from 13.8 % for E-BP electrode to 34.8 % for E-BP/PEDOT* electrode and 51.5% for E-BP/PEDOT electrode. Note that the

Figure 4.14. *Ex situ* XRD patterns of the E-BP/PEDOT electrode taken before and after one discharging-charging cycle.

relatively lower initial CE of the H/E-BP electrode (11.4%) compared to that of pure E-BP (13.8%) electrode might be due to some irreversible reactions between the surface hydroxyl groups of H/E-BP and sodium. Importantly, the reversible capacity of E-BP/PEDOT (1597 mAh g⁻¹) is almost 4.6 times that of E-BP electrode (345 mAh g⁻¹), indicating the significant enhancement of reversible reaction kinetics after surface engineering. To probe the great improvement of initial and reversible specific capacity for E-BP/PEDOT, the E-BP and E-BP/PEDOT electrodes after first discharging process are characterized by SEM measurements. As shown in Figure 4.15a-b, both electrodes before discharge

show clear presence of nanosheets. After discharging to 0.01 V at 100 mA g^{-1} , no sheets can be observed in the E-BP electrode and cracks appear obviously due to the huge volume change (**Figure 4.15c**). On the contrary, nanosheets are still present in the E-BP/PEDOT

Figure 4.15. SEM images of the E-BP and E-BP/PEDOT electrodes (a, b) before and (c, d) after the discharging process.

electrode (**Figure 4.15d**) despite of some blur edges, which might be due to the SEI formation and the adhesion of organic electrolyte on the sheet surface. The much improved structural durability could be ascribed to the coated PEDOT nanofibers as a barrier to prevent the aggregation of sodiation product. For the E-BP electrode, the severe contact loss with the current collector due to crack generation hinders the desodiation reaction, resulting in lower reversible capacity

and thus poor initial CE was obtained. Therefore, the improved specific capacities and 1st-cycle CE for E-BP/PEDOT electrode can be ascribed to this special nanoscale design with conductive surface network and super wettability, preserving the electrode structure and inducing fast sodiation/desodiation reaction.

The rate capabilities of both E-BP and E-BP/PEDOT electrodes for SIBs are also investigated at various current densities. As shown in **Figure 4.13d**, a low 5th-cycle discharge capacity of 201 mAh g⁻¹ for E-BP electrode is obtained at a current density of 100 mA g⁻¹. The capacity decreases obviously at increased current densities. The specific capacities change to 104.5 and 54.2 mAh g⁻¹ at 200 and 500 mA g⁻¹, respectively. And only 13.1 mA g⁻¹ is delivered at 10 A g⁻¹, indicating poor rate capability of pristine E-BP as anodes for SIBs. On the contrary, for E-BP/PEDOT, a high 5th-cycle discharge capacity of 1397 mAh g⁻¹ can be obtained at a current density of 100 mA g⁻¹. Notably, high specific capacities of 1250 mAh g⁻¹ (a capacity retention of 89.7 %) at 200 mA g⁻¹, 1000 mAh g⁻¹ (71.6 %) at 500 mA g⁻¹, 750 mAh g⁻¹ (53.7 %) at 1 A g⁻¹, 700 mAh g⁻¹ (50.1 %) at 2 A g⁻¹, 450 mAh g⁻¹ (32.2 %) at 5 A g⁻¹, and 370 mAh g⁻¹ (26.5 %) at 10 A g⁻¹ can be delivered. When the current density returns to 100 mA g⁻¹, a specific capacity of 1048 mAh g⁻¹ can still be obtained, implying the excellent reversible Na storage properties of the E-BP/PEDOT electrode.

Figure 4.16. a) Galvanostatic intermittent titration technique (GITT) profile of the E-BP and E-BP/PEDOT electrodes in the second cycle. Low current density of 50 mA g⁻¹ (~ C/50 rate) was applied for 1 h and followed by resting the cell for 4 h to reach the quasi-equilibrium state. b) Overpotential (η) values estimated from the GITT results for the 2nd cycle of E-BP and E-BP/PEDOT electrodes. c) EIS measured at the third fully charged state and corresponding fitted equivalent circuit model (inset). R_s , bulk resistance; R_{ct} , charge transfer resistance; CPE1, constant phase element; and W_0 , Warburg impedance. d) Cycling life of E-BP/PEDOT and E-BP/graphene hybrids electrodes with different ratios at 100 mA g⁻¹.

To further verify the improved electrochemical performances of E-BP/PEDOT compared to bare E-BP nanosheets for SIBs, galvanostatic intermittent titration technique (GITT) measurements were conducted by passing a low current density of 50 mA g⁻¹ (~ C/50 rate) for 1 h and resting the cell for 4 h to reach the quasi-equilibrium state. The potential response of both electrodes during 2nd-cycle GITT measurement was obtained as shown in the **Figure 4.16a**. Overpotential (η) values (**Figure 4.16b**) for the 2nd cycle of E-BP and E-

BP/PEDOT electrodes are estimated from the GITT results by determining the difference between the cut-off voltage and the open circuit voltage measured after 4 h relaxation. It is found that the overpotentials of E-BP and E-BP/PEDOT electrodes during the discharging process are 0.23 ± 0.05 V and 0.22 ± 0.09 V, respectively. However, the overpotentials of E-BP electrode rise fast during the charging process and finally reach its maximum of 1.07 V, which is almost 1.6 times that of E-BP/PEDOT electrode (0.66 V). The lower overpotential of E-BP/PEDOT suggests that the reaction kinetics was significantly accelerated. The electrochemical impedance spectra (EIS) were performed to further evidence the fast reaction kinetics of E-BP/PEDOT. As shown in **Figure 4.16c**, the semicircle in the high-middle frequency range represents the charge transfer resistance (R_{ct}) between the electrolyte and the electrodes and the low frequency line stands for the Warburg resistance (W_o) related to the Na ion diffusion inside the electrode materials. According to the fitted equivalent circuit in the inset of Figure 4.16c, the R_{ct} of E-BP/PEDOT (61 Ω) and E-BP (129 Ω) electrodes can be determined. It indicates that the E-BP/PEDOT possesses lower charge transfer resistance than the E-BP, which mainly originates from the conductive matrix as well as the super wettability of E-BP/PEDOT with the electrolyte.

One of the key features of the E-BP/PEDOT electrode is that a high reversible capacity can be delivered, which was usually realized by coupling BP with conductive carbon materials. Actually, the absolute specific capacity will be reduced due to the relatively low specific capacities of these carbon materials for SIBs. As discussed above, the high mass percentage of BP (90.2%) in E-

BP/PEDOT could be beneficial to achieve high specific capacity based on the overall weight of the whole electrode. To verify the advantages of E-BP/PEDOT as anodes for SIBs, the cycling performance of E-BP/PEDOT was carried out at a current density of 100 mA g^{-1} . As shown in **Figure 4.16d**, a high reversible specific capacity of 1600 mAh g^{-1} can be achieved for the E-

Figure 4.17. Cycling performance of the pure PEDOT electrode for SIBs at a current density of 100 mA g^{-1} .

BP/PEDOT. However, it fades to 1094 mAh g^{-1} after 20 cycles, which could be ascribed to the large volume change of BP during sodiation/desodiation process. After 30 cycles, the discharge capacity became stable and maintained to be 1078 mAh g^{-1} during the 100th cycle. In addition, the cycling performance of the pure PEDOT electrode for SIBs was also studied. As shown in **Figure 4.17**, a specific capacity of 72 mAh g^{-1} was achieved for PEDOT during the 200th cycle at 100 mA g^{-1} . For comparison, we investigated the cycling performance of BP nanosheets-graphene hybrids with various G/P (graphene/BP nanosheets) ratios.

It is found that sample with a high G/P ratio can achieve good cycling stability, given that graphene can effectively increase the conductivity of the electrode. However, based on the overall mass of the electrode, the sample containing 75 % graphene depicts a specific capacity of 289 mAh g^{-1} (based on the overall weight of the whole electrode) after 100 cycles, which is much lower than that of E-BP/PEDOT. The Na storage properties of pure graphene is also evaluated and shown in **Figure 4.18**. It is seen that a specific capacity of 206 mAh g^{-1} can be achieved at 100 mA g^{-1} over 100 cycles, which is much lower than the theoretical capacity of BP. Thus, high percent of graphene incorporated in BP-based composites will largely reduce the specific capacity based on the overall mass of the electrode. Therefore, the outstanding Na storage properties of the E-BP/PEDOT electrode demonstrate the favorable features of this smart surface engineering approach.

The lithium storage ability of E-BP/PEDOT electrodes was also evaluated *via* coin-type half cells with Li metal as counter electrode. As shown in the first-cycle galvanostatic charge-discharge profiles of E-BP and E-BP/PEDOT electrodes (**Figure 4.19a**), the initial reversible specific capacities of E-BP and E-BP/PEDOT electrodes are 210 and 1631 mAh g^{-1} with CEs of 11.4% and 51%, respectively. In addition, their rate capabilities were also evaluated at various current densities. As shown in **Figure 4.19b**, E-BP electrode exhibits 100 mAh g^{-1} at 100 mA g^{-1} , 51 mAh g^{-1} at 200 mA g^{-1} , 30.5 mAh g^{-1} at 500 mA g^{-1} , 15.7 mAh g^{-1} at 10 A g^{-1} and finally returns to 63 mAh g^{-1} at 100 mA g^{-1} . Therefore,

the low specific capacities of E-BP electrode at different current densities reveal its poor rate capabilities. On the contrary, E-BP/PEDOT

Figure 4.18. Cycling performance of the pure graphene electrode for SIBs at a current density of 100 mA g^{-1} .

electrode exhibits excellent rate capabilities for LIBs (**Figure 4.19b**) with high specific capacities of 1408 mAh g^{-1} at 100 mA g^{-1} , 1080 mAh g^{-1} at 200 mA g^{-1} , 872 mAh g^{-1} at 500 mA g^{-1} , 751 mAh g^{-1} at 1 A g^{-1} , 652 mAh g^{-1} at 2 A g^{-1} , 512 mAh g^{-1} at 5 A g^{-1} and 434 mAh g^{-1} at a high current density of 10 A g^{-1} . When the current density returns to 100 mA g^{-1} , a high specific capacity of 1043 mAh g^{-1} can still be achieved, indicating its excellent rate capability. Furthermore, good cycling performance of E-BP/PEDOT electrode can also be obtained with a high specific capacity of 1092 mAh g^{-1} after 100 cycles at 100 mA g^{-1} , as shown in **Figure 4.19c**. However, for E-BP electrode, only a specific capacity of 46.7 mAh g^{-1} is achieved after 100 cycles at 100 mA g^{-1} .

Figure 4.19. Electrochemical activities of LIBs. a) The first-cycle galvanic charge/discharge profiles of the E-BP/PEDOT and E-BP electrodes at 100 mA g^{-1} . b) Rate capabilities of the E-BP/PEDOT and E-BP electrodes at various current densities. c) Cycling performance of the E-BP/PEDOT and E-BP electrodes and their corresponding CEs at 100 mA g^{-1} .

4.4 Conclusion

In summary, we prepared the E-BP/PEDOT composites *via in situ* polymerization of EDOT molecules on the surface of few-layer BP, which achieves simultaneously enhanced charge transfer kinetics and super wettability towards electrolyte. Accordingly, high reversible specific capacities as well as excellent rate capabilities can be achieved when E-BP/PEDOT is tested as anodes for SIBs and LIBs. Due to the high mass percentage of the BP in the sample, the Na storage properties of E-BP/PEDOT outperform that of the E-BP/graphene composites based on the overall mass of whole electrodes. Our encouraging

results may inspire an effective nanoscale surface engineering strategy towards advanced electrode for rechargeable batteries.

Chapter 5 0D–2D Ni₂P Nanocrystals–Black Phosphorus Heterostructure

In this chapter, zero-dimensional (0D) transition metal phosphides (TMPs) nanocrystals (NCs)–two-dimensional (2D) ultrathin black phosphorus (BP) heterostructure (Ni₂P@BP) has been synthesized via a facile sonication-assisted exfoliation followed by a solvothermal process. Compared with the bare BP, the specially designed Ni₂P@BP architecture shows enhanced electrical conductivity. As a result, the Ni₂P@BP exhibits excellent Li storage properties, such as improved Li diffusion kinetics and prolonged cyclability.

5.1 Introduction

Phosphorene, monolayer or few-layer black phosphorus (BP), is an emerging class of two-dimensional (2D) materials that is well-known for its intriguing physical and chemical properties, such as high mobility, tunable direct band gap, large field effect transistors (FET) on-off ratios, and in-plane highly anisotropic behaviours.^{61, 261-269} Nevertheless, further improvement of its functionality is needed to meet the dynamic demands of a wide range of applications, including FET, photodetectors, solar cells, sensors, energy storage and conversion devices.²⁷⁰⁻²⁷² For example, as a promising anode for reversible batteries, the performance of BP is still compromised owing to its relatively high volume change and sluggish reaction kinetics during charging and discharging process. Thus, continual effort in developing effective strategies to optimize the properties

of BP including its intrinsically charge carrier concentration and electrical conductivity could be the answer to fulfill the needs of specific applications. In this regard, integration of nanoscale building blocks into a composite provides a promising platform for rationally engineering artificial heterosystems with distinct properties in a controlled manner, which might establish itself as stronger contender in various fields.²⁷³⁻²⁸⁰

Recently, transition metal phosphides (TMPs) with high activity and conductivity have been considered as high performance electrode materials for Li-ion batteries (LIBs) or Na-ion batteries (NIBs).²⁸¹⁻²⁸⁵ Driven by the upward trend of nanotechnology, downsizing TMPs into zero-dimensional (0D) nanocrystals (NCs) has endowed them with large surface-to-volume ratio, large quantity of active sites and prominent edges. Owing to their high surface energy, the number of active surface is inevitably affected as the results of agglomeration. Moreover, the transport kinetics of charge carriers is greatly reduced in presence of increasing number of interfaces after TMPs NCs assemblies. As mentioned earlier, hybridization has been identified as a possible route to engineer the properties of heterostructures. Inspired by this concept, these and other problems can be circumvented by creating heterostructures of BP nanosheets and TMPs NCs is expected to bring about some advantageous features: (1) metallic TMPs NCs can inject electrons into BP nanosheets and effectively tune the charge carrier concentration while BPs nanosheets can provide long diffusion paths for charge carriers with less interface scattering, which is beneficial for increasing the electrical conductivities; (2) re-stacking of BP nanosheets can be prevented

after the deposition of TMPs NCs on the surface of BP nanosheets while agglomeration of TMPs NCs can be suppressed when they are anchored onto the BP nanosheets, which effectively maintains the high surface area and large number of active sites. However, such interesting heterostructures and their properties have not been well demonstrated.

In this work, we demonstrate a facile strategy to construct a 0D-2D heterostructure, Ni₂P NCs–BP nanosheets (denoted as Ni₂P@BP), study their electrical conductivities and investigate its properties the electrodes materials for LIBs. The heterostructure is synthesized by using BP nanosheets as precursor (exfoliated from the high-quality BP single crystals) to react with NiCl₂, resulting in Ni₂P NCs homogeneously embedded in the BP nanosheets. In such a heterostructure, the 2D morphology of BP nanosheets is well maintained the 2D morphology and Ni₂P NCs display an average diameter of ~ 5 nm. The effective charge carrier concentration increases from $1.25 \times 10^{17} \text{ cm}^{-3}$ for the pure BP nanosheets to $1.37 \times 10^{20} \text{ cm}^{-3}$ for the Ni₂P@BP heterostructure. As a result, the electrical conductivity is enhanced from 2.12×10^2 to $6.25 \times 10^4 \text{ S m}^{-1}$ at 300 K. The above properties were measured in a pellet sample prepared by spark plasma sintering (SPS) of either pure BP nanosheets or Ni₂P@BP heterostructure. As a demonstration of its viability, the Ni₂P@BP was tested as electrode materials for LIBs. The Ni₂P@BP shows much improved Li storage properties versus the bare BP, such as high reversible capacities (1196.3 mAh g⁻¹ at 0.1 A g⁻¹; about 4 times higher than that of the pure BP nanosheets), good rate capabilities (322.0 mAh g⁻¹ at 10 A g⁻¹) and outstanding long-term cycling performance of 743.7 mAh g⁻¹

¹ (94.1 % capacity retention) after 1000 cycles at 1 A g⁻¹.

Scheme 5.1. Schematic illustration for the synthesis process of the Ni₂P@BP heterostructure: (1) chemical vapor transport deposition process; (2) liquid exfoliation; and (3) solvothermal synthesis with NiCl₂.

5.2 Experimental Section

5.2.1 Materials

Red phosphorus (P, Sigma-Aldrich), tin (Sn, Sigma-Aldrich), stannic iodide (SnI₄, Sigma-Aldrich), nickel chloride (NiCl₂, Sigma-Aldrich), nickel phosphide (Ni₂P, 98%, Sigma-Aldrich), dimethylformamide (DMF, 99.8%, anhydrous), polyvinylidene fluoride (PVDF), N-methyl pyrrolidone (Sigma-Aldrich), absolute ethyl alcohol, sulfuric acid (H₂SO₄, 98%), Nafion solution (5 wt% in deionized water, Sigma-Aldrich), Li ions battery electrolyte (Chasrlton Technologies Pte Ltd., Singapore), Li and copper foil (ACME Research Support

Pte Ltd, Singapore), polypropylene (PP) film (Celgard 2300, North Carolina, USA), were used as received without further purification. The high-purity deionized water was purified using the Milli-Q system (Millipore, Billerica, MA, USA).

5.2.2 Vapor Transport Deposition Process of Bulk BP Crystals

Bulk BP crystals were prepared through a facile low-pressure transport route according to the literature.²⁸⁶⁻²⁸⁷ Briefly, 500 mg of bulk red phosphorus, 10 mg of SnI₄, and 20 mg of Sn were placed into a predried silica tube and then sealed under 10⁻⁴ Torr. The tube was heated to 873 K within 15 h and dwelled at that temperature for 8 h, and then was cooled down to 773 K in a period of 15 h. Eventually, the tube was cooled down to room temperature in 20 h. The layered black crystals were then collected and kept in a glovebox for further analysis.

5.2.3. Preparation of BP Nanosheets

The BP nanosheets were prepared by a liquid exfoliation of the as-synthesized bulk BP crystals. In detail, for the synthesis of few-layer BP nanosheets, 50 mg of the obtained bulk BP crystals were added into 2 mL of DMF in an agate mortar and then manually ground for 30 mins. Then the mixture was transferred in a bottle with 60 mL of DMF that bubbled with argon atmosphere about 10 mins to eliminate the dissolved oxygen molecules to prevent the bulk BP crystals from the oxidation. Next, the mixture solution was sealed and sonicated in an ice-bath

for 10 h at a power of 200 W. Afterwards, the resultant brown suspension was centrifuged at 2000 rpm for 15 mins to remove the residual unexfoliated bulk BP.

5.2.4 Preparation of 0D-2D Ni₂P@BP Heterostructure

Ni₂P@BP hybrid nanostructures were prepared via a solvothermal synthesis according to a method described as follows. In an autoclave equipped with a Teflon Inliner, 0.2 g of NiCl₂ (excess reactants) were added to 55 mL of BP nanosheets DMF solution. After stirring for 30 mins, the suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and heated at 160 °C for 3 h. After cooling down, the product was centrifuged and washed several times with absolute ethanol to remove the solvent and unreacted solutes. The sample was dried at 60 °C overnight in a vacuum oven.

5.2.5 Characterization

The morphology of materials were determined by field emission SEM (JEOL, JSM-7600F) and TEM (JEOL, model JEM-2100F) operating at 200 kV. The crystal structural characterization of the samples was investigated by a Shimadzu XRD-600 with Cu K_α radiation ($\lambda = 0.15404$ nm) operated at 40 kV and 30 mA. Nitrogen adsorption/desorption isotherms were conducted at 77 K (ASAP Tri-star II 3020 model). Raman spectroscopy was measured by using a confocal Raman microscopy system (WITec CRM200) with the excitation line of 532 nm and an air-cooling charge-coupled device as the detector (WITec Instruments Corp, Germany). The surface area analysis was performed using N₂

adsorption/desorption isotherm measurements at $-196\text{ }^{\circ}\text{C}$ on a Micrometrics Tri-star II 3020 model equipment.

5.2.6 Electrochemical Measurement.

The sample is mixed with acetylene black and PVDF binder which dissolved in NMP (as a solvent). The mass ratio of the active material (Ni₂P@BP), acetylene black (Timcal), and PVDF in the mixed slurry is 7:2:1. In order to improve the homogeneity, the mixture was reground by using a mortar and pestle about half an hour. The resulting slurry (about 1.1 mg) was then uniformly coated on a copper foil (the diameter of 12 mm) and vacuum oven dried at $100\text{ }^{\circ}\text{C}$ overnight. CR2032-type coin cells were assembled with Li foil as the counter and reference electrode, PP film as the separator, and 1M LiPF₆ into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte (around 250 μL) in an argon-filled glove box with concentrations of moisture and oxygen below 1.0 ppm. CV was performed using the electrochemical workstation (CHI 660C) at different scan rates ($0.1\text{--}2.0\text{ mVs}^{-1}$). The constant-current charge-discharge tests were performed in the range of $0.005\text{--}3.0\text{ V}$ using a NEWARE multichannel battery test system. EIS was performed using an Ametek PARSTAT 2273 electrochemistry workstation (a Bio-Logic SP-150 potentiostat). The AC amplitude of 5 mV and frequency range of $1\text{ MHz--}0.01\text{ Hz}$ was applied in this measurement. The BP nanosheets electrode was prepared in the same way as the Ni₂P@BP electrode.

5.3 Results and Discussion

The layered BP single crystals (Figure 5.1a) were prepared by a chemical vapor transport deposition process. The morphology and composition of the crystals was measured by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) mapping. As illustrated in Figure 5.1b, the SEM image clearly shows the layered structure of the BP crystals. The EDX analysis suggests the sole existence of P with the C and O elements originated from the background (Figure 5.2a). The ultrathin BP nanosheets were prepared

Figure 5.1. a) Digital image images of the BP crystals. b) Low-magnification SEM image of the BP crystals. c) TEM image of the exfoliated BP nanosheets with the size of several micrometers. d) HRTEM image of the BP nanosheets (The insets are corresponding SAED patterns). e) TEM images of the Ni₂P@BP with EDS mapping. f) and g) Typical TEM images of the Ni₂P@BP. h) and i) HRTEM images of the Ni₂P@BP (The inset in h are corresponding SAED patterns, red planes for BP and green planes for Ni₂P).

by liquid exfoliation of high-quality BP single crystals. The morphological and structural details of the BP nanosheets were analyzed by high-resolution transmission electron microscopy (HRTEM) with selective area electron

diffraction (SAED). As shown in Figure 5.1c, the exfoliated BP nanosheets show a typical few-layer nanosheet with a size of several micrometers. The HRTEM of the BP (Figure 5.1d) shows the lattice spacing of 0.259 nm which corresponds to that of the (040) crystal planes. The corresponding SAED pattern is made up of discrete spots, which confirms that each nanosheet is mostly single-crystalline (inset in Figure 5.1d). Raman spectroscopy of the BP nanosheets was conducted with and calibrated using a bare silicon wafer. As shown in Figure 5.2b, the phonon modes are located at 362.3, 439.3 and 466.9 cm⁻¹ for A_g¹ (out-of-plane mode), B_{2g} and A_g² (in-plane modes), respectively, which are in good accordance with previous observations for BP.^[46-48] The crystal structures of the BP crystals and Ni₂P@BP are characterized by powder X-ray diffraction (XRD). XRD patterns of the BP crystals, simulated BP (JCPDS no. 76-1957), Ni₂P (JCPDS no. 74-1385) and Ni₂P@BP heterostructure are shown in Figure 5.3, in which the diffraction peaks of Ni₂P@BP are well indexed to orthorhombic BP (JCPDS no. 76-1957) and hexagonal Ni₂P (JCPDS no. 74-1385). The sharp diffraction peaks of BP at 17.1°, 34.6°, and 52.9° can be indexed to the diffractions arise from (020), (040) and (060) planes, respectively, which reveals the preferential orientation along the *c*-direction, highly anisotropic properties, and confirms the layered nature of the BP crystals.

Figure 5.2. a) The EDS spectrum of the BP crystal. b) Raman spectrum at $\lambda = 532$ nm of the BP nanosheets. c) A digital image of a pellet samples after SPS process.

Figure 5.3. XRD patterns of the Ni₂P@BP (black), BP crystal (green), simulated BP (blue), Ni₂P (red). All the peaks in the patterns can be indexed to layered BP (JCPDS no. 76-1957) and Ni₂P (JCPDS no. 74-1385).

The low-resolution TEM images in Figures 5.1f, 5.1g and Figure 5.4 depict that the as-made Ni₂P@BP heterostructure adopts a typical few-layer nanosheet orientation with a lateral size of ~ 1 μm and plenty of tiny nanoparticles uniformly embedded on the surface of the BP nanosheets. In order to clearly visualize the interior structure of the Ni₂P@BP, HRTEM was carried out (Figures 5.1h and

5.1i). Highly single-crystalline Ni₂P NCs with an average diameter of 5 nm can be clearly observed. The lattice spacing of Ni₂P NCs is 0.224 nm, which is assignable to the (111) planes of hexagonal Ni₂P.²⁸⁸ Furthermore, the SAED pattern (inset in Figure 5.1h) indicates that the major diffraction peaks match well with the structures of both orthorhombic BP and hexagonal Ni₂P. EDX mapping analysis (Figure 5.1e) presents the homogeneous distribution of Ni and P elements. The textural properties of the Ni₂P@BP were obtained based on the nitrogen adsorption/desorption isotherms curves (Figure 5.5). The Ni₂P@BP gives a typical type IV isotherm, which is indicative of its mesoporous nature. The as-synthesized Ni₂P@BP possesses a Brunauer-Emmett-Teller (BET) surface area of 41.2846 m² g⁻¹. Meanwhile, the Barrett-Joyner-Halenda (BJH) pore-size distribution of the as-synthesized Ni₂P@BP is centered at ~ 22 nm (inset in Figure 5.5).

Figure 5.4. TEM images of the Ni₂P@BP.

Figure 5.5. Nitrogen adsorption/desorption isotherms and BJH pore size distribution of the Ni₂P@BP (Inset is the corresponding pore size distribution).

Electrical conductivities and Hall measurements of the BP single crystal, BP nanosheets and Ni₂P@BP were performed on a physical properties measurement system (PPMS, Quantum Design). For the latter two samples, the measurements were carried out in pellet form prepared by SPS (**Figure 5.2c**). The carrier concentration (n) was calculated using the formula, $n = 1/(e R_H)$, where e is the elementary charge, R_H is measured Hall coefficient. As shown in Figure 2a, the electrical conductivities are 1.10×10^3 , 2.12×10^2 and 6.25×10^4 S m⁻¹ for the BP single crystal, BP nanosheets and Ni₂P@BP at 300 K, respectively. **Figure 5.6** clearly reveals that the electrical conductivity of the Ni₂P@BP heterostructure can improve the electrical conductivity by two orders of magnitude compared to the bare BP nanosheets. Further, the decreasing electrical conductivity as a function of temperature signifies metallic behavior, in sharp contrast to the pure BP crystal as well as the BP nanosheets.

Figure 5.6. a) Electrical conductivity and b) Total thermal conductivity versus temperature of the BP single crystal, BP nanosheets and Ni₂P@BP, respectively.

Indeed, Hall measurements show that the charge carrier concentrations of the BP single crystal, BP nanosheets and Ni₂P@BP are 5.00×10^{17} , 1.25×10^{17} , and $1.37 \times 10^{20} \text{ cm}^{-3}$ at 300K, respectively, indicating that the Ni₂P NCs act as electron donors to the BP nanosheets. The carrier concentration of the Ni₂P@BP heterostructure is about three orders of magnitude higher than that of the bare BP. Such high electrical conductivity and tunable carrier concentration are very beneficial for improving the performances in LIBs.

Figure 5.7. a) CVs of the Ni₂P@BP for Li-ion batteries in the first 5 cycles at a scan rate of 0.1 mV s⁻¹. b) CV curves of the Ni₂P@BP electrode at various scan rates. c) Linear relationship of the cathodic and anode peaks current (*i_p*) and the square root of the scan rate (*v*^{1/2}) fitted by the Randles-Sevcik equation for the Ni₂P@BP. d) EIS plots of the Ni₂P@BP and BP nanosheets electrodes measured at the third fully discharged state (The inset displays a corresponding fitted equivalent circuit).

Figure 5.8. a) CV curves of the BP nanosheets electrode for LIBs in the first 5 cycles at a scan rate of 0.1 mV s⁻¹. b) CV curves of the BP nanosheets electrode at various scan rates. c) Linear relationship of the cathodic and anode peaks current (*i_p*) and the square root of the scan rate (*v*^{1/2}) fitted by the Randles-Sevcik equation for the BP.

To evaluate the Li ions storage ability, the cyclic voltammetry (CV) measurements of the Ni₂P@BP electrode were tested in a potential window

between 0.01 and 3.0 V at a scan rate of 0.1 mV s⁻¹. The first five CV curves of the Ni₂P@BP are shown in **Figure 5.7a**. During the first cycle, there are three cathodic peaks located at 2.04, 1.50 (split into 1.64 and 1.38) and 0.72 V, and then three anodic peaks at around 1.04, 1.89 and 2.36 V. The broad cathodic peak at 0.72 V and anodic peak at 1.04 V can be assigned to the conversion reaction of the BP → Li_xP → Li₃P.^{96, 199, 289-291} The cathodic peak at 1.50 V (split into 1.64 and 1.38 V, which merge into one peak at 1.60 V after the initial activation cycle) and anodic peak at 1.89 V can be identified as P-based alloying/dealloying reaction as Ni₂P + 3Li⁺ + 3e⁻ → Li₃P + 2Ni.^[58-64] Moreover, the reversible redox peaks at 2.04 and 2.36 V, which are attributed to the lithium-ion intercalation reaction and the re-formation of Ni₂P, respectively, gradually disappear, which may be caused by pulverization during the discharge/charge process.²⁹²⁻²⁹³ Meanwhile, from the second cycle onwards, the CV curves are almost stable and mostly overlap with each other, suggesting the excellent reversible Li storage property of the Ni₂P@BP electrode. In addition, judging from the current of different peaks, it is well illustrated that the BP has a greater contribution to Li ions storage compared with the Ni₂P. To test the ability of quick CV response, scan rates ranging from 0.1 to 2.0 mV s⁻¹ were carried out on the Ni₂P@BP and BP nanosheets electrodes (**Figures 5.7b** and **5.8**). It can be observed that the intensities of the redox peaks and polarization increase with the increasing scan rate for the Ni₂P@BP electrode (**Figure 5.7b**). Meanwhile, the positions of the cathodic peaks shift to lower potentials, while the anodic peaks shift to higher potentials with the increasing sweep rate. As shown in **Figure 5.7c**, the linear

relationships between the peak currents (i_p , A) and the square root of the scan rate are fitted for both cathodic and anodic peaks at 0.72 and 1.04 V with slopes of 1.97 and 1.29, respectively, which clearly demonstrates that the lithiation/delithiation reaction of the Ni₂P@BP electrode are diffusion-controlled. Herein, the i_p can be described by using the Randles-Sevcik equation:²⁹⁴

$$i_p = 2.69 \times 10^5 n_e^{3/2} S D^{1/2} C v^{1/2}$$

where n_e is the number of charge transferred, S is the effective electrode area (cm²), D is the diffusion coefficient of Li ions (cm² s⁻¹), C is the concentration of Li ions (mol cm⁻³), and v is the scan rate of the CV test (V s⁻¹). In comparison, the CV profile of the BP nanosheets electrode is seriously distorted and the oxidation and reduction peaks cannot be distinguished when the scan rate is higher than 0.4 mV s⁻¹, in conjunction with the presence of small slopes of 0.23 (cathodic) and 0.16 (anodic) at 0.74 and 1.07 V, respectively (Figure 5.8). Furthermore, the average D value (8.02×10^{-13} cm² s⁻¹) of the Ni₂P@BP electrode is nearly two orders of magnitude higher than that of the BP nanosheets electrode (1.14×10^{-14} cm² s⁻¹). Evidently, the Ni₂P@BP is more competent to sustain a quicker CV response compared with the BP nanosheets, suggesting high ions diffusion efficiency and excellent rate capability of the Ni₂P@BP.

In order to have in-depth understanding on the Li ions and electron transport kinetics of Ni₂P@BP, electrochemical impedance spectroscopy (EIS) measurements were carried out from 100 KHz to 0.01 Hz at the third fully discharged state. The EIS spectra, fitted results and an equivalent circuit are shown in Figure 5.7d. As can be seen, the depressed semicircle in the high-middle

frequency range can be assigned to the charge transfer resistance (R_{ct}) at electrode-electrolyte interface. Meanwhile, the R_{ct} for the Ni₂P@BP (97.1 Ω) is found to be lower than that of the BP nanosheets electrode (182.7 Ω). Furthermore, the Warburg impedance, ascribed to the semi-infinite Li ions diffusion in the Ni₂P@BP is also lower than BP nanosheets electrode. Thus, EIS results indicate that the Ni₂P@BP possesses better charge transfer kinetics within the electrode and at the electrode/electrolyte interface compared with the BP nanosheets.

The rate capability of the Ni₂P@BP as LIBs electrode was tested at various current densities. As shown in Figure 5.9a, the capacity of the Ni₂P@BP electrode decreases slowly with the increasing scan rate. Remarkably, a high reversible specific capacity of 1196.3 mAh g⁻¹ is achieved at 0.1 A g⁻¹. With increasing current density, specific capacities of 1034.7 mAh g⁻¹ at 0.2 A g⁻¹,

Figure 5.9. a) Rate capabilities of the Ni₂P@BP at varying discharge rates. b) Cycling performances of the Ni₂P@BP between 0.005 and 3.0 V vs. Li/Li⁺ at a cycling rate of 1 A g⁻¹ and cycling performances of the BP nanosheets at a cycling rate of 0.1 A g⁻¹.

833.7 mAh g⁻¹ at 0.5 A g⁻¹, 753.4 mAh g⁻¹ at 1 A g⁻¹, 602.8 mAh g⁻¹ at 2 A g⁻¹, 423.8 mAh g⁻¹ at 5 A g⁻¹, 322.0 mAh g⁻¹ at 10 A g⁻¹, can be retained, implying

excellent rate capability of the Ni₂P@BP for Li ions storage. Simultaneously, the first galvanic discharge/charge measurements of Ni₂P@BP and BP nanosheets at a current density of 0.1 A g⁻¹ and the discharge/charge curves of Ni₂P@BP at different rates are shown in **Figure 5.10**. In comparison, the specific capacity of the bare BP rapidly reduces to 290.9 mAh g⁻¹ after the first discharge at 0.1 A g⁻¹ and subsequently drops to 68.6 mAh g⁻¹ at a current density of 2 A g⁻¹. After cycling at high current densities, a specific capacity of 1115.5 mAh g⁻¹ can still be achieved when the current density reduces to 0.1 A g⁻¹, which means that the Ni₂P@BP electrode could also reversibly discharge/charge at a wide range of current densities. The cycling performances are shown in Figure 5.9b. The Ni₂P@BP electrode exhibits a specific capacity

Figure 5.10. a) The first galvanic discharge/charge measurements of Ni₂P@BP and BP nanosheets at a current density of 0.1 A g⁻¹. b) The discharge/charge curves of Ni₂P@BP at different rates.

of 743.7 mAh g⁻¹ after 1000 cycles at a current density of 1 A g⁻¹. In contrast, the bare BP electrode only exhibits a low specific capacity of 218 mAh g⁻¹ after 5 cycles at a current density of 0.1 A g⁻¹ (**Figure 5.9b**).

5.4 Conclusion

In summary, we have demonstrated a novel design of 0D-2D Ni₂P@BP heterostructure, which shows promising lithium storage properties. Comparing with the pure BP nanosheets, the Ni₂P@BP heterostructure enhances the electrical conductivity (from 2.12×10^2 to $6.25 \times 10^4 \text{ S m}^{-1}$) by tuning the charge carrier concentration (from 1.25×10^{17} to $1.37 \times 10^{20} \text{ cm}^{-3}$). As an anode of LIB, the Ni₂P@BP shows quick electrochemical response with improved Li ion diffusion kinetics, which yields an excellent rate capability (e.g., 322.0 mAh g^{-1} at 10 A g^{-1}), high reversible capacity of around $1196.3 \text{ mAh g}^{-1}$ at 0.1 A g^{-1} and outstanding cycle life of 743.7 mAh g^{-1} after 1000 cycles at 1 A g^{-1} .

Chapter 6 Conclusion and Future Work

In this chapter, the conclusion of my thesis studies is presented, including the high-yield preparation of phosphorene, design and fabrication of air-stable PG-SPS, nanoscale surface engineering of E-BP/PEDOT with enhanced reaction kinetics as well as constructing 0D-2D architecture of Ni₂P@BP. In addition, future work was also recommended, including design and preparation of Sn nanoparticles growing on BP nanosheets (Sn@E-BP) and exploring phosphorene for other energy storage.

6.1 Conclusion

This PhD research work mainly focuses on the studies of BP as anodes for LIBs and SIBs. Phosphorene, as another elementary 2D material after graphene, has been considered as a promising anode for reversible batteries owing to its high theoretical specific capacity (2596 mAh g⁻¹) and ultrafast Li/Na ions diffusion along the zigzag direction. However, the major challenges of low-yield preparation of phosphorene and the poor air-stability largely hinder its practical application. Furthermore, when phosphorene is tested as anodes for LIBs and SIBs, it exhibits low CE, low initial reversible capacities as well as fast capacity fading owing to the sluggish reaction kinetics and large volume change (~300%). Therefore, thesis studies herein mainly focus on the aims of large-scale preparation, effective passivation approaches and advanced strategies towards improved electrochemical performance of BP as anodes for LIBs and SIBs.

Firstly, formamide was identified as an appropriate solvent to produce high-yield phosphorene. The yield of the as-obtained phosphorene largely outperforms the commonly used ones (e.g., NMP, DMF, IPA) in previous reports. In addition, good crystallinity and tunable size distributions of phosphorene were also realized. And also, phosphorene obtained in formamide was stable for further processing and applications.

Furthermore, a densely-packed graphene-phosphorene composite (PG-SPS) is designed and prepared via a facile spark plasma sintering (SPS) method. As a result, much improved air-stability for PG-SPS sample was achieved due to that its high packing density (0.6 g cm^{-3}) could effectively suppress the permeation of water or oxygen molecules into the sample. Importantly, improved volumetric capacities could be achieved for PG-SPS as anodes of LIBs without scarifying its electrochemical performance.

In addition, enhanced charge transfer kinetics and surface wettability with electrolyte were realized by effective nanoscale surface engineering of exfoliated few-layer BP, which is performed by homogeneous deposition of horizontally aligned PEDOT nanofibers on surface-modified BP nanosheets. The as-obtained BP/PEDOT composites exhibit much improved wettability towards the electrolyte compared to that of the pure BP nanosheets. Accordingly, the purposely engineered E-BP/PEDOT architecture could achieve simultaneously: (1) enhanced charge transfer kinetics and (2) super surface wettability with electrolyte. As a result, the reaction kinetics are greatly enhanced accordingly for both sodium and lithium storage. Importantly, the Na storage properties of E-

BP/PEDOT outperform that of the E-BP/graphene composites based on the overall mass of whole electrodes due to the high mass percentage of BP in this architecture.

Finally, a 0D-2D heterostructure of $\text{Ni}_2\text{P}@BP$ was also constructed via a facile strategy. In such a heterostructure, the 2D morphology of BP nanosheets is well maintained and Ni_2P NCs display an average diameter of ~ 5 nm. With enhanced electrical conductivity as well as synergistic effect from both building blocks, the $\text{Ni}_2\text{P}@BP$ shows much improved Li storage properties versus the bare BP when tested as electrode materials for LIBs.

6.2 Recommendation for Future Work

Present works have been successfully proven that BP could be a promising anode for high-performance LIBs and SIBs by combining BP nanosheets with carbon materials, conductive polymers, and metal phosphides. The following section recommends future work to further develop advanced BP-based materials in energy research field.

6.2.1 Preparation of Sn Nanoparticles Growing on BP Nanosheets

Tin is one of the most intensively studied anode materials for LIBs and SIBs among the alloy-type anodes due to its relatively high theoretical capacity of 992 mA h g^{-1} based on the formation of $\text{Li}_{4.4}\text{Sn}$. It is much higher than that of conventional graphite (LiC_6 , 372 mAh g^{-1}). In addition, Sn has higher operating voltage than graphite, improving the safety of batteries during fast charging and

discharging process. However, the severe volume expansion (around 420%) upon repeated charge and discharge cycles leads to a continuous and accumulated agglomeration of Sn nanoparticles and thus fast capacity fading.²⁹⁵ To overcome the adverse issues associated with such degradation of electrodes, tremendous efforts have been made in the latest years, including preparing tin-based nanostructures and employing matrixes (e.g., carbon) to accommodate volume change. Recently, Sn nanoparticles encapsulated elastic hollow carbon spheres were prepared by *in situ* reducing SnO₂ hollow spheres with carbon coating, as shown in Figure 6.1.²⁹⁶ This void volume could efficiently accommodate the huge volume change of Sn nanoparticles and thus prevent the pulverization of electrode. Therefore, high specific capacities and excellent cycling performance were achieved.

Figure 6.1. a) SEM image of SnO₂ coated SiO₂ spheres; b) TEM image of the hollow SnO₂ spheres; c) and d) SEM and TEM image of TNHCs, respectively. The inset in (c) is a close view of a single broken carbon spherical shell studded with Sn particles. Reproduced with permission from Ref. [296]. Copyright 2008, John Wiley & Sons, Inc.

In this regard, an idea of constructing Sn nanoparticles uniformly growing on ultrathin BP nanosheets is proposed. In this architecture, BP nanosheets could be utilized as a helpful substrate that accommodates the volume change of Sn during charging and discharging process. In addition, with the high electrical conductivity of Sn nanoparticles, the reaction kinetics of the electrode will be largely promoted, endowing improved electrochemical performance when Sn@E-BP is tested as anodes for LIBs and SIBs.

6.2.2 Exploration of BP Nanosheets in Other Energy Research Fields

Exploring phosphorene or phosphorene-based materials in a variety of applications is one of the most active research areas. In addition to LIBs, SIBs and thermoelectric, phosphorene has been demonstrated as a promising candidate for many other energy storage and conversion devices (e.g., modern reversible batteries,²⁹⁷ electrocatalysis,¹³¹ photocatalysis,²⁹⁸⁻²⁹⁹ solar cells,³⁰⁰ etc.) due to its intriguing properties. For example, Li-S batteries have attracted intensive research as a promising alternative of the current LIBs due to their superior theoretical capacity (1675 mAh g^{-1}) and high energy density (2600 Wh kg^{-1}).³⁰¹⁻³⁰³ However, the dissolution of intermediate polysulfides into the electrolyte results in gradual loss of active sulfur and rapid capacity fade accordingly. Recently, Li *et al.* demonstrated the incorporation of phosphorene into a porous carbon nanofiber network could serve as an effective polysulfides immobilizer due to a high binding energy of LiS_x to phosphorene, largely enhancing the cycling performance of Li-S batteries.¹³² Very recently, a phosphorene as a

coating layer, with high electrical conductivity and ultrahigh Li diffusion, was also introduced onto a commercial polypropylene separator to trap and activate the soluble polysulfides in Li-S batteries.³⁰⁴ Phosphorene has also been explored as a promising anode of Mg-ion batteries, but current studies are mainly focused on the theoretical calculations by means of first-principles analysis.³⁰⁵⁻³⁰⁷

Supercapacitors are another important energy-storage system due to their high power density, fast charging/discharging rate and excellent cycle stability.³⁰⁸ According to the charge storage mechanism, supercapacitors are classified into electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs work based on the charge storage at the interface of electrodes and electrolyte, while pseudocapacitors are based on the reversible redox process at or near the electrode surface. Very recently, a flexible all-solid-state supercapacitor was reported based on the exfoliated phosphorene as electrode materials.³⁰⁹ As shown in **Figure 6.2**, typically, the as-obtained dispersion of phosphorene in acetone was drop-casted on a Pt-coated PET substrate. Subsequently, PVA/H₃PO₄ as the gel electrolyte was sandwiched between the two as-prepared BP films on PET, followed by protection against the ambient exposure. As a result, the fabricated device based on EDLCs exhibited a high stack capacitance of 13.75 F cm⁻³ at a scan rate of 0.01 V s⁻¹, good mechanical flexibility as well as outstanding cycling stability over 30000 cycles with only 28.2 % capacity decay.

To further improve the capacitance of BP-based materials for supercapacitors, the architecture of E-BP/conductive polymer (e.g., E-BP/PEDOT established above) could be beneficial due to the pseudocapacitive behaviors and enhanced

charge transfer from the conductive polymer. In addition, such material design may effectively avoid the restacking of BP nanosheets, endowing fast ion access to the active sites. Therefore, higher capacitance as well as good rate capability of E-BP/conductive polymer for flexible supercapacitor could be achieved.

Figure 6.2. Schematic illustration for fabrication process of the BP-ASSP devices. a) A rectangular flexible polyethylene terephthalate (PET) substrate. b) Growing Pt film on PET by magnetron sputtering. c) Drop casting of dispersed BP nanosheets or ground BP powders in acetone on Pt-coated PET, and the copper tape is adhered to one edge of the device by silver plastic to improve the electrical contacts. d) Drop-casting and solidification of PVA/H₃PO₄ gel electrolyte. e) Assembly of the sandwich structure device with two pieces of PETs. f) Cross section of the sandwich structure. Reproduced with permission from Ref. [309]. Copyright 2016, John Wiley & Sons, Inc.

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1. One-Pot Synthesis of Tunable Crystalline Ni₃S₄@ Amorphous MoS₂ Core/Shell Nanospheres for High-Performance Supercapacitors
Y. Zhang, W. P. Sun, X. H. Rui, B. Li, H. T. Tan, G. L. Guo, S. Madhavi, Y. Zong, Q. Y. Yan,* *Small*, **2015**, 11, 3720-3720.
2. An Air-Stable Densely Packed Phosphorene-Graphene Composite Toward Advanced Lithium Storage Properties
Y. Zhang, H. W. Wang, Z. Z Luo, H. T. Tan, B. Li, S. N. Sun, Z. Li, Y. Zong, Z. C. Xu, Y. H. Yang, K. A. Khor, Q. Y. Yan,* *Adv. Energy Mater.* **2016**, 6, 1600453.
3. Two-Dimensional Black Phosphorus for Energy Storage and Thermoelectric Applications
Y. Zhang, Y. Zheng, K. Rui, H. H. Hng, K. Hippalgaonkar, J. W. Xu, W. P. Sun, J. X. Zhu,* Q. Y. Yan*, W. Huang, *Small*, **2017**, accepted.
4. Alloy-based Anode Materials towards Advanced Sodium-ion Batteries
M. M. Lao,† Y. Zhang† (Co-first Author), W. B. Luo*, Q. Y. Yan*, W. P. Sun*, S. X. Dou, *Adv. Mater.* **2017**, DOI: 10.1002/adma.201700622.
(Co-first Author)
5. A Crystalline Cu–Sn–S Framework for High-Performance Lithium Storage
L. N. Nie,† Y. Zhang† (Co-first Author), K. Q. Ye, J. Y. Han, Y. Wang, G. Rakesh, Y. X. Li, R. Xu, Q. Y. Yan,* Q. C. Zhang,* *J. Mater. Chem. A*, **2015**, 3, 19410-19416. (Co-first Author)

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6. A Surfactant-Thermal Method to Prepare Crystalline Tthioantimonate for High-Performance Lithium-Ion Batteries
L. N. Nie,[†] **Y. Zhang**[†] (Co-first Author), W. W. Xiong, T. T. Lim, R. Xu, Q. Y. Yan,^{*} Q. C. Zhang,^{*} *Inorg. Chem. Front.*, **2016**, 3, 111-116. (Co-first Author)
7. Functionalized Few-layer Black Phosphorus with Super-wettability towards Enhanced Reaction Kinetics for Rechargeable Batteries
Y. Zhang, W. P. Sun, Z. Z. Luo, Y. Zheng, Z. W. Yu, D. Zhang, H. T. Tan, J. X. Zhu, X. L. Wang, Q. Y. Yan, S. X. Dou, **2017** (submitted).
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