Multifunctional 0D–2D Ni₂P Nanocrystals–Black Phosphorus Heterostructure

Zhong-Zhen Luo, Yu Zhang, Chaohua Zhang, Hui Teng Tan, Zhong Li, Anas Abutaha, Xing-Long Wu, Qihua Xiong, Khiam Aik Khor, Kedar Hippalgaonkar, Jianwei Xu, Huey Hoon Hng, and Qingyu Yan*

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1. Introduction

Phosphorene, monolayer or few-layer black phosphorus (BP), is an emerging class of 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 behaviors.[1–12] 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, conversion devices, and so on.[13–15] For example, as a promising low-temperature thermoelectric material with high Seebeck coefficient, the performance of BP is still compromised owing to its relatively high thermal conductivity.[16–18] Thus, continual effort in developing effective strategies to optimize the properties of BP including its intrinsically charge carrier concentration, electrical conductivity, and thermal 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.[19–28]

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).[18,29–32] and hydrogen evolution reaction (HER).[33–45] Driven by the upward trend of nanotechnology, downsizing TMPs into 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) TMPs NCs attached onto or embedded in BP nanosheets can substantially increase the scattering of phonons, which can decrease the thermal conductivity; (3) restacking 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 and thermal conductivities and investigate its properties as thermoelectric materials and the electrodes materials for LIBs or HER catalyst. 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 × 10¹⁷ cm⁻³ for the pure BP nanosheets to 1.37 × 10²⁰ cm⁻³ for the Ni₂P@BP heterostructure. As a result, the electrical conductivity is enhanced from 2.12 × 10² to 6.25 × 10⁴ S m⁻¹ at 300 K. Also, the thermal conductivity decreases from 11.1 to 7.69 W m⁻¹ K⁻¹ at this temperature, which reduces sharply compared with the value of BP single crystal (44.5 W m⁻¹ K⁻¹). The above three 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 and HER catalyst. The Ni₂P@BP shows much improved Li storage properties versus the bare BP, such as high reversible capacities (1196.3 mA h g⁻¹ at 0.1 A g⁻¹; about four times higher than that of the pure BP nanosheets), good rate capabilities (322.0 mA h g⁻¹ at 10 A g⁻¹), and outstanding long-term cycling performance of 743.7 mA h g⁻¹ (94.1% capacity retention) after 1000 cycles at 1 A g⁻¹. Moreover, the Ni₂P@BP also exhibits superior electrochemical HER activity versus the commercial nickel phosphide with a current density of 10 mA cm⁻² at an overpotential of only 107 mV, small Tafel slope of 38.6 mV dec⁻¹, and outstanding long-term operational stability.

2. Results and Discussion

The layered BP single crystals (Figure 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 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 S1a, Supporting Information). The ultrathin BP nanosheets were prepared 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 1c, the exfoliated BP nanosheets show a typical few-layer nanosheet with a size of several micrometers. The HRTEM of the BP (Figure 1d) shows the lattice spacing of

![Figure 1](https://example.com/fig1.png)

**Figure 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,g) Typical TEM images of the Ni₂P@BP. h,i) HRTEM images of the Ni₂P@BP (the inset in h are corresponding SAED patterns, red planes for BP, and green planes for Ni₂P).
The low-resolution TEM images in Figure 1f,g and Figure S3 (Supporting Information) depict that the as-made Ni$_2$P@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 Ni$_2$P@BP, HRTEM was carried out (Figure 1h). Raman spectroscopy of the BP nanosheets was conducted with and calibrated using a bare silicon wafer. As shown in Figure S1b (Supporting Information), the phonon modes are located at 362.3, 439.3, and 466.9 cm$^{-1}$ for A$_g^1$ (out-of-plane mode), B$_{2g}$ and A$_g^2$ (in-plane modes), respectively, which are in good accordance with previous observations for BP.\cite{46-48} The crystal structures of the BP crystals and Ni$_2$P@BP are characterized by powder X-ray diffraction (XRD). XRD patterns of the BP crystals, simulated BP (JCPDS no. 76–1957), Ni$_2$P (JCPDS no. 74–1385) and Ni$_2$P@BP heterostructure are shown in Figure S2 (Supporting Information), in which the diffraction peaks of Ni$_2$P@BP are well indexed to orthorhombic BP (JCPDS no. 76–1957) and hexagonal Ni$_2$P (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 2. a) Electrical conductivity and b) total thermal conductivity versus temperature of the BP single crystal, BP nanosheets, and Ni$_2$P@BP, respectively. The dotted lines in (b) are the simulated curves to show trend of $T^{-1}$ region and of $T^{-1}$ at different temperature regions.

The corresponding SAED pattern is made up of discrete spots, which confirms that each nanosheet is mostly single-crystalline (inset in Figure 1d). As shown in Figure S1b (Supporting Information), the phonon modes are located at 362.3, 439.3, and 466.9 cm$^{-1}$ for A$_g^1$ (out-of-plane mode), B$_{2g}$ and A$_g^2$ (in-plane modes), respectively, which are in good accordance with previous observations for BP.\cite{46-48} The crystal structures of the BP crystals and Ni$_2$P@BP are characterized by powder X-ray diffraction (XRD). XRD patterns of the BP crystals, simulated BP (JCPDS no. 76–1957), Ni$_2$P (JCPDS no. 74–1385) and Ni$_2$P@BP heterostructure are shown in Figure S2 (Supporting Information), in which the diffraction peaks of Ni$_2$P@BP are well indexed to orthorhombic BP (JCPDS no. 76–1957) and hexagonal Ni$_2$P (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.

The low-resolution TEM images in Figure 1f,g and Figure S3 (Supporting Information) depict that the as-made Ni$_2$P@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 Ni$_2$P@BP, HRTEM was carried out (Figure 1h). Highly single-crystalline Ni$_2$P NCs with an average diameter of 5 nm can be clearly observed. The lattice spacing of Ni$_2$P NCs is 0.224 nm, which is assignable to the (111) planes of hexagonal Ni$_2$P.\cite{49} Furthermore, the SAED pattern (inset in Figure 1h) indicates that the major diffraction peaks match well with the structures of both orthorhombic BP and hexagonal Ni$_2$P. EDX mapping analysis (Figure 1e) presents the homogeneous distribution of Ni and P elements. The textual properties of the Ni$_2$P@BP were obtained based on the nitrogen adsorption/desorption isotherms curves (Figure S4, Supporting Information). The Ni$_2$P@BP gives a typical type IV isotherm, which is indicative of its mesoporous nature. The as-synthesized Ni$_2$P@BP possesses a Brunauer–Emmett–Teller (BET) surface area of 41.2846 m$^2$ g$^{-1}$. Meanwhile, the Barrett–Joyner–Halenda (BJH) pore-size distribution of the as-synthesized Ni$_2$P@BP is centered at =22 nm (inset in Figure S4, Supporting Information).

Electrical conductivities and Hall measurements of the BP single crystal, BP nanosheets and Ni$_2$P@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 S1c, Supporting Information). The carrier concentration ($n$) was calculated using the formula, $n = 1/\epsilon R_H$, where $\epsilon$ is the elementary charge, $R_H$ is measured Hall coefficient. As shown in Figure 2a, the electrical conductivities are $1.10 \times 10^3$, $2.12 \times 10^4$, and $6.25 \times 10^4$ S m$^{-1}$ for the BP single crystal, BP nanosheets, and Ni$_2$P@BP at 300 K, respectively. Figure 2a clearly reveals that the electrical conductivity of the Ni$_2$P@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. Indeed, Hall measurements show that the charge carrier concentrations of the BP single crystal, BP nanosheets, and Ni$_2$P@BP are $5.00 \times 10^{17}$, $1.25 \times 10^{17}$, and $1.37 \times 10^{20}$ cm$^{-3}$ at 300 K, respectively, indicating that the Ni$_2$P NCs act as electron donors to the BP nanosheets. The carrier concentration of the Ni$_2$P@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 various potential applications, including thermoelectric materials and the electrodes for LIBs or HER that require highly efficient charge transfer.

The thermal conductivities are also evaluated. Temperature dependence of the total thermal conductivity ($\kappa = \kappa_e + \kappa_l$), where $\kappa_e$ and $\kappa_l$ are the electronic and the lattice contributions, respectively, of all samples was measured using a four-probe steady-state method in the PPMS. It is worth noting that $\kappa_e$, calculated by Wiedemann–Franz law, is expected to be only as large as $=0.4$ W m$^{-1}$ K$^{-1}$ at all temperatures, indicating that phonons are the major heat carriers in all samples. As shown in Figure 2b, thermal conductivity of the BP single crystal was measured in the zigzag (ZZ) lattice direction and it possesses the highest $\kappa$ in the whole temperature range compared to other samples. This is expected since it has a highly crystalline lattice with negligible amount of defects and impurities that
may act as phonon scattering centers. The room-temperature $\kappa$ of BP single crystal matches well with that reported for BP in the ZZ lattice direction.\cite{90} On the other hand, BP nanosheets and Ni$_2$P@BP show a substantially reduced $\kappa$ of 11.1 and 7.69 W m$^{-1}$ K$^{-1}$ at 300 K, respectively. At low temperature, both samples show the expected $\kappa \sim T^3$ relationship as expected for bulk samples (Figure 2b). The lattice thermal conductivity, under the diffuse scattering, average bulk mean free path approximation, can be expressed as $\kappa_l = (1/3) c_v g^2 \tau$, where $c$, $v_g$, and $\tau$ are the specific heat, phonon group velocity, and phonon relaxation time, respectively. The total phonon relaxation times due to phonon–phonon scattering ($\tau_\text{u}$), boundary scattering ($\tau_\text{bd}$), and impurity scattering ($\tau_\text{i}$) can be summed up using Matthiesen’s rule $\tau^{-1} = \tau_\text{i}^{-1} + \tau_\text{bd}^{-1} + \tau_\text{u}^{-1}$. Since the temperature dependent values of $\kappa$ for BP single crystal at temperatures higher than 150 K (Figure 2b) can be fitted to a $T^{-1}$ law, which is evidence of phonon–phonon (Umklapp) scattering, $\tau_\text{i}$ can therefore be estimated from the measured values of $\kappa_l$ (negligible contribution from $\kappa_\text{e}$, Figure S5, Supporting Information), specific heat and group velocity from the phonon modes in the ZZ direction.\cite{51,52} Consequently, for BP nanosheets, boundary scattering adds a temperature-independent term ($\tau_\text{bd}$) to the total $\tau$. The boundary size ($\Delta = v_g \tau_{\text{bd}}$) is therefore calculated to be $\approx 6-9$ nm. In contrast, due to the presence of Ni$_2$P NCSs, all scattering mechanisms are active in Ni$_2$P@BP, which results in a further reduction in $\kappa$ (31% less than that of pure BP nanosheets). Therefore, the 0D–2D Ni$_2$P@BP heterostructure effectively decreases the thermal conductivity to about one-sixth that of BP single crystal, while enhancing the electrical conductivity by 3 orders of magnitude; the approach of 0D–2D heterostructuring provides great potential in improving the thermoelectric properties of materials.

To evaluate the Li ions storage ability, the cyclic voltammetry (CV) measurements of the Ni$_2$P@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 Ni$_2$P@BP are shown in Figure 3a. 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 $\rightarrow$ Li$_x$P $\rightarrow$ Li$_3$P.\cite{53–57} 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 Ni$_2$P $+$ 3Li$^+$ $+$ 3e$^-$ $\rightarrow$ Li$_3$P $+$ 2Ni.\cite{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 Ni$_2$P, respectively, are gradually disappear, which may be caused by pulverization during the discharge/charge process.\cite{58,65,66} Meanwhile, from the second cycle onwards, the CV curves are almost stable and mostly overlap with each other, suggesting

![Figure 3.](image-url)

Figure 3. a) CVs of the Ni$_2$P@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 Ni$_2$P@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 ($\nu_{1/2}$) fitted by the Randles–Sevcik equation for the Ni$_2$P@BP. d) EIS plots of the Ni$_2$P@BP and BP nanosheets electrodes measured at the third fully discharged state. (The inset displays a corresponding fitted equivalent circuit.)
the excellent reversible Li storage property of the Ni$_2$P@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 Ni$_2$P. To test the ability of quick reaction, scan rates ranging from 0.1 to 2.0 mV s$^{-1}$ were carried out on the Ni$_2$P@BP and BP nanosheets electrodes (Figure 3b and Figure S6, Supporting Information). It can be observed that the intensities of the redox peaks and polarization increase with the increasing scan rate for the Ni$_2$P@BP electrode (Figure 3b). 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 3c, 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 Ni$_2$P@BP electrode are diffusion-controlled. Herein, the $i_p$ can be described by using the Randles–Sevcik equation$^{[67]}$

$$i_p = 2.69 \times 10^{5} n^3/2 D^{1/2} S^{1/2} C^{1/2} \nu^{1/2}$$  \hspace{1cm} (1)

where $n_p$ is the number of charge transferred, $S$ is the effective electrode area (cm$^2$), $D$ is the diffusion coefficient of Li ions (cm$^2$ s$^{-1}$), $C$ is the concentration of Li ions (mol cm$^{-3}$), and $\nu$ 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 S6, Supporting Information). Furthermore, the average $D$ value ($8.02 \times 10^{-13}$ cm$^2$ s$^{-1}$) of the Ni$_2$P@BP electrode is nearly two orders of magnitude higher than that of the BP nanosheets electrode ($1.14 \times 10^{-14}$ cm$^2$ s$^{-1}$). Evidently, the Ni$_2$P@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 Ni$_2$P@BP.

In order to have in-depth understanding on the Li ions and electron transport kinetics of Ni$_2$P@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 3d. 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 Ni$_2$P@BP (97.1 $\Omega$) is found to be lower than that of the BP nanosheets electrode (182.7 $\Omega$). Furthermore, the Warburg impedance, ascribed to the semi-infinite Li ions diffusion in the Ni$_2$P@BP is also lower than BP nanosheets electrode. Thus, EIS results indicate that the Ni$_2$P@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 Ni$_2$P@BP as LIBs electrode was tested at various current densities. As shown in Figure 4a, the capacity of the Ni$_2$P@BP electrode decreases slowly with the increasing scan rate. Remarkably, a high reversible specific capacity of 1196.3 mA h g$^{-1}$ is achieved at 0.1 A g$^{-1}$. With increasing current density, specific capacities of 1034.7 mA h g$^{-1}$ at 0.2 A g$^{-1}$, 833.7 mA h g$^{-1}$ at 0.5 A g$^{-1}$, 753.4 mA h g$^{-1}$ at 1 A g$^{-1}$, 602.8 mA h g$^{-1}$ at 2 A g$^{-1}$, 423.8 mA h g$^{-1}$ at 5 A g$^{-1}$, and 322.0 mA h g$^{-1}$ at 10 A g$^{-1}$, can be retained, implying excellent rate capability of the Ni$_2$P@BP for Li ions storage. Simultaneously, the first galvanic discharge/charge measurements of Ni$_2$P@BP and BP nanosheets at a current density of 0.1 A g$^{-1}$ and the discharge/charge curves of Ni$_2$P@BP at different rates are shown in Figure S7b (Supporting Information). In comparison, the specific capacity of the bare BP rapidly reduces to 290.9 mA h g$^{-1}$ after the first discharge at 0.1 A g$^{-1}$ and subsequently drops to 68.6 mA h g$^{-1}$ at a current density of 2 A g$^{-1}$. After cycling at high current densities, a specific capacity of 1115.5 mA h g$^{-1}$ can still be achieved when the current density reduces to 0.1 A g$^{-1}$, which means that the Ni$_2$P@BP electrode could also reversibly discharge/charge at a wide range of current densities. The cycling performances are shown in Figure 4b. The Ni$_2$P@BP electrode exhibits a specific capacity of 743.7 mA h 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 mA h g$^{-1}$ after 5 cycles at a current density of 0.1 A g$^{-1}$ (Figure 4b).

The electrocatalytic HER activities of the Ni$_2$P@BP were examined in a 0.5 m H$_2$SO$_4$ solution using a typical three-electrode setup with graphite rod as the counter electrode. For comparison, similar measurements were also carried out for the commercial Pt catalyst (20 wt% Pt/Vulcan XC-72), commercial Ni$_3$P particles and BP nanosheets under the same conditions and their polarization curves were displayed in Figure 5 and Figure S8 (Supporting Information), respectively. As expected, the commercial Pt catalyst shows the highest HER activity.

![Figure 4](https://www.advenergymat.de)  
Figure 4. a) Rate capabilities of the Ni$_2$P@BP at varying discharge rates. b) Cycling performances of the Ni$_2$P@BP between 0.005 and 3.0 V versus 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$^{-1}$.
The Ni$_2$P@BP demonstrates a much lower overpotential of ≈107 mV at a current density of 10 mA cm$^{-2}$. In addition, the stability of the Ni$_2$P@BP electrode was further investigated in 0.5 M H$_2$SO$_4$ at a scan rate of 2 mV s$^{-1}$. Meanwhile, in sharp contrast, the commercial Ni$_2$P exhibits a high overpotential of ≈311 mV at a current density of 10 mA cm$^{-2}$ and the BP nanosheets also exhibits poor HER activity by showing an overpotential of 600 mV (Figure S8, Supporting Information). Although the BP nanosheets are easily oxidized in oxygen- and water-rich environment to form oxidized phosphorus species, the reducing operating condition of the negative electric potential for such HER electrode may suppress the degradation process. As revealed in Figure 5b, after 3000 consecutive cycles, the Ni$_2$P@BP only exhibits a slight decrease in the slope of the polarization curve. Moreover, the current density at the overpotential of 107 mV for the Ni$_2$P@BP electrode remains stable with the continuous sweeps for 24 h (Figure 5d). In addition, the morphology and crystallinity of the Ni$_2$P@BP are well retained after such stability test, manifesting its excellent stability in electrochemical process.

The Tafel slope represents an inherent property of an electrocatalyst and is used as a significant standard to assess the HER kinetics of electrocatalysts. The Tafel plots of the Ni$_2$P@BP and Pt/C were shown in Figure 5c. The Ni$_2$P@BP electrode exhibits a very small Tafel slope of 38.6 mV dec$^{-1}$ with the measured value about 30 mV dec$^{-1}$ for 20% Pt/C as the reference. These values were obtained by fitting the linear portions of Tafel plots to the Tafel equation, $\eta = b \log (j) + a$ ($\eta$ (V) is the overpotential, $b$ (V dec$^{-1}$) is the Tafel slope, $j$ (A cm$^{-2}$) is the current density, and $a$ is the intercept with respect to the exchange current density $j_0$). The Tafel slope value of 38.6 mV dec$^{-1}$ suggests that the electrocatalytic HER process of the Ni$_2$P@BP electrode is based on the Volmer–Tafel mechanism ($\eta = 30–120$ mV)\cite{69,70}. The HER activity of the Ni$_2$P@BP surpasses most of the Ni$_2$P-based HER catalysts tested in acidic solutions (Table S1, Supporting Information).

The outstanding electrochemical performance of the Ni$_2$P@BP heterostructure can be mainly attributed to its superior structural characteristics: (1) such Ni$_2$P@BP heterostructure can effectively prevent the stacking of the BP and agglomeration of the Ni$_2$P NCs, which maximize the specific surface area with effective electrolyte–electrode interaction for Li storage and more exposed active sites for electrocatalytic HER; (2) The Ni$_2$P NCs anchored on the BP nanosheets could effectively tune the charging carrier concentration of the heterostructure and the 2D morphology of the BP nanosheets provide long charge carrier diffusion path to induce improved charge carrier transfer kinetics.

3. Conclusions

In summary, we have demonstrated a novel design of 0D–2D Ni$_2$P@BP heterostructure, which shows promising multifunctional properties. Comparing with the pure BP nanosheets, the Ni$_2$P@BP heterostructure enhances the electrical conductivity (from 2.12 $\times$ 10$^4$ to 6.25 $\times$ 10$^4$ S m$^{-1}$) by tuning the charge carrier concentration (from 1.25 $\times$ 10$^{17}$ to 1.37 $\times$ 10$^{20}$ cm$^{-3}$), and reduces the thermal conductivity (from 11.1 to 7.69 W m$^{-1}$ K$^{-1}$) at 300 K. As an anode of LIB, the Ni$_2$P@BP shows quick electrochemical
response with improved Li ion diffusion kinetics, which yields an excellent rate capability (e.g., 322.0 mA h g\(^{-1}\) at 10 A g\(^{-1}\)), high reversible capacity of around 1196.3 mA h g\(^{-1}\) 0.1 A g\(^{-1}\) and outstanding cycle life of 743.7 mA h g\(^{-1}\) after 1000 cycles at 1 A g\(^{-1}\). In addition, as a HER electrocatalyst, the Ni\(_2\)P@BP shows excellent electrocatalytic performance with a current density of 10 mA cm\(^{-2}\) at an overpotential of only 107 mV, small Tafel slope of 38.6 mV dec\(^{-1}\), as well as remarkable stability in acidic solution.

4. Experimental Section

**Chemicals and Reagents:** Red phosphorus (P, Sigma-Aldrich), tin (Sn, Sigma-Aldrich), stannic iodide (SnI\(_4\), Sigma-Aldrich), nickel chloride (NiCl\(_2\), Sigma-Aldrich), nickel phospide (Ni\(_2\)P, 98%, Sigma-Aldrich), dimethylformamide (DMF, 99.8%, anhydrous), polyvinylidene fluoride (PVDF), N-methyl pyrrolidone (Sigma-Aldrich), absolute ethyl alcohol, polyvinylidenefluoride (PVDF), Nafion solution (5 wt% in deionized water, Sigma-Aldrich), Li ions battery electrolyte (Charslton Technologies Pte Ltd., Singapore), Li and copper foil (ACME Research Support Pte Ltd, Singapore), and 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).

**Vapor Transport Deposition Process of Bulk BP Crystals:** Bulk BP crystals were prepared through a facile low-pressure transport route according to the literature.(21,22) Briefly, 500 mg of bulk red phosphorus, 10 mg of SnI\(_4\), and 20 mg of Sn were placed into a predrilled 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. This process was shown in **Scheme 1** (1).

**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 min. Then the mixture was transferred in a bottle with 60 mL of DMF that bubbled with argon atmosphere about 10 min 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. Afterward, the resultant brown suspension was centrifuged at 2000 rpm for 15 min to remove the residual unexfoliated bulk BP. This process was shown in **Scheme 1** (2).

**Preparation of 0D–2D Ni\(_2\)P@BP Heterostructure:** Ni\(_2\)P@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 NiCl\(_2\) (excess reactants) were added to 55 mL of BP nanosheets DMF solution. After stirring for 30 min, 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. This process was shown in **Scheme 1** (3).

**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\(_\alpha\) radiation (\(\lambda = 0.15404 \text{nm}\)) 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 N\(_2\) adsorption/desorption isotherm measurements at −196 °C on a Micrometrics Tri-star II 3020 model equipment.

**Thermal and Electrical Properties Measurement:** Ni\(_2\)P@BP and BP nanosheets powders were filled in graphite die (10.5 mm in inner diameter) and sintered to compact bulk disk (about 2 mm in thickness) using SPS (Dr. Sinter 1050, Sumitomo Coal Mining, Osaka, Japan) system. In detail, the sample was heated to 250 °C in 5 min and maintained for 5 min at the pressure of 50 MPa. Then, the temperature was cooled to 50 °C in 4 min with the applied pressure of 10 MPa. All of the sintering steps were performed under the vacuum about 6 × 10\(^{-2}\) mbar. The bulk disk sample was cut and polished to bar with length =9 mm, width =3 mm, and thickness =2 mm by using the cutting machine and sandpapers. Finally, four-probe leads as the measuring electrodes were attached to the bar by applying the silver-filled H20E-HCepoxy. The temperature dependence of the thermal conductivity (\(k\)) and electrical conductivity (\(\sigma\)) were measured by using the continuous mode in a Quantum Design PPMS with thermal transport option. The room temperature Hall coefficient (\(R_\text{H}\)) was performed in the same PPMS equipment using AC transport option.

**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 (Ni\(_2\)P@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 °C overnight. CR2032-type coin cells were assembled with Li foil as the counter and reference electrode, PP film as the separator, and 1M LiPF\(_6\) into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte (around 250 \(\mu\)L) 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 (0.1–2.0 mV s\(^{-1}\)). The constant-current charge–discharge tests were performed in the range of 0.005–3.0 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 MHz–0.01 Hz was applied in this measurement. The AC amplitude charge–discharge tests were performed in the same PPMS equipment using AC transport option.

The electrode for electrocatalytic HER activities test was prepared as the following steps. The dispersions of catalyst materials were prepared by sonicating a mixture containing 4 mg of electrocatalyst in 0.9 mL ethanol, 0.1 mL \(\text{H}_2\text{O}\), and 20 \(\mu\)L Nafion for about 30 min to form homogenous ink. Then, 5 \(\mu\)L of the catalyst suspension was spread onto the surface of the glassy carbon electrode (GCE, 3 mm in diameter).
by a micropipette and dried at ambient temperature overnight. Linear sweep voltammetry were carried out on a Solartron analytical equipment (Model 1470E) with a scan rate of 2 mV s\(^{-1}\) in 0.5 M H\(_2\)SO\(_4\) (p-purge with argon gas) using a typical three-electrode system that uses Ag/AgCl as the reference electrode and graphite rod as the counter electrode. The measured potential versus Ag/AgCl was converted to a reversible hydrogen electrode (RHE) scale by using \(E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V}\) in 0.5 M H\(_2\)SO\(_4\). For comparison, the commercial Pt catalyst (20 wt% Pt/ Vulcan XC-72), commercial NiP and BP nanosheets electrodes were also tested using similar measurement. All the HER results measured in a three-electrode configuration were IR-corrected. EIS was performed with frequency ranging from 0.01 to 10\(^5\) Hz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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