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A self-assembled nanoflower-like Ni₅P₄@NiSe₂ heterostructure with hierarchical pores triggering high-efficiency electrocatalysis for Li–O₂ batteries

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Abstract

The remarkably high theoretical energy densities of $\text{Li}-O_2$ batteries have triggered tremendous efforts for next-generation conversion devices. Discovering efficient oxygen reduction reaction and oxygen evolution reaction (ORR/OER) bifunctional catalysts and revealing their internal structure-property relationships are crucial in developing high-performance $\text{Li}-O_2$ batteries. Herein, we have prepared a nanoflower-like Ni₅P₄@NiSe₂ heterostructure and employed it as a cathode catalyst for Li–O₂ batteries. As expected, the three-dimensional biphasic Ni₅P₄@NiSe₂ nanoflowers facilitated the exposure of adequate active moieties and provide sufficient space to store more discharge products. Moreover, the strong electron redistribution between Ni₅P₄ and NiSe₂ heterojunctions could result in the built-in electric fields, thus greatly facilitating the ORR/OER kinetics. Based on the above merits, the Ni₅P₄@NiSe₂ heterostructure catalyst improved the catalytic performance of Li–O₂ batteries and holds great promise in realizing their practical applications as well as inspiration for the design of other catalytic materials.

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Keywords: Li– O_2 batteries, electrocatalysis, cathode catalysts, Ni₅P₄@NiSe₂ heterostructure, hierarchical porous nanoflowers

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Future perspectives

To counter the excessive depletion of traditional fossil fuels and environmental contamination, exploring new energy storage systems has attracted more and more research interests. Li-O₂ batteries with ultra-high energy density are expected to replace Li-ion batteries in modern applications such as static electricity storage or electric vehicles. However, their poor rate capability, low specific capacities and inferior cycling stability have largely hindered their practical applications. To solve those aforementioned obstacles, designing and constructing efficient cathode electrocatalysts are highly desired, and heterostructured electrocatalysts not only accelerate the interfacial charge transport, but also significantly regulate the adsorption strength to oxygencontaining intermediates, thus boosting the reaction kinetics and enhancing the electrocatalytic performance of Li–O₂ batteries. Therefore, developing heterostructures with fancy architecture is of great importance to the field of electrocatalysis for Li-O₂ batteries and other energy-related devices as well.

1. Introduction

Nowadays, the excessive consumption of fossil energy and serious environmental pollution has drawn our attention to developing energy storage devices with high energy densities [1-3]. It is evident that Li-O₂ batteries hold great potential for nextgeneration battery systems, mainly due to their extra-high theoretical energy density (3500 Wh kg^{-1}), which is related to the reversible redox reaction of $2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$ [4-6]. However, some problems still need to be solved, including low specific capacities, inferior rate capacity, high discharge/charge overpotentials and limited cycle life, which can be generated from the slow reaction kinetics towards oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) processes [7–9]. To overcome these obstacles, numerous researches have been carried out in recent years, in which the construction of efficient electrocatalysts can not only significantly improve the sluggish kinetics towards ORR/OER, but also limit the adverse parasitic reactions [10–12]. In other words, exploiting appropriate catalysts is crucial for improving the performance of Li–O₂ batteries.

Among them, noble metals (Pd, Pt, Au) [13-15] are considered as ideal cathode catalysts to mitigate polarization and improve battery efficiency cycling performance, but the high price and scarcity restrain their large-scale application. Various alternatives have thus been extensively studied in Li-O₂ batteries, such as carbon composites [16–18], alloys [19, 20], transition metal oxides [21–23], nitrides [24–26], sulfides [27-29], carbides [30-32] and phosphide [33-35], etc. Actually, it is well known that carbon materials are too sensitive to generate unwanted by-products, which could largely deteriorate the battery performance. According to recent literature reports, it is universally acknowledged that transition metal compounds are promising catalyst materials for electrical storage and electrocatalytic systems due to their excellent physicochemical properties, including tunable active centers and high catalytic activity. Among the transition metals, Ni element are moderately reserved and more affordable than Co element, and Ni-based compounds exhibit high catalytic activity

when used as redox reaction sites [36, 37]. Most importantly, the presence of Ni³⁺ and Ni²⁺ redox couples could be easily obtained in the catalyst materials, realizing impressive electrocatalytic activities through promoting the formation/ decomposition of Li₂O₂ [38]. Besides, Ni-based compounds have been intensively investigated and evaluated as cathode catalysts of Li-O2 batteries due to the environmental benignity, high chemical and thermal stability, as well as facile fabrication protocols [39-41]. As reported, transition metal selenides typically exhibit superior electrical conductivity due to their exceptional D-electron configuration and suitable energy position, which in turn leads to excellent electrocatalytic performance [42, 43]. Yoo's [44] groups demonstrated that FeSe hollow spheroids delivered excellent stable cycle performance without significant changes in the overpotentials during cycling in Li– O_2 batteries, and the Se O_x on the surfaces of FeSe hollow spheroids contributed to facilitating ORR/OER bifunctional catalytic activities. Notably, transition metal phosphide surface polarization at the phosphorus terminus normally leads to negatively charged phosphorus centers, and the P sites with high electronegativity usually act as proton receptors, which facilitates the adsorption and desorption of intermediate species in oxygen electrocatalysis [35, 45]. For example, Du et al [46] successfully synthesized concave polyhedrons CoP with a high-index facet (211), which presented favorable electrocatalytic ability in Li–O₂ batteries.

Since electrochemical reactions in Li-O2 batteries occur essentially at the three-phase interfaces, surface modifications, including defect engineering, heterogeneous atom doping and heterostructure construction, are proposed to effectively improve catalytic performance. In recent years, heterojunction engineering has received considerable research interests due to its unique physicochemical properties and practicality in designing unique electrocatalysts [47–50]. First, the built-in electric fields at the heterointerfaces could modulate the interfacial electronic structure and promote the reaction kinetics in the ORR/OER processes [51-53]. Besides, due to the high difference of electronegativity between Se (2.55) and P (2.19), the heterojunction interfaces could present two electrical regions of opposite charges [54, 55]. The strongly charged regions of Ni₅P₄ show the potential to optimize the chemisorption of reaction intermediates, and the electrondeficient regions of NiSe2 may act as active sites for continuity and accessibility via electron transfer, thus positively affecting the performance of $Li-O_2$ batteries [56]. The conventional strategies for forming heterogeneous interfaces, however, are generally to employ the epitaxial growth methods in solution, and they cannot be widely applied in practical production due to the complicated processes [57, 58]. Therefore, it remains a challenge to effectively fabricate heterostructured catalysts with rich heterogeneous interfaces.

Herein, nanoflower-like Ni_5P_4 @NiSe₂ heterostructure was prepared and acted as a cathode catalyst for Li–O₂ batteries, which delivered superior specific capacities and extended cycling life, compared with the Ni_5P_4 and $NiSe_2$ counterparts. The improved catalytic activity of the nanoflowerlike Ni_5P_4 @NiSe₂ heterostructure mainly stemmed from the built-in electric fields at the heterojunction interfaces, which effectively enhanced the electrical conductivity and thus improved the slow reaction kinetics in the charge and discharge processes. Moreover, the disordered atomic arrangement and the slight lattice distortion triggered by the Jahn-Teller effect at the heterogeneous interfaces could enable additional active sites to facilitate the regulation of the adsorption of oxygen-containing intermediates, which significantly improving the ORR/OER bifunctional catalytic activity. In addition, the constructed flower-like structure facilitate the construction of three-dimensional (3D) diffusion paths of Li⁺/O₂ and provided sufficient room for the storage of discharge products. These results inspire promising strategies to develop new sufficiently stable electrocatalysts for Li–O₂ batteries.

2. Experimental section

2.1. Fabrication of Ni(OH)₂ precursor

The precursor solution was obtained by dissolving 1 mmol Ni(NO₃)₂·6H₂O, 8 mmol CH₄N₂O and 3 mmol NH₄F into 30 ml of deionized water at room temperature with stirring for 20 min. Then, it was transferred into a 50 ml Teflon-lined stainless-steel autoclave and heated at 120 °C for 24 h. After cooling down to room temperature, the as-prepared Ni(OH)₂ was washed with deionized water and ethanol three times and dried at 50 °C for 12 h in a vacuum oven.

2.2. Synthesis of Ni₅P₄@NiSe₂ nanoflowers

 $Ni_5P_4@NiSe_2$ nanoflowers were prepared by simultaneous phosphorylation and selenization treatment. In brief, its fabrication was carried out in a tube furnace with as-prepared $Ni(OH)_2$ precursor at the downstream and a mixture of Se powder and NaH_2PO_2 at the upstream at 350 °C for 2.5 h with a heating rate of 2 °C min⁻¹ under an Ar atmosphere.

2.3. Materials characterizations

Field-emission scanning electron microscope (FESEM, Hitachi, S-4800, Japan) coupled with energy-dispersive x-ray spectroscope (EDX, Oxford Materials Analysis, UK) and high-resolution transmission electron microscope (HRTEM, JEOL-JEM 2100F, 200 kV, Japan) were used to investigate the morphologies and structures of the samples. The crystalline structures were recorded via x-ray diffraction (XRD, D/Max-IIIC, 36 kV and 20 mA, Japan). The Brunauer-Emmett-Teller (BET) specific surface areas and pore size distribution were examined by nitrogen adsorption/desorption isotherm (BET, Micromeritics ASAP2020). X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+) was collected to characterize the surface chemical states, and all binding energies of the XPS spectra were adjusted by the carbon peak (C 1s) at around 284.8 eV. Exact two-phase ratio of Ni₅P₄@NiSe₂ was obtained by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Agilent-5110, USA).

2.4. Electrochemical measurements

To evaluate the electrochemical performance of the cathode catalysts for Li-O₂ batteries, modified 2032 coin-type cells with holes on the cathode lid were assembled. To prepare the Ni₅P₄@NiSe₂ cathodes, 40 wt % Ni₅P₄@NiSe₂ powder, 40 wt % Ketjen black (KB) and 20 wt % poly-1,1,2,2-tetrafluoroethylene were mixed in 3 ml isopropanol under ultrasonic condition. The slurry was then uniformly dispersed on carbon papers and dried under vacuum at 120 °C for 12 h. The Ni₅P₄ and NiSe₂ cathodes were also prepared by the same method as above for comparison. The Li-O₂ cells were assembled in a glovebox (Mbraun) with the prepared cathodes, Li sheet anodes and glass fiber separators with 1 M lithium bis(trifluoromethanesulfonyl)imide in triethylene glycol dimethyl ether (LTFSI/TEGDME) electrolyte. The electrochemical performance was measured by using a multi-channel cell test system (LAND CT 2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (CHI 660E, frequency region: 10⁵-0.01 Hz, amplitude voltage: 10 mV).

3. Result and discussion

Here, heterostructures can be described as the unique structures that consist of heterointerfaces formed by different materials through chemical or physical combinations. It is evident that the different work function (Φ) of Ni₅P₄ and NiSe₂ are 4.97 and 6.88 eV, respectively [59, 60]. Meanwhile, NiSe₂ presents semiconductor characteristics with a wide band gap energy (E_g) of about 1.96 eV, while Ni₅P₄ shows metallic properties due to the Femi level of Ni₅P₄ passed through the conduction band [61, 62]. Therefore, when they contacted with each other closely, a thermodynamic equilibrium was gained, and a space charge region would be formed, in which electrons were injected from $NiSe_2$ to Ni_5P_4 [63]. And the builtin fields work mechanism of interfacial NiSe2 and Ni5P4 in equilibrium as shown in scheme 1. As a result, the surface of Ni₅P₄@NiSe₂ heterostructure exhibits enriched electron density, and this implies a significant increase in electrical conductivity, which can further improve the electrocatalytic activity of the cell. The synthetic process of the Ni₅P₄@NiSe₂ heterostructure was schematically illustrated in scheme 1, and its fabrication photograph was included in figure S1. First, Ni(NO₃)₂·6H₂O, CH₄N₂O and NH₄F were ultrasonically dispersed in deionized water under stirring, and the precursor of Ni(OH)₂ was achieved after the hydrothermal treatment, evidenced by the data in figure S2. It was then further converted to Ni₅P₄@NiSe₂ heterostructure by a simultaneous phosphorylation and selenization process at 350 °C under the Ar atmosphere for 2.5 h. For comparison, Ni₅P₄ and NiSe₂ nanoflowers were also obtained via the same fabrication route with phosphorylation or selenization, respectively.

It can be observed in figure S3 that the precursors were assembled in a nanoflower-like structure with an average diameter of 5 μ m, consisting of many smooth nanosheets with the thickness of 3–5 nm. Compared with the smooth and granular



Scheme 1. Synthetic procedure for $Ni_5P_4@NiSe_2$ heterostructure.



Figure 1. (a), (b) SEM images, (c) EDS profiles, (d), (e) TEM images with corresponding (f) SAED pattern and (g)–(k) element mapping images of $Ni_5P_4@NiSe_2$ heterostructure.

nanosheets of Ni₅P₄ in figure S4 and NiSe₂ in figure S5, those of the Ni₅P₄@NiSe₂ heterostructure in figures 1(a) and (b) shows smooth surfaces with many nanopores and large available space, which could be conducive to effective electrolyte penetration, boosted mass transfer and effective discharge products accommodation [64–66]. The N₂ adsorption/ desorption isotherms (figure 2(b)) of Ni₅P₄@NiSe₂ heterostructure show the IV-type H3 hysteresis loop. In the observed isotherms, the hysteresis curves exhibit a saturated adsorption plateau, indicating homogeneous pore formation [4, 67]. Its pore size distribution result demonstrates that the pores are mainly mesoporous, which could provide abundant mass diffusion tunnels and expose more active sites for LOBs. The overall molar ratio of $Ni_5P_4/NiSe_2$ is approximately 57/43 according to EDX result in figure 1(c), which is close to those of XPS and ICP-AES results in figure S6. The EDX-elemental mapping images of $Ni_5P_4@NiSe_2$ heterostructure suggest that the Ni, P, and Se elements are uniformly dispersed on the whole architecture.

To further investigate the more detail microstructure of $Ni_5P_4@NiSe_2$ heterostructure, the TEM image in figure 1(d) shows 3D hierarchical porous nanoflower-like morphology,



Figure 2. (a) XRD patterns of different samples; (b) N_2 adsorption-desorption isotherms with the pore size distribution, (c) XPS survey and (f) high-resolution P 2p spectra of $Ni_5P_4@NiSe_2$ heterostructure; XPS high-resolution (d) Ni 2p and (e) Se 3d spectra of $Ni_5P_4@NiSe_2$ and $NiSe_2$ samples.

which is well consistent with the SEM results. In figure 1(e), the lattice fringes with well-defined interfacial distances of 0.223 nm can be clearly described to the spacing of the (210) crystal planes of Ni₅P₄, meanwhile the lattice fringes of approximately 0.299 nm can be consistent with the (200) planes of NiSe₂. Interestingly, figure 1(e) also depicts clear interfacial regions owing to the mismatch of the different phases, and the resulting strong electronic interaction between Ni₅P₄ and NiSe₂ may lead to an increase in the active sites [43, 68, 69]. Figure 1(f) exhibits the corresponding selected area electron diffraction pattern of Ni₅P₄@NiSe₂ heterostructure, which can be unambiguously indexed into (002), (201), (211), (302), (204) planes of the Ni₅P₄ and (200), (211) planes of the NiSe₂, respectively, further demonstrating that Ni₅P₄@NiSe₂ heterostructure was successfully synthesized.

The crystalline structure and phase of Ni₅P₄@NiSe₂, Ni₅P₄ and NiSe₂ were tested by XRD measurement. As depicted in figure 2(a), all diffraction peaks of Ni₅P₄@NiSe₂ heterostructure correspond perfectly to hexagonal Ni₅P₄ (JCPDS. no 18-0883) and cubic NiSe₂ (JCPDS. no 89-3058), which is identical to the HRTEM data. As we all know, electrocatalytic reactions in Li-O₂ batteries generally mainly occur at the three-phase interfaces, and it is thus critical to analyze the surface elemental states of different samples [70]. XPS testing was used to study the bonding configuration and elemental composition of Ni₅P₄@NiSe₂ and NiSe₂. Figure 2(c) reveals the presence of C, O, Ni, P and Se elements on the asprepared Ni₅P₄@NiSe₂ heterostructure. Its Ni 2p spectrum in figure 2(d) shows two spin-orbit peaks, which are assigned to $2p_{3/2}$ and $2p_{1/2}$ signals. Moreover, the peaks can be respectively fitted to Ni^{3+} (855.9 and 873.9 eV), Ni^{2+} (852.7 and 869.8 eV) and the associated satellite (861.1 and 879.6 eV) peaks. Compared with those of pure NiSe₂, the two-orbit doublets in the XPS spectrum of Ni₅P₄@NiSe₂ heterostructure are slightly shifted to negative binding energies [55], which can be attributed to electronic structure changes caused by the interfacial charge redistribution of Ni₅P₄ and NiSe₂. The high-resolution XPS spectrum of Se 3d (figure 2(e)) splits into two-component peaks at about 54.5 and 53.5 eV, related to Se $3d_{3/2}$ and Se $3d_{1/2}$ of Se²⁻. The Se 3d peak of Ni₅P₄@NiSe₂ is normally accompanied by a 58.5 eV characteristic peak assigned to the Se–O bond, confirming that the surfaces of some Se species were oxidized to SeO_x during the synthesis route [44, 66]. As can be seen in the high-resolution XPS spectrum of P 2p in figure 2(f), the peak of Ni₅P₄@NiSe₂ heterostructure at 129.35 eV is ascribed to the Ni–P bond, and the peak at 133.7 eV demonstrates the presence of oxidation on the material surfaces [55, 71].

The electrocatalytic activity of Ni₅P₄@NiSe₂ heterostructure was measured in Li–O₂ batteries placed in a testing box purchased from NJZH (Shenzhen) Scientific Ltd, as displayed in figure S7. CV profiles of Ni₅P₄@NiSe₂, Ni₅P₄, NiSe₂ and pure KB cathodes within 2.35–4.5 V at 0.15 mV s⁻¹ are depicted in figure 3(a). The Ni₅P₄@NiSe₂ cathode exhibits the highest ORR/OER current densities, proving that it can significantly promote the electrocatalytic reaction kinetics. Specifically, the Ni₅P₄@NiSe₂ cathode distinctly exhibits two negative peaks for OER, which are attributed to the different decomposition stages of discharge products [72–74]. It is proposed that the peak at ~4.2 V is attributed to the delithiation process of Li₂O₂ (Li₂O₂ \rightarrow Li_{2-x}O₂ + x Li⁺ + x e⁻), while the lower peak at 3.78 V is ascribed to a further delithiation process (Li_{2-x}O₂ \rightarrow O₂ + (2 - x) Li⁺ + (2 - x) e⁻) [7, 8].

The discharge/charge plots of $\text{Li}-\text{O}_2$ batteries based on various cathodes were tested at the current density of 100 mA g⁻¹ with the voltage range of 2.35–4.5 V



Figure 3. (a) CV curves, (b) initial discharge/charge profiles, (c) rate capability and (e) cycling performance of different cathodes; (d) rate performance and (g) cycling stability with (f) corresponding typical discharge/charge profiles of the Ni_5P_4 @NiSe₂ cathode.

versus Li⁺/Li. It is apparent in figure S8 that the initial discharge/charge specific capacities of carbon paper cathodes are negligible, which proves their contribution mainly comes from the active materials. As presented in figure 3(b), the Ni₅P₄@NiSe₂ cathode exhibits the largest discharge/charge capacities of 19 090/19 031 mAh g^{-1} at 100 mA g^{-1} , while those of Ni₅P₄, NiSe₂ and pure KB cathodes are 16 831.5/14 153.5, 12 469.5/12 284 and 6689.75/5519.25 mAh g^{-1} , respectively, with corresponding columbic efficiencies of 99.7%, 84.1%, 98.5% and 82.5%, illustrate superior eletrocatalytic activities of composite cathode. Moreover, the discharge/charge potentials of Ni₅P₄@NiSe₂ cathode are about 2.74/4.20 V with the overpotentials of 0.20/1.26 V, respectively, which are significantly lower than those of Ni_5P_4 (0.25/1.42 V), $NiSe_2$ (0.20/1.45 V) and pure KB (0.32/1.47 V) counterparts. Figure 3(c) shows the rate performance of Ni₅P₄@NiSe₂, Ni₅P₄, NiSe₂ and pure KB cathodes under different current densities with the cutoff capacity of 1000 mAh g⁻¹. It can be seen that at current densities of 100, 200, 400, 800, 1000 and 100 mA g^{-1} , the Ni₅P₄@NiSe₂ cathode exhibits the largest/lowest terminal discharge/charge voltages. When the current density returns to 100 mA g^{-1} , the terminal voltages remained almost unchanged compared to the initial values. Those differences in electrochemical properties demonstrate that the built-in electric fields with charge redistribution on heterostructure could improve the electrical conductivity of the cathode catalyst materials, thus effectively facilitating the formation and decomposition of discharge products [69]. In addition, the disordered atomic arrangement and the slight lattice distortion triggered by the Jahn-Teller effect at the heterogeneous interfaces could increase the reaction activity centers to boost electrocatalytic reactions [75–77]. It is thus concluded that the synergy of these two factors endowed the heterostructure cathodes excellent electrocatalytic performance. Figure 3(d) further shows the rate capability of Ni₅P₄@NiSe₂ cathodes at different current densities under the voltage window of 2.35-4.5 V, and the pure KB cathode (figure S9) was also tested under the same conditions. As the current densities increased from 100 to 800 mA g^{-1} , the ORR/OER overpotentials of Ni₅P₄@NiSe₂ cathode increased to 0.20/1.45 V, and impressive discharge/charge specific capacities of 19 090/19 031, 18 026/17 802, 16 620/15 788 and 14 379/12 844 mAh g^{-1} at the current densities of 100, 200, 400 and 800 mA g^{-1} were also yielded, respectively. Moreover, the voltage platforms in the galvanostatic ORR/OER profiles of the Ni₅P₄@NiSe₂ cathodes match well with the peaks of CV curves.

The cycle stability of different cathodes were evaluated with the fixed capacity of 1000 mAh g⁻¹ at 200 mA g⁻¹, as shown in figure 3(e). The terminal discharge/charge plots of Ni₅P₄@NiSe₂ cathode was the most stable during cycling and can be effectively cycled up to 128 cycles, while those of Ni₅P₄, NiSe₂ and pure KB cathodes dropped down quickly after 64, 28 and 20 cycles, respectively. Moreover, the excellent cycling performance of 202 cycles at a lower limiting capacity of 600 mAh g⁻¹ with 100 mA g⁻¹ was



Figure 4. (a) XRD patterns, (b) EIS plots, (c) initial discharge/charge plots with (d)–(f) corresponding high-resolution Li 1s spectra and (g)–(i) FESEM images of Ni_5P_4 @NiSe₂ cathodes at different states.

also included in figure 3(f). Table S1 shows a comparison of the battery performance in this work with previously reported similar counterparts. It can be well noticed that the Ni₅P₄@NiSe₂ cathode exhibits long cycle stability and ultra-high discharge specific capacities, compared to those of transition metal phosphide and selenide cathodes. It is believed that the nanoflower-like Ni₅P₄@NiSe₂ heterostructure with more free space and nanopores could construct a large amount of 3D channels for the fast Li⁺/O₂ transport. Additionally, the built-in electric fields between Ni₅P₄ and NiSe₂ can largely improve the slow redox kinetics of the cathode reactions, resulting in excellent electrochemical performance of Li–O₂ batteries.

To explain the formation/decomposition mechanism and reason for the excellent electrocatalytic performance of Ni₅P₄@NiSe₂ cathodes, *ex-situ* XRD, XPS and EIS at different stages during cycling were characterized. Figure 4(a) shows the XRD patterns of the Ni₅P₄@NiSe₂ cathode at different stages, where two new diffraction peaks located at 32.9 and 35.0° after first discharging, indexed to (100) and (101) planes of Li₂O₂ (JCPDS. no 09-0355), respectively, and those of the fresh carbon paper cathode was also given in figure S10 for comparison. After 1st and 60th recharging, the diffraction peaks of Li₂O₂ fully disappeared, and almost no peaks of high crystalline by-products were traced. Meanwhile, EIS testing was carried out to measure the intrinsic kinetics characteristic at different discharge/charge stages. Typically, the EIS diagram contains two parts, the semicircle at high-frequency is associated with charge-transfer resistance (R_{ct}) , and the diagonal line at low-frequency is related to the ion diffusion properties. The date was fitted using the equivalent series circuit (inset of figure 4(b)). As shown in figure 4(b), the semicircles in the Ni₅P₄@NiSe₂-based cell were greatly enlarged from 14.5 to 82.5 Ω after first discharging, mainly due to the coverage and accumulation of insulating Li_2O_2 [18, 23]. Besides, it also shows that after first recharging and even after 100 cycles of prolonged cycling, the R_{ct} of Ni₅P₄@NiSe₂ cathode is close to its initial stage, demonstrating that the discharge products were almost decomposed. To further shed light on the composition of discharge products on Ni₅P₄@NiSe₂ cathode, ex situ XPS experiments were studied, and the discharge/charge profiles with corresponding selected states are listed in figures 4(c)-(f). For discharged figure 4(e) relative to the initial stage, indicates that the main discharge products were Li₂O₂ and almost no by-products generation at this stage. After recharging (figure 4(f)), this peak no longer appeared, whereas the Se $3d_{3/2}$ and Se $3d_{1/2}$ peaks of the pristine cathode (figure 4(d)) can be detected at 54.5 and 53.5 eV. Those results further explain the ultra-long cycle life and stable cycling performance of Ni₅P₄@NiSe₂ cathodes.

According to previous reports in the literature, the morphology of Li_2O_2 plays an essential role in affecting the subsequent charging process. Whether discharge products Li_2O_2 formed film- or disc-shaped was controlled by the adsorption energy of LiO_2 . The disc-shaped Li_2O_2 grew through the solution growth model due to the weak adsorption energy

of the LiO₂ intermediate, while the film-shaped Li₂O₂ was formed via a surface mechanism with strong adsorption energy of LiO_2 . As can be seen in figure 4(h), the surfaces of the Ni₅P₄@NiSe₂ cathode were covered with film-like discharge products with great contact after being fully discharged distinct different from that at the fresh stage in figure 4(g). It is noteworthy that the evenly deposited film-like discharge products could facilitate the establishment of a good contact interface with the Ni₅P₄@NiSe₂ cathode, which can make fully utilized of active centers and maximize the synergistic effect between Ni₅P₄, NiSe₂ and the heterogeneous interfaces [7]. At the following recharging in figure 4(i), the film-like discharge products completely disappeared, showing almost the same nanoflower-like morphology as initial appearance, indicting the excellent reversibility of Li-O2 batteries with Ni₅P₄@NiSe₂ cathodes.

Based on the above results, the superior electrocatalytic performance of Ni₅P₄@NiSe₂ cathodes would be attributed to their unique architecture. The 3D nanoflower-like structure with self-assembled nanosheets not only promoted the diffusion of O₂/Li⁺ throughout the cathode, but also provided sufficient active sites for storing the discharge products. Besides, the excellent electrical conductivity of the heterostructure can accelerate the charge transfer during the charge/discharge processes and enhance the electrochemical reaction kinetics [78, 79]. More importantly, the unique heterostructure shows a significant effect on the electron redistribution and disordered atomic arrangement, which can provide additional active sites to improve the ORR/OER bifunctional catalytic activity [66]. Additionally, the Ni₅P₄ and NiSe₂ heterostructure can modulate the growth pathway of Li₂O₂ and induce their tight coating with low crystallinity structure along the 3D selfassembled nanosheets, building homogeneous low-impedance cathode/Li₂O₂ interfaces and promoting the efficient formation/decomposition of Li₂O₂ [80]. The possible formation/ decomposition mechanisms of the Li2O2 on the Ni5P4@NiSe2 cathode are shown in figure S11. First, O2(sol) was adsorbed to the active sites to form adsorbed oxygen $(O_2^*, * represents)$ surface adsorbed species) based on equation (1):

$$O_2$$
 + surface active sites $\rightarrow O_2^*$. (1)

Second, O_2^* captured one electron and reacted with Li⁺ to generate LiO₂* based on equation (2):

$$O_2^* + e^- + Li^+ \to LiO_2^*.$$
 (2)

Third, $Li_2O_2^*$ was formed by electrochemical reduction of LiO_2^* based on equation (3):

$$LiO_2^* + e^- + Li^+ \to Li_2O_2^*.$$
 (3)

4. Conclusion

In summary, the nanoflower-like $Ni_5P_4@NiSe_2$ heterostructure was successfully synthesized via hydrothermal method combining simultaneous phosphating/selenization treatment. The 3D hierarchical porous structure of $Ni_5P_4@NiSe_2$ heterostructure can facilitate barrier-free Li⁺/O₂ transport and provide sufficient specific surface area for the storage of discharge products. Moreover, the unique heterostructure shows a significant effect on the electron redistribution and disordered atomic arrangement, which can provide additional active sites to perfect the ORR/OER bifunctional catalytic activity. The Ni₅P₄@NiSe₂ cathode delivered superior electrochemical performance, including an ultra-high discharge/charge specific capacity of 19 090/19 031 mAh g⁻¹ and extended cycling life of 202 cycles at 100 mA g⁻¹. The above results demonstrate that interfacial electron structure modulation by the construction of the heterogeneous structure with rational architecture design is a promising way of developing highly-efficient bifunctional electrode materials, which can also be expected to be employed in other energy catalytic applications.

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Conflict of interest

The authors declare no conflict of interest.

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References

- Asadi M et al 2018 A lithium-oxygen battery with a long cycle life in an air-like atmosphere Nature 555 502–6
- [2] Liu Q C, Liu T, Liu D P, Li Z J, Zhang X B and Zhang Y 2016 A flexible and wearable lithium-oxygen battery with record energy density achieved by the interlaced architecture inspired by bamboo slips *Adv. Mater.* 28 8413–8
- [3] Qiao Y, Wang Q F, Mu X W, Deng H, He P, Yu J H and Zhou H S 2019 Advanced hybrid electrolyte Li–O₂ battery realized by dual superlyophobic membrane *Joule* 3 2986–3001
- [4] Xia Q et al 2021 MnCo₂S₄-CoS_{1.097} heterostructure nanotubes as high efficiency cathode catalysts for stable and long-life lithium-oxygen batteries under high current conditions Adv. Sci. 8 2103302
- [5] Ran Z Q, Shu C Z, Hou Z Q, Cao L J, Liang R X, Li J B, Hei P, Yang T S and Long J P 2020 Ni₃Se₂/NiSe₂ heterostructure nanoforests as an efficient bifunctional electrocatalyst for high-capacity and long-life Li–O₂ batteries J. Power Sources 468 228308
- [6] Hu A J et al 2020 Heterostructured NiS₂/ZnIn₂S₄ realizing toroid-like Li₂O₂ deposition in lithium-oxygen batteries with low-donor-number solvents ACS Nano 14 3490–9

- [7] Li D Y et al 2022 CoS₂ nanoparticles anchored on MoS₂ nanorods as a superior bifunctional electrocatalyst boosting Li₂O₂ heteroepitaxial growth for rechargeable Li–O₂ batteries Small 18 2105752
- [8] Liu X M, Zhao L L, Xu H R, Huang Q S, Wang Y Q, Hou C X, Hou Y Y, Wang J, Dang F and Zhang J T 2020 Tunable cationic vacancies of cobalt oxides for efficient electrocatalysis in Li–O₂ batteries *Adv. Energy Mater.* 10 2001415
- [9] Gu T H, Agyeman D A, Shin S J, Jin X, Lee J M, Kim H, Kang Y M and Hwang S J 2018 α-MnO₂ nanowire-anchored highly oxidized cluster as a catalyst for Li–O₂ batteries: superior electrocatalytic activity and high functionality *Angew. Chem., Int. Ed. Engl.* 57 15984–9
- [10] He B, Wang J, Fan Y Q, Jiang Y L, Zhai Y J, Wang Y, Huang Q S, Dang F, Zhang Z D and Wang N 2018 Mesoporous CoO/Co–N–C nanofibers as efficient cathode catalysts for Li–O₂ batteries *J. Mater. Chem.* A 6 19075–84
- [11] Hou Y, Wang J, Hou C X, Fan Y, Zhai Y J, Li H Y, Dang F and Chou S L 2019 Oxygen vacancies promoting the electrocatalytic performance of CeO₂ nanorods as cathode materials for Li–O₂ batteries J. Mater. Chem. A 7 6552–61
- [12] Sennu P, Park H S, Park K U, Aravindan V, Nahm K S and Lee Y S 2017 Formation of NiCo₂O₄ rods over Co₃O₄ nanosheets as efficient catalyst for Li–O₂ batteries and water splitting *J. Catal.* **349** 175–82
- [13] Liu X M, Huang Q S, Wang J, Zhao L L, Xu H R, Xia Q, Li D Y, Qian L, Wang H S and Zhang J 2021 *In-situ* deposition of Pd/Pd₄S heterostructure on hollow carbon spheres as efficient electrocatalysts for rechargeable Li–O₂ batteries *Chin. Chem. Lett* **32** 2086–90
- [14] Zhao W, Wang J, Yin R, Li B, Huang X S, Zhao L and Qian L 2020 Single-atom Pt supported on holey ultrathin g-C₃N₄ nanosheets as efficient catalyst for Li–O₂ batteries *J. Colloid Interface Sci.* 564 28–36
- [15] Wang P, Li C X, Dong S H, Ge X L, Zhang P, Miao X G, Zhang Z W, Wang C X and Yin L W 2019 One-step route synthesized Co₂P/Ru/N-doped carbon nanotube hybrids as bifunctional electrocatalysts for high-performance Li–O₂ batteries *Small* 15 1900001
- [16] Wang J, Liu L L, Chou S L, Liu H K and Wang J Z 2017 A 3D porous nitrogen-doped carbon-nanofiber-supported palladium composite as an efficient catalytic cathode for lithium–oxygen batteries J. Mater. Chem. A 5 1462–71
- [17] Xu H R, Zhao L L, Liu X M, Li D Y, Xia Q, Cao X Y, Wang J, Zhang W B, Wang H S and Zhang J T 2021 CoMoP₂ nanoparticles anchored on N, P doped carbon nanosheets for high-performance lithium-oxygen batteries *FlatChem* 25 100221
- [18] Zhai Y J *et al* 2019 Highly efficient cobalt nanoparticles anchored porous N-doped carbon nanosheets electrocatalysts for Li–O₂ batteries *J. Catal.* **377** 534–42
- [19] Leng L M, Li J, Zeng X Y, Song H Y, Shu T, Wang H S and Liao S L 2017 Enhancing the cyclability of Li–O₂ batteries using PdM alloy nanoparticles anchored on nitrogen-doped reduced graphene as the cathode catalyst *J. Power Sources* 337 173–9
- [20] Li K, Dong H Y, Wang Y W, Yin Y H and Yang S T 2020 Preparation of low-load Au–Pd alloy decorated carbon fibers binder-free cathode for Li–O₂ battery *J. Colloid Interface Sci.* 579 448–54
- [21] Yao W T *et al* 2019 Tuning Li₂O₂ formation routes by facet engineering of MnO₂ cathode catalysts *J. Am. Chem. Soc.* 141 12832–8
- [22] Yang Z D, Chang Z W, Xu J J, Yang X Y and Zhang X B 2017 CeO₂@NiCo₂O₄ nanowire arrays on carbon textiles as high performance cathode for Li–O₂ batteries *Sci. China Chem.* 60 1540–5

- [23] Zhao W, Li X M, Yin R, Qian L, Huang X S, Liu H, Zhang J X, Wang J, Ding T and Guo Z H 2018 Urchin-like NiO–NiCo₂O₄ heterostructure microsphere catalysts for enhanced rechargeable non-aqueous Li–O₂ batteries *Nanoscale* 11 50–59
- [24] Guo Z Y, Wang F M, Li Z J, Yang Y, Tamirat A G, Qi H C, Han J S, Li W, Wang L and Feng S H 2018 Lithiophilic Co/Co₄N nanoparticles embedded in hollow N-doped carbon nanocubes stabilizing lithium metal anodes for Li-air batteries J. Mater. Chem. A 6 22096–105
- [25] Xu S M et al 2016 Toward lower overpotential through improved electron transport property: hierarchically porous CoN nanorods prepared by nitridation for lithium-oxygen batteries Nano Lett. 16 5902–8
- [26] Dong S M et al 2011 Molybdenum nitride based hybrid cathode for rechargeable lithium-O₂ batteries Chem. Commun. 47 11291–3
- [27] Shombe G B, Khan M D, Choi J, Gupta R K, Opallo M and Revaprasadu N 2022 Tuning composition of CuCo₂S₄-NiCo₂S₄ solid solutions via solvent-less pyrolysis of molecular precursors for efficient supercapacitance and water splitting *RSC Adv.* **12** 10675–85
- [28] Dou Y Y, Lian R Q, Zhang Y T, Zhao Y Y, Chen G, Wei Y J and Peng Z Q 2018 Co₉S₈@carbon porous nanocages derived from a metal–organic framework: a highly efficient bifunctional catalyst for aprotic Li–O₂ batteries *J. Mater. Chem.* A 6 8595–603
- [29] Hou Z Q, Feng S, Hei P, Yang T S, Ran Z Q, Zheng R X, Liao X, Shu C Z and Long J P 2019 Morphology regulation of Li₂O₂ by flower-like ZnCo₂S₄ enabling high performance Li–O₂ battery J. Power Sources 441 227168
- [30] Jiao W C, Su Q M, Ge J J, Dong S J, Wang D, Zhang M, Ding S K, Du G H and Xu B S 2021 Mo₂C quantum dots decorated ultrathin carbon nanosheets self-assembled into nanoflowers toward highly catalytic cathodes for Li–O₂ batteries *Mater. Res. Bull.* 133 111020
- [31] Lai Y Q, Jiao Y F, Song J X, Zhang K, Li J and Zhang Z A 2018 Fe/Fe₃C@graphitic carbon shell embedded in carbon nanotubes derived from Prussian blue as cathodes for Li–O₂ batteries *Mater. Chem. Front.* 2 376–84
- [32] Liu C J, Qiu Z, Brant W R, Younesi R, Ma Y, Edström K, Gustafsson T and Zhu J 2018 A free standing Ru-TiC nanowire array/carbon textile cathode with enhanced stability for Li–O₂ batteries *J. Mater. Chem.* A 6 23659–68
- [33] Huang H B, Luo S H, Liu C L, Yi T F and Zhai Y C 2018 High-surface-area and porous Co₂P nanosheets as cost-effective cathode catalysts for Li–O₂ batteries ACS Appl. Mater. Interfaces 10 21281–90
- [34] Hou Z Q, Shu C Z, Hei P, Yang T S, Zheng R X, Ran Z Q and Long J P 2020 A 3D free-standing Co doped Ni₂P nanowire oxygen electrode for stable and long-life lithium-oxygen batteries *Nanoscale* 12 6785–94
- [35] Ran Z Q, Shu C Z, Hou Z Q, Zhang W B, Yan Y, He M and Long J P 2021 Modulating electronic structure of honeycomb-like Ni₂P/Ni₁₂P₅ heterostructure with phosphorus vacancies for highly efficient lithium-oxygen batteries *Chem. Eng. J.* **413** 127404
- [36] Liu G X, Zhang L, Wang S Q, Ding L X and Wang H H 2017 Hierarchical NiCo₂O₄nanosheets on carbon nanofiber films for high energy density and long-life Li–O₂ batteries *J. Mater. Chem.* A 5 14530–6
- [37] Li J B, Shu C Z, Liu C H, Chen X F, Hu A J and Long J P 2020 Rationalizing the effect of oxygen vacancy on oxygen electrocatalysis in Li–O₂ battery *Small* 16 2001812
- [38] Wang L J *et al* 2016 Facile synthesis of flower-like hierarchical NiCo₂O₄ microspheres as high-performance cathode materials for Li–O₂ batteries *RSC Adv.* 6 98867–73

- [39] Li B, Zheng M B, Xue H G and Pang H 2016 High performance electrochemical capacitor materials focusing on nickel based materials *Inorg. Chem. Front.* 3 175–202
- [40] Zhang L Y, Shi D W, Liu T, Jaroniec M and Yu J G 2019 Nickel-based materials for supercapacitors *Mater. Today* 25 35–65
- [41] Zhao C L, Lu Y X, Chen L Q and Hu Y S 2019 Ni-based cathode materials for Na-ion batteries *Nano Res.* 12 2018–30
- [42] Wen X J, Ran Z Q, Zheng R X, Du D Y, Zhao C, Li R J, Xu H Y, Zeng T and Shu C Z 2022 NiSe₂@NiO heterostructure with optimized electronic structure as efficient electrocatalyst for lithium-oxygen batteries *J. Alloys Compd.* **901** 163703
- [43] Yu J, Tian Y M, Lin Z W, Liu Q, Liu J Y, Chen R R, Zhang H S and Wang J 2021 NiSe₂/Ni₅P₄ nanosheets on nitrogen-doped carbon nano-fibred skeleton for efficient overall water splitting *Colloids Surf.* A 614 126189
- [44] Yoo H, Lee G H and Kim D W 2021 FeSe hollow spheroids as electrocatalysts for high-rate Li–O₂ battery cathodes *J. Alloys Compd.* 856 158269
- [45] Yan Y T, Lin J H, Bao K, Xu T X, Qi J L, Cao J, Zhong Z X, Fei W D and Feng J C 2019 FeSe hollow spheroids as electrocatalysts for high-rate Li–O₂ battery cathodes J. Colloid Interface Sci. 552 332–6
- [46] Du D Y, Wang L, Zheng R X, Li M L, Ran Z Q, Ren L F, He M, Yan Y and Shu C Z 2021 Surface atomic modulation of CoP bifunctional catalyst for high performance Li–O₂ battery enabled by high-index (2 1 1) facets J. Colloid Interface Sci. 601 114–23
- [47] Yan Y, Ran Z Q, Zeng T, Wen X J, Xu H Y, Li R J, Zhao C and Shu C Z 2022 Interfacial electron redistribution of hydrangea-like NiO@Ni₂P heterogeneous microspheres with dual-phase synergy for high-performance lithium-oxygen battery *Small* 18 2106707
- [48] Veeramani V, Chen Y H, Wang H C, Hung T F, Chang W S, Wei D H, Hu S F and Liu R S 2018 CdSe/ZnS QD@CNT nanocomposite photocathode for improvement on charge overpotential in photoelectrochemical Li–O₂ batteries *Chem. Eng. J.* 349 235–40
- [49] Zhu G J, Guo R, Luo W, Liu H K, Jiang W, Dou S X and Yang J 2021 Boron doping-induced interconnected assembly approach for mesoporous silicon oxycarbide architecture *Natl Sci. Rev.* 8 152
- [50] Wang T Z, Cao X J and Jiao L F 2021 Ni₂P/NiMoP heterostructure as a bifunctional electrocatalyst for energy-saving hydrogen production *eScience* 1 69–74
- [51] Xu J J, Wang Z L, Xu D, Zhang L L and Zhang X B 2013 Tailoring deposition and morphology of discharge products towards high-rate and long-life lithium-oxygen batteries *Nat. Commun.* 4 2438
- [52] Xu S M, Liang X, Liu X, Bai W L, Liu Y S, Cai Z P, Zhang Q, Zhao C, Wang K X and Chen J S 2020 Surface engineering donor and acceptor sites with enhanced charge transport for low-overpotential lithium–oxygen batteries *Energy Storage Mater.* 25 52–61
- [53] Cheng H, Xie J, Cao G S, Lu Y H, Zheng D, Jin Y, Wang K Y and Zhao X B 2019 Realizing discrete growth of thin Li₂O₂ sheets on black phosphorus quantum dots-decorated δ-MnO₂ catalyst for long-life lithium-oxygen cells *Energy Storage Mater.* 23 684–92
- [54] Liu C C, Gong T, Zhang J, Zheng X R, Mao J, Liu H, Li Y and Hao Q Y 2020 Engineering Ni₂P-NiSe₂ heterostructure interface for highly efficient alkaline hydrogen evolution *Appl. Catal.* B 262 118245
- [55] Yang J, Yang N, Xu Q, Pearlie L S, Zhang Y Z, Hong Y, Wang Q, Wang W J, Yan Q Y and Dong X C 2019 Bioinspired controlled synthesis of NiSe/Ni₂P nanoparticles

decorated 3D porous carbon for Li/Na ion batteries ACS Sustain. Chem. Eng. 7 13217–25

- [56] Cui X H, Luo Y N, Zhou Y, Dong W H and Chen W 2021 Application of functionalized graphene in Li–O₂ batteries *Nanotechnology* **32** 132003
- [57] Yang Y, Zhang T, Wang X C, Chen L F, Wu N, Liu W, Lu H L, Xiao L, Fu L and Zhuang L 2016 Tuning the morphology and crystal structure of Li₂O₂: a graphene model electrode study for Li–O₂ battery ACS Appl. Mater. Interfaces 8 21350–7
- [58] Ye S F, Wang L F, Liu F F, Shi P C and Yu Y 2021 Integration of homogeneous and heterogeneous nucleation growth via 3D alloy framework for stable Na/K metal anode *eScience* 1 75–82
- [59] Ni S, Qu H N, Xu Z H, Zhu X Y, Xing H F, Wang L, Yu J M, Liu H Z, Chen C M and Yang L R 2021 Interfacial engineering of the NiSe₂/FeSe₂ p-p heterojunction for promoting oxygen evolution reaction and electrocatalytic urea oxidation *Appl. Catal.* B 299 120638
- [60] Feng C J, Wang Y N, Lu Z W, Liang Q, Zhang Y Z, Li Z Y and Xu S 2022 Nanoflower Ni₅P₄ coupled with GCNQDs as Schottky junction photocatalyst for the efficient degradation of norfloxacin Sep. Purif. Technol. 282 120107
- [61] Liu X, Zhao Y X, Yang X F, Liu Q Q, Yu X H, Li Y Y, Tang H and Zhang T R 2020 Porous Ni₅P₄ as a promising cocatalyst for boosting the photocatalytic hydrogen evolution reaction performance *Appl. Catal.* B 275 119144
- [62] Zhang X, Cheng Z W, Deng P H, Zhang L P and Hou Y 2021 NiSe₂/Cd_{0.5}Zn_{0.5}S as a type-II heterojunction photocatalyst for enhanced photocatalytic hydrogen evolution *Int. J. Hydrog. Energy* **46** 15389–97
- [63] Li S Z, Zang W J, Liu X M, Pennycook S J, Kou Z K, Yang C H, Guan C and Wang J 2019 Heterojunction engineering of MoSe₂/MoS₂ with electronic modulation towards synergetic hydrogen evolution reaction and supercapacitance performance *Chem. Eng. J.* 359 1419–26
- [64] He B et al 2020 Superassembly of porous Fe_{tet}(NiFe)_{oct}O frameworks with stable octahedron and multistage structure for superior lithium-oxygen batteries Adv. Energy Mater. 10 1904262
- [65] Li G Y, Li N, Peng S T, He B, Wang J, Du Y, Zhang W B, Han K and Dang F 2020 Highly efficient Nb₂C MXene cathode catalyst with uniform O-terminated surface for lithium-oxygen batteries Adv. Energy Mater. 11 20022721
- [66] Zhang G L, Li G Y, Wang J, Tong H, Wang J C, Du Y, Sun S H and Dang F 2022 2D SnSe cathode catalyst featuring an efficient facet-dependent selective Li₂O₂ growth/decomposition for Li–oxygen batteries Adv. Energy Mater. 12 2103910
- [67] Zhao X J *et al* 2021 Favorable anion adsorption/desorption of high rate NiSe₂ nanosheets/hollow mesoporous carbon for battery-supercapacitor hybrid devices *Nano Res.* 14 2574–83
- [68] Xie H, Chen M and Wu L 2019 Hierarchical nanostructured NiS/MoS₂/C composite hollow spheres for high performance sodium-ion storage performance ACS Appl. Mater. Interfaces 11 41222–8
- [69] Yang Y, Kang Y K, Zhao H H, Dai X P, Cui M, Luan X B, Zhang X, Nie F, Ren Z T and Song W Y 2019 An interfacial electron transfer on tetrahedral NiS₂/NiSe₂ heterocages with dual-phase synergy for efficiently triggering the oxygen evolution reaction *Small* 16 1905083
- [70] Xia Q et al 2022 Recent advances in heterostructured cathodic electrocatalysts for non-aqueous Li–O₂ batteries Chem. Sci. 13 2841–56
- [71] Zhou Q *et al* 2022 Engineering in-plane nickel phosphide heterointerfaces with interfacial sp H-P hybridization for

highly efficient and durable hydrogen evolution at 2 A cm^{-2} *Small* **18** 2105642

- [72] Huang H C, Cheng C J, Zhang G L, Guo L, Li G Y, Pan M, Dang F and Mai X M 2022 Surface phosphatization for a sawdust-derived carbon catalyst as kinetics promoter and corrosion preventer in lithium-oxygen batteries Adv. Funct. Mater. 32 2111546
- [73] Wang Y, Li N, Hou C X, He B, Li J J, Dang F, Wang J and Fan Y Q 2020 Nanowires embedded porous TiO₂@C nanocomposite anodes for enhanced stable lithium and sodium ion battery performance *Ceram. Int.* 46 9119–28
- [74] Dang C C, Wang Y, He B, Zhang W B, Dang F, Wang H C and Du Y 2020 Novel MoSi₂ catalysts featuring surface activation as highly efficient cathode materials for long-life Li–O₂ batteries *J. Mater. Chem.* A 8 259–67
- [75] Liang R X, Shu C Z, Hu A J, Li M L, Ran Z Q, Zheng R X and Long J P 2020 Interface engineering induced selenide lattice distortion boosting catalytic activity of heterogeneous CoSe₂@NiSe₂ for lithium-oxygen battery *Chem. Eng. J.* **393** 124592

- [76] Jin Y C, Liu Y, Song L, Yu J H, Li K R, Zhang M D and Wang J L 2022 Interfacial engineering in hollow NiS₂/FeS₂-NSGA heterostructures with efficient catalytic activity for advanced Li–CO₂ battery *Chem. Eng. J.* 430 133029
- [77] Wang W X, Xiong F Y, Zhu S H, Chen J H, Xie J and An Q Y 2022 Defect engineering in molybdenum-based electrode materials for energy storage eScience 2 278–94
- [78] Zhang F Z, Ma Y Y, Jiang M M, Luo W and Yang J P 2022 Boron heteroatom-doped silicon–carbon peanut-like composites enables long life lithium-ion batteries *Rare Met.* 41 1276–83
- [79] Zhang F Z, Sherrell P C, Luo W, Chen J, Li W, Yang J P and Zhu M F 2021 Organic/inorganic hybrid fibers: controllable architectures for electrochemical energy applications *Adv. Sci.* 8 2102859
- [80] Li D Y, Zhao L L, Xia Q, Wang J, Liu X M, Xu H R and Chou S L 2021 Activating MoS₂ nanoflakes via sulfur defect engineering wrapped on CNTs for stable and efficient Li–O₂ batteries Adv. Funct. Mater. **32** 2108153