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

Xue Han¹, Yanjie Liang¹, Lanling Zhao², Jun Wang¹,* Qing Xia¹, Deyuan Li¹, Yao Liu¹,* Zhaorui Zhou¹, Yuxin Long¹, Yebing Li¹, Yiming Zhang¹ and Shulei Chou¹,*

¹ Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, People’s Republic of China
² School of Physics, Shandong University, Jinan 250061, People’s Republic of China
³ Institute for Carbon Neutralization, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, People’s Republic of China

E-mail: jw707@sdu.edu.cn, liuyao@sdu.edu.cn and chou@wzu.edu.cn

Received 19 June 2022, revised 10 July 2022
Accepted for publication 15 July 2022
Published 8 August 2022

Abstract
The remarkably high theoretical energy densities of Li–O₂ 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 Li–O₂ 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.

Supplementary material for this article is available online

Keywords: Li–O₂ batteries, electrocatalysis, cathode catalysts, Ni₅P₄@NiSe₂ heterostructure, hierarchical porous nanoflowers

* Authors to whom any correspondence should be addressed.

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
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–O\(_2\) 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 these 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 oxygen-containing intermediates, thus boosting the reaction kinetics and enhancing the electrocatalytic performance of Li–O\(_2\) batteries. Therefore, developing heterostructures with fancy architecture is of great importance to the field of electrocatalysis for Li–O\(_2\) 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–O\(_2\) batteries hold great potential for next-generation 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\(_2\) ↔ Li\(_2\)O\(_2\) [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 OER and ORR, but also limit the adverse parasitic reactions [10–12]. In other words, exploiting appropriate catalysts is crucial for improving the performance of Li–O\(_2\) 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–O\(_2\) 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 Ni\(^{3+}\) and Ni\(^{2+}\) redox couples could be easily obtained in the catalyst materials, realizing impressive electrocatalytic activities through promoting the formation/decomposition of Li\(_2\)O\(_2\) [38]. Besides, Ni-based compounds have been intensively investigated and evaluated as cathode catalysts of Li–O\(_2\) 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 SeO\(_2\) on the surfaces of FeSe hollow spheroids contributed to facilitating ORR/OER bifunctional catalytic activities. Notably, transition metal phosphate 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–O\(_2\) batteries.

Since electrochemical reactions in Li–O\(_2\) 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 S (2.55) and P (2.19), the heterojunction interfaces could present two electrical regions of opposite charges [54, 55]. The strongly charged regions of Ni\(_3\)P\(_4\) show the potential to optimize the chemisorption of reaction intermediates, and the electron-deficient regions of NiSe\(_2\) 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\(_3\)P\(_4\)@NiSe\(_2\) heterostructure was prepared and acted as a cathode catalyst for Li–O\(_2\) batteries, which delivered superior specific capacities and extended cycling life, compared with the Ni\(_3\)P\(_4\) and NiSe\(_2\) counterparts. The improved catalytic activity of the nanoflower-like Ni\(_3\)P\(_4\)@NiSe\(_2\) 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 facilitated 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 Ni5P2@NiSe2 nanoflowers

Ni5P2@NiSe2 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 NaH2PO2 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 spectroscopy (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 Ni5P2@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 Ni5P2@NiSe2 cathodes, 40 wt % Ni5P2@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 Ni5P2 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 (LTF5/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 Ni5P2 and NiSe2 are 4.97 and 6.88 eV, respectively [59, 60]. Meanwhile, NiSe2 presents semiconductor characteristics with a wide band gap energy (Eg) of about 1.96 eV, while Ni5P2 shows metallic properties due to the Fermi level of Ni5P2 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 NiSe2 to Ni5P2 [63]. And the built-in fields work mechanism of interfacial NiSe2 and Ni5P2 in equilibrium as shown in scheme 1. As a result, the surface of Ni5P2@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 Ni5P2@NiSe2 heterostructure was schematically illustrated in scheme 1, and its fabrication photograph was included in figure S1. First, Ni(NO3)2·6H2O, CH3N2O 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 Ni5P2@NiSe2 heterostructure by a simultaneous phosphorylation and selenization process at 350 °C under the Ar atmosphere for 2.5 h. For comparison, Ni5P2 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 μm, consisting of many smooth nanosheets with the thickness of 3–5 nm. Compared with the smooth and granular
Scheme 1. Synthetic procedure for Ni$_5$P$_4$@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$_5$P$_4$@NiSe$_2$ heterostructure.

nanosheets of Ni$_5$P$_4$ in figure S4 and NiSe$_2$ in figure S5, those of the Ni$_5$P$_4$@NiSe$_2$ 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 N$_2$ adsorption/desorption isotherms (figure 2(b)) of Ni$_5$P$_4$@NiSe$_2$ 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$_5$P$_4$/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$_5$P$_4$@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$_5$P$_4$@NiSe$_2$ heterostructure, the TEM image in figure 1(d) shows 3D hierarchical porous nanoflower-like morphology,
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 Ni$_3$P$_4$, meanwhile the lattice fringes of approximately 0.299 nm can be identified with the (200) planes of NiSe$_2$. Interestingly, figure 1(e) also depicts clear interfacial regions owing to the mismatch of the different phases, and the resulting strong electronic interaction between Ni$_3$P$_4$ and NiSe$_2$ may lead to an increase in the active sites [43, 68, 69]. Figure 1(f) exhibits the corresponding selected area electron diffraction pattern of Ni$_3$P$_4$@NiSe$_2$ heterostructure, which can be unambiguously indexed into (0002), (201), (211), (302), (204) planes of the Ni$_3$P$_4$ and (200), (211) planes of the NiSe$_2$, respectively, further demonstrating that Ni$_3$P$_4$@NiSe$_2$ heterostructure was successfully synthesized.

The crystalline structure and phase of Ni$_3$P$_4$@NiSe$_2$, Ni$_3$P$_4$ and NiSe$_2$ were tested by XRD measurement. As depicted in figure 2(a), all diffraction peaks of Ni$_3$P$_4$@NiSe$_2$ heterostructure correspond perfectly to hexagonal Ni$_3$P$_4$ (JCPDS no 18-0883) and cubic NiSe$_2$ (JCPDS no 89-3058), which is identical to the HRTEM data. As we all know, electrocatalytic reactions in Li–O$_2$ 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 Ni$_3$P$_4$@NiSe$_2$ and NiSe$_2$. Figure 2(c) reveals the presence of C, O, Ni, P and Se elements on the as-prepared Ni$_3$P$_4$@NiSe$_2$ 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 NiSe$_2$, the two-orbit doublets in the XPS spectrum of Ni$_3$P$_4$@NiSe$_2$ heterostructure are slightly shifted to negative binding energies [55], which can be attributed to electronic structure changes caused by the interfacial charge redistribution of Ni$_3$P$_4$ and NiSe$_2$. 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$_{5/2}$ and Se 3d$_{3/2}$ of Se$^{2-}$. The Se 3d peak of Ni$_3$P$_4$@NiSe$_2$ 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$_2$ 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 Ni$_3$P$_4$@NiSe$_2$ 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 Ni$_3$P$_4$@NiSe$_2$ heterostructure was measured in Li–O$_2$ batteries placed in a testing box purchased from NJZH (Shenzhen) Scientific Ltd, as displayed in figure S7. CV profiles of Ni$_3$P$_4$@NiSe$_2$, Ni$_3$P$_4$, NiSe$_2$ and pure KB cathodes within 2.35–4.5 V at 0.15 mV s$^{-1}$ are depicted in figure 3(a). The Ni$_3$P$_4$@NiSe$_2$ cathode exhibits the highest ORR/OER current densities, proving that it can significantly promote the electrocatalytic reaction kinetics. Specifically, the Ni$_3$P$_4$@NiSe$_2$ 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 $\sim$4.2 V is attributed to the delithiation process of Li$_2$O$_2$ (Li$_2$O$_2$ $\rightarrow$ Li$_{2\cdot x}$O$_2$ $+$ x Li$^+$ $+$ x e$^-$), while the lower peak at 3.78 V is ascribed to a further delithiation process (Li$_{2\cdot x}$O$_2$ $\rightarrow$ O$_2$ $+$ (2 $-$ x) Li$^+$ $+$ (2 $-$ x) e$^-$) [7, 8].

The discharge/charge plots of Li–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
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 16 831.5/15 3.5, 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 electrocatalytic 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, which are significantly lower than those of Ni₅P₄ (0.25/1.42 V), NiSe₂ (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 cut-off capacity of 1000 mAh g⁻¹. It can be seen that at current densities of 100, 200, 400, 800 and 1000 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$_5$P$_4$@NiSe$_2$ 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 Ni$_5$P$_4$@NiSe$_2$ 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 Ni$_5$P$_4$@NiSe$_2$ heterostructure with more free space and nanopores could construct a large amount of 3D channels for the fast Li$^+$/O$_2$ transport. Additionally, the built-in electric fields between Ni$_5$P$_4$ and NiSe$_2$ can largely improve the slow redox kinetics of the cathode reactions, resulting in excellent electrochemical performance of Li–O$_2$ batteries.

To explain the formation/decomposition mechanism and reason for the excellent electrocatalytic performance of Ni$_5$P$_4$@NiSe$_2$ cathodes, ex-situ XRD, XPS and EIS at different stages during cycling were characterized. Figure 4(a) shows the XRD patterns of the Ni$_5$P$_4$@NiSe$_2$ cathode at different stages, where two new diffraction peaks located at 32.9 and 35.0$^\circ$ after first discharging, indexed to (100) and (101) planes of Li$_2$O$_2$ (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 Li$_2$O$_2$ 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 Ni$_5$P$_4$@NiSe$_2$-based cell were greatly enlarged from 14.5 to 82.5 $\Omega$ after first discharging, mainly due to the coverage and accumulation of insulating Li$_2$O$_2$ [18, 23]. Besides, it also shows that after first recharging and even after 100 cycles of prolonged cycling, the $R_{ct}$ of Ni$_5$P$_4$@NiSe$_2$ 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 Ni$_5$P$_4$@NiSe$_2$ 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 Li$_2$O$_2$ 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 Ni$_5$P$_4$@NiSe$_2$ cathodes.

According to previous reports in the literature, the morphology of Li$_2$O$_2$ plays an essential role in affecting the subsequent charging process. Whether discharge products Li$_2$O$_2$ formed film- or disc-shaped was controlled by the adsorption energy of LiO$_2$. The disc-shaped Li$_2$O$_2$ grew through the solution growth model due to the weak adsorption energy
of the LiO$_2$ intermediate, while the film-shaped Li$_2$O$_2$ 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 Ni$_3$P$_4$@NiSe$_2$ 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 unevenly deposited film-like discharge products could facilitate the establishment of a good contact interface with the Ni$_3$P$_4$@NiSe$_2$ cathode, which can make fully utilized of active centers and maximize the synergistic effect between Ni$_3$P$_4$, NiSe$_2$ 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, indicing the excellent reversibility of Li–O$_2$ batteries with Ni$_3$P$_4$@NiSe$_2$ cathodes.

Based on the above results, the superior electrocatalytic performance of Ni$_3$P$_4$@NiSe$_2$ cathodes would be attributed to their unique architecture. The 3D nanoflower-like structure with self-assembled nanosheets not only promoted the diffusion of O$_2$/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 Ni$_3$P$_4$ and NiSe$_2$ heterostructure can modulate the growth pathway of Li$_2$O$_2$ and induce their tight coating with low crystallinity structure along the 3D self-assembled nanosheets, building homogeneous low-impedance cathode/Li$_2$O$_2$ interfaces and promoting the efficient formation/decomposition of Li$_2$O$_2$ [80]. The possible formation/decomposition mechanisms of the Li$_2$O$_2$ on the Ni$_3$P$_4$@NiSe$_2$ cathode are shown in figure S11. First, O$_2$(sol) was adsorbed to the active sites to form adsorbed oxygen (O$_2$*, * represents surface adsorbed species) based on equation (1):

$$O_2 + \text{surface active sites} \rightarrow O_2^*. \quad (1)$$

Second, O$_2^*$ captured one electron and reacted with Li$^+$ to generate LiO$_2$* based on equation (2):

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

Third, Li$_2$O$_2$* was formed by electrochemical reduction of LiO$_2$* based on equation (3):

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

4. Conclusion

In summary, the nanoflower-like Ni$_3$P$_4$@NiSe$_2$ heterostructure was successfully synthesized via hydrothermal method combining simultaneous phosphating/seleнизation treatment. The 3D hierarchical porous structure of Ni$_3$P$_4$@NiSe$_2$ heterostructure can facilitate barrier-free Li$^+/O_2$ 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 Ni$_3$P$_4$@NiSe$_2$ cathode delivered superior electrochemical performance, including an ultra-high discharge/charge specific capacity of 19 090/19 031 mA h 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.

Acknowledgments

Funding support is gratefully acknowledged by the National Natural Science Foundation of China (51971119, 52171141, U21A20311), the Natural Science Foundation of Shandong Province (ZR2020YQ32, ZR2020QB122), the China Postdoctoral Science Foundation (2020M672054), the Guangdong Basic and Applied Basic Research Foundation (2021A1515111124), the Young Scholars Program of Shandong University (2019WLJH21) and Project of Introducing Urgently Needed Talents in Key Supporting Regions of Shandong Province (2203-371703-04-01-786537).

Conflict of interest

The authors declare no conflict of interest.

ORCID iD

Jun Wang © https://orcid.org/0000-0003-4954-2794

References

[1] 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–O$_2$ battery realized by dual superlyophobic membrane Joule 3 2986–3001
[4] Xia Q et al 2021 MnCo$_2$S$_4$–CoS$_2$催he 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 NiSe$_2$/NiSe$_2$ heterostructure nanostructures as an efficient bifunctional electrocatalyst for high-capacity and long-life Li–O$_2$ batteries J. Power Sources 468 228308
[6] Hu A J et al 2020 Heterostructured NiSe$_2$/ZnIn$_2$S$_4$ realizing toroid-like Li$_2$O$_2$ deposition in lithium-oxygen batteries with low-donor-number solvents ACS Nano 14 3490–9
[7] Li D Y et al 2022 CoS$_2$ nanoparticles anchored on MoS$_2$ nanorods as a superior bifunctional electrocatalyst boosting Li$_2$O$_2$ heteroepitaxial growth for rechargeable Li–O$_2$ 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–O$_2$ batteries Adv. Energy Mater. 10 2000145

[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-MnO$_2$ nanowire-anchored highly oxidized cluster as a catalyst for Li–O$_2$ 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–O$_2$ 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 CeO$_2$ nanorods as cathode materials for Li–O$_2$ batteries J. Mater. Chem. A 7 6552–61

[12] Senju P, Park H S, Park K U, Aravindan V, Nahm K S and Lee Y S 2017 Formation of NiCo$_2$O$_4$ rods over Co$_3$O$_4$ nanosheets as efficient catalyst for Li–O$_2$ 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/Pd$_3$S heterostructure on hollow carbon spheres as efficient electrocatalysts for rechargeable Li–O$_2$ 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-C$_3$N$_4$ nanosheets as efficient catalyst for Li–O$_2$ 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 Co$_2$P/Ru/N-doped carbon nanotube hybrids as bifunctional electrocatalysts for high-performance Li–O$_2$ 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 14562–71

[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 CoMo$_2$ 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–O$_2$ 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–O$_2$ batteries using PdM alloy nanoparticles anchored on nitrogen-doped reduced graphene as the cathode catalyst J. Power Sources 337 173–89

[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–O$_2$ battery J. Colloid Interface Sci. 579 448–54

[21] Yao W T et al 2019 Tuning Li$_2$O$_2$ formation routes by facet engineering of MnO$_2$ 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 CeO$_2$@NiCo$_2$O$_4$ nanowire arrays on carbon textiles as high performance cathode for Li–O$_2$ 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–NiCo$_2$O$_4$ heterostructure microsphere catalysts for enhanced rechargeable non-aqueous Li–O$_2$ 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/Co$_3$N$_4$ 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 Co$_3$N 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-O$_2$ batteries Chem. Commun. 47 11291–3

[27] Shombe G B, Khan M D, Choi J, Gupta R K, Oparro M and Revaprasadu N 2022 Tuning composition of CuCo$_2$S$_4$–NiCo$_2$S$_4$ solid solutions via solvent-less pyrolysis of molecular precursors for efficient supercapacitance and water splitting RSC Adv. 12 10675–85

[28] Dou H Y, Lian R Q, Zhang Y T, Zhao Y Y, Chen W J, Wei Y J and Peng Z Q 2018 CoB$_2$O$_4$ carbon porous nanocages derived from a metal–organic framework: a highly efficient bifunctional catalyst for aprotic Li–O$_2$ batteries J. Mater. Chem. A 6 8859–603

[29] Hou 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 Li$_2$O by flower-like ZnCo$_2$S$_4$ enabling high-performance Li–O$_2$ 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, Gu G H and Xu B S 2021 Mo$_x$C quantum dots decorated ultrathin carbon nanosheets self-assembled into nanoflowers toward highly catalytic cathodes for Li–O$_2$ 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/Fe$_2$O$_3$@graphitic carbon shell embedded in carbon nanotubes derived from Prussian blue as cathodes for Li–O$_2$ 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–O$_2$ 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 Co$_2$P nanosheets as cost-effective cathode catalysts for Li–O$_2$ batteries ACS Appl. Mater. Interfaces 10 21281–90

[34] Hou Z Q, Shu C Z, Hei P, Yang T S, Zheng R X and Long J P 2020 A 3D free-standing Co doped Ni$_2$P$_2$O$_7$ nanowire electrode for stable and long-life lithium-oxygen batteries Nano lett. 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 NiS/Ni$_2$P$_2$S$_4$ 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 NiCo$_2$O$_4$ nanosheets on carbon nanofiber films for high energy density and long-life Li–O$_2$ 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–O$_2$ battery Small 16 2001812

[38] Wang L J et al 2016 Facile synthesis of flower-like hierarchical NiCo$_2$O$_4$ microspheres as high-performance cathode materials for Li–O$_2$ 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, Jaromec M and Yu J G 2019 Nickel-based materials for supercapacitors Mater. Today 25 55–65

[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 J X, Ran Z Q, Zheng R X, Du D Y, Zhao C, Li R J, Xu H Y, Zeng T and Shu C Z 2022 NiS$_2$/Ni$_2$P 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 NiS$_2$/Ni$_2$P$_2$ 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–O$_2$ 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–O$_2$ 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–O$_2$ 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 Interfaceal electronic redistribution of hydrangea-like NiO@Ni$_2$P$_2$ 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–O$_2$ battery 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 Ni$_2$P/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, Bui 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 B X 2019 Realizing discrete growth of thin Li$_2$O$_2$ sheets on black phosphorus quantum dots–decorated δ-MnO$_2$ catalyst for long-life lithium-oxygen cells Energy Storage Mater. 23 684–92

[54] Liu C C, Gong T, Zhang J, Zheng R X, Mao J, Liu H, Li Y and Hao Q Y 2020 Engineering Ni$_2$P/NiSe$_2$ heterostructure interface for highly efficient alkaline hydrogen evolution Appl. Catal. B 262 118245

[55] Yang J, Yang N, Xu Q, Pearle L S, Zhang Y Z, Hong Y, Wang Q, Wang W J, Yan Y Q and Dong X C 2019 Bioinspired controlled synthesis of NiSe/Ni$_2$P 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–O$_2$ 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 Zhang L 2016 Tuning the morphology and crystal structure of Li$_2$O$_2$: a graphene model electrode study for Li–O$_2$ 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, Zou X Y, Xing H F, Wang H L, Yu J M, Liu H Z, Chen C M and Yang L R 2021 Interfacial engineering of the NiSe$_2$/FeSe$_2$ 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 Ni$_3$P$_2$ coupled with GNQDs as Schottky junction photocatalyst for the efficient degradation of norfloxacin Sep. Purif. Technol. 282 121017

[61] Liu X, Zhao Y X, Yang X F, Liu Q Q, Yu X H, Li Y, Yang H and Zhang T R 2020 Porous Ni$_3$P$_2$ 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 NiSe$_2$/Cd$_{0.5}$Zn$_{0.5}$S as a type-II heterojunction photocatalyst for enhanced photocatalytic hydrogen evolution Int. J. Hydrog. Energy 46 15380–97

[63] Li S Z, Zang W J, Liu X M, Penncook S J, Kou Z K, Yang C H, Guan C and Wang J 2019 Heterojunction engineering of MoSe$_2$/MoS$_2$ 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$_{33}$Ni$_{33}$Fe$_{33}$O frameworks with stable octahedron and multi-stage 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 NbC/MXene cathode catalyst with uniform O-terminated surface for lithium-oxygen batteries Adv. Energy Mater. 11 2002272

[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 Li$_2$O$_2$ 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 NiSe$_2$ 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 Ni/Si/MoS$_2$/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 Ni$_2$S$_2$/Ni$_2$Se$_2$ 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–O$_2$ 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 TiO$_2$@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 MoSi$_2$ catalysts featuring surface activation as highly efficient cathode materials for long-life Li–O$_2$ 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 in hollow NiS$_2$@FeS$_2$-NSGA heterostructures with efficient catalytic activity for advanced Li–CO$_2$ 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 J 2022 Interfacial engineering in hollow NiS$_2$/FeS$_2$-NSGA heterostructures with efficient catalytic activity for advanced Li–CO$_2$ 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 Novel Mo and B doped carbon–porous TiO$_2$ nanocomposite anode for long life lithium-ion batteries Chem. Eng. J. 430 133029

[78] Zhang F Z, Ma Y Y, Jiang M M, Luo W and Yang J P 2022 Novel Mo and B doped carbon–porous TiO$_2$ nanocomposite anode for 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 MoS$_2$ nanoflakes via sulfur defect engineering wrapped on CNTs for stable and efficient Li–O$_2$ batteries Adv. Funct. Mater. 32 2108153