1. Introduction

With the increasing demands of human society, non-renewable energy resources are gradually exhausted. As a consequence, electrochemical water splitting provides a good alternative for an efficient conversion of water into sustainable chemicals and fuels with renewable electricity, including both the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). In particular, the OER generally suffers from a bottleneck, *i.e.*, a four-electron proton-coupled process, which results in its sluggish kinetics and a substantially high activation energy barrier (namely, higher overpotential) based on the theoretical decomposition voltage of water (1.23 V vs. RHE). Up to now, the state-of-the-art Ir-/Ru-based oxides have exhibited excellent OER performance with smaller overpotentials, *i.e.*, ~312 mV for IrO$_2$ and ~350 mV for RuO$_2$, for attaining a current density of 10 mA cm$^{-2}$ and superior catalytic stability. However, the high cost and scarcity of noble metals limit their practical utilization. Therefore, development of earth-abundant, non-noble OER catalysts with desirable electrocatalytic performances for practical applications is of great significance.

In recent years, various transition metal (TM) phosphides, oxides, chalcogenides, borides, nitrides and their composites have emerged as effective OER catalysts. Among these cost-efficient catalysts, TM phosphides are regarded as catalysts with superior electrocatalytic activity and stability in alkaline media to effectively promote the OER process in terms of thermodynamics and kinetics. Moreover, from the view of catalyst structure, the number of active centers, as a momentous factor, must be taken into consideration for any electrocatalyst to render remarkable OER performance. To this end, two effective strategies, *i.e.*, construction of three dimensional (3D) hierarchical porous (particularly hollow architectures) and multi-component hetero-interfaces, have been proposed. Concretely, the former can maximally expose active edge sites on the catalyst surface. The latter can effectively reduce the chemisorption free energy of OH$^-$, promote the desorption of the intermediates from active centers, bring strong synergistic effects, and even increase the number of active centers. For instance, 3D Fe$_2$O$_3$@Ni$_2$P/Ni(PO$_4$)$_2$/nickel foam (NF) achieved a current density of 10 mA cm$^{-2}$ with a low overpotential of 177 mV. 3D FeP@Ni$_3$P/NF only needed an overpotential of 290 mV to reach a current density of 50 mA cm$^{-2}$ in 1 M KOH. 3D NiSe$_2$-Ni$_3$P/NF merely required an ultralow overpotential of 220 mV to reach a current density of 50 mA cm$^{-2}$. Therefore, the purposeful design of 3D hierarchical hollow structures has a direct effect on the electrochemical performance. However, it is highly challengeable to develop a simple but efficient methodology to

Design and construction of bi-metal MOF-derived yolk–shell Ni$_2$P/ZnP$_2$ hollow microspheres for efficient electrocatalytic oxygen evolution†

Jinyang Zhang, Xuan Sun, Yang Liu, Linrui Hou and Changzhou Yuan*

It is highly challengeable to explore and design high-performance non-noble metal electrocatalysts for the oxygen evolution reaction (OER) towards highly efficient water electrolysis. Herein, we design and synthesize, for the first time, a novel cost-efficient electrocatalyst, *i.e.*, hierarchical yolk–shell Ni$_2$P/ZnP$_2$ hollow microspheres (NZP HMSs), via a two-step strategy involving a solvothermal process and subsequent phosphatization. When utilized as a promising electrocatalyst for the OER, the yolk–shell NZP HMS specimen exhibits more exceptional OER performances than its solid Ni$_2$P counterpart, including a lower overpotential of 210 mV at 10 mA cm$^{-2}$, a smaller Tafel slope of 57.8 mV dec$^{-1}$ and more superior electrochemical stability in 1 M KOH. The superb electrocatalytic OER properties are attributed to the synergistic contributions from the Ni$_2$P/ZnP$_2$ hetero-interface at the nanoscale, favorable electronic conductivity and high electroactive surface area. More significantly, we strongly envision that this simple synthetic methodology can be highly versatile for other hierarchical yolk–shell hollow phosphides towards the OER and beyond.

School of Materials Science and Engineering, University of Jinan, Jinan 250022, P. R. China. E-mail: mse_yuancz@ujn.edu.cn, ayuancz@163.com
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0qm00128g
fabricate hierarchical hollow TM phosphides with heterointerfaces at the nanoscale as highly efficient OER catalysts.

In this work, we firstly synthesized hierarchical yolk–shell Ni$_2$P/Zn$_2$P hollow microspheres (NZP HMSs) via a facile low-temperature phosphatization of a bimetallic (Ni, Zn) organic framework precursor, and further investigated their OER performances in 1 M KOH electrolyte as an electrocatalyst. When evaluated as a competitive catalyst for the OER, the resultant yolk–shell NZP HMSs displayed excellent OER performance with a low overpotential of 210 mV at a current density of 10 mA cm$^{-2}$ and a small Tafel slope of 57.8 mV dec$^{-1}$ as well as excellent electrochemical stability, benefiting from the concerted contributions from their large electroactive surface, nanoscale Ni$_2$P/Zn$_2$P hetero-interface and exceptional electrical conductivity.

2. Experimental section

2.1 Chemicals

All chemicals including Ni(NO$_3$)$_2$·6H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, dimethylformamide (DMF), 1,3,5-benzene tricarboxylic acid (BTC), polyvinylpyrrolidone (PVP), absolute alcohol and NaH$_2$PO$_2$ were purchased from Sinopharm Chemical Reagent Co. Ltd, and used as received without further purification. All aqueous solutions were freshly prepared by using high-purity water (18.25 MΩ cm$^{-1}$ as received without further purification. All aqueous solutions were kept the same as those of yolk–shell NZP HMSs. And the precursor for the solid NP MSs was designed as pre-NP MSs. And the Zn$_3$(PO$_4$)$_2$ hollow microspheres (ZOP HMSs) were prepared as well but changing the ramp rate to 5 mV at 5 min$^{-1}$.

2.2 Synthesis of yolk–shell NZP HMSs

Typically, 215 mg of Ni(NO$_3$)$_2$·6H$_2$O, 215 mg of Zn(NO$_3$)$_2$·6H$_2$O, and 140 mg of BTC were dissolved in 30 mL of DMF under magnetic stirring for 30 min. Then, the mixture was sealed in a green precipitate was separated by centrifugation, washed with DMF and absolute alcohol several times, dried in a vacuum oven at 60 °C overnight, and denoted as pre-NZP. Then, pre-NZP (100 mg) was mixed well with 300 mg of NaH$_2$PO$_2$. The mixture was further annealed at 600 °C for 2 h at a ramp rate of 3 °C min$^{-1}$ under a N$_2$ atmosphere. After washing the mixture with 0.5 M HCl and water, and drying at 80 °C, yolk–shell NZP HMSs were obtained. For comparison, solid Ni$_2$P microspheres (NP MSs) were prepared as well but using 430 mg of Ni(NO$_3$)$_2$·6H$_2$O instead. The yolk–shell Ni$_2$P/Zn$_2$P hollow microspheres (NZP-5 HMSs) were produced by changing the ramp rate to 5 °C min$^{-1}$. The solid Ni$_2$P/Zn$_2$P microspheres (NZP MSs) were produced by using Ni(NO$_3$)$_2$·6H$_2$O (280 mg) and Zn(NO$_3$)$_2$·6H$_2$O (150 mg). The yolk–shell Ni$_2$P hollow microspheres (NP HMSs) were obtained with 15 mL of DMF and 15 mL of absolute alcohol instead of 30 mL of DMF. And the Zn$_3$(PO$_4$)$_2$ hollow microspheres (ZOP HMSs) were obtained without the addition of Ni species. One especially notes that other synthetic parameters for all the above products were kept the same as those of yolk–shell NZP HMSs. And the precursor for the solid NP MSs was designed as pre-NP for convenience.

2.3 Material characterization

Morphologies of the samples were investigated with a field-emission scanning electron microscope (FESEM, JEOL-6300F), a transmission electron microscope (TEM) and a high-resolution TEM (HRTEM, TECNAI-20) system equipped with an energy dispersive X-ray (EDX) analysis setup (Genesis XM2). The X-ray diffraction (XRD) patterns of the products were recorded with a Bruker D8 Focus Diffraction System using a Cu Kα source ($λ$ = 0.15406 nm). Nitrogen adsorption–desorption tests were determined on a surface area analyzer (TriStar II 3020) at 77 K. The mesopore and micropore size distributions were derived by the Barrett–Joyner–Halenda (BJH) and density functional theory (DFT) methods, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on a photoelectron spectrometer using Al Kα radiation as the excitation source (a VGESCALAB MKII X-ray photoelectron). All the peaks were calibrated with the C 1s spectrum at a binding energy of 284.8 eV. Thermogravimetric and differential scanning calorimetry (TG-DSC) analyses were performed on a STA449 F5 (NETZSCH, Germany).

2.4 Electrochemical measurements

The catalyst suspension was prepared from a solution (1 mL) consisting of 2.5 mg of catalyst, 100 μL of Nafion and 900 μL of ethanol. A Ni foam (porosity 95% and purity 95%) was pre-treated and then used as a catalyst support. Specifically, the purchased NF was immersed in 12 M HCl for 10 min, then rinsed well with water, and finally, cut for determining the geometric surface area. The remaining surface was isolated from the electrolyte using hot glue as the insulator to ensure an exposed surface area of 1.0 cm$^2$ for subsequent electrochemical tests. Electrochemical measurements were carried out in a standard three-compartment electrochemical cell consisting of a working electrode, a Pt counter electrode, and an Ag/AgCl (saturated KCl aqueous solution) reference electrode on an IVIUM electrochemical workstation (Netherlands).

The catalyst was typically loaded on the pretreated NF via drop-casting 40 μL of the catalyst ink, equivalent to a loading of 0.1 mg cm$^{-2}$. The electrochemical OER experiments over the solid NP MSs and yolk–shell NZP HMSs were conducted in 250 mL of 1 M KOH aqueous solution ($pH = 13.6$). Before the OER test, the NF was first activated with 100 cyclic voltammetry (CV) sweeps at a scan rate of 100 mV s$^{-1}$. Linear sweep voltammetry (LSV) curves were produced at a scan rate of 5 mV s$^{-1}$ across a potential window of 1.20–1.75 V (vs. reversible hydrogen electrode, RHE) without iR compensation. The cycle stability of the yolk–shell NZP HMSs was evaluated by a long-term durability test at 1.44 V (vs. RHE). Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 100 kHz to 0.01 Hz with an AC signal amplitude of 5 mV at 1.44 V (vs. RHE). During electrochemical experiments, the electrolyte was always agitated using a magnetic stirrer rotating at 350 rpm at room temperature (RT, 25 °C).

The current density was normalized over the geometric surface area of the electrode. The Ag/AgCl electrode was calibrated to
1.001 ± 0.002 V vs. RHE in a standard three-electrode system: the Ag/AgCl electrode as the reference electrode and two polished Pt plates as the working and counter electrodes in H$_2$-saturated 1 M KOH solution. All potentials measured were calibrated to the RHE using the following eqn (1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH}$$ \hspace{1cm} (1)

The electrochemical active surface area (EASA) was evaluated in terms of double layer capacitance ($C_{\text{dl}}$), assuming a $C_{\text{dl}}$ capacitance of 60 $\mu$F cm$^{-2}$. The CV scans were performed at different scan rates within a potential window of 0.1 V, where no faradaic process occurred. The CV scanning sequence was in the order of 20, 40, 60, 80, 100 and 120 mV s$^{-1}$. The turnover frequency (TOF) values were calculated by the following equation:\hspace{1cm} (2)

$$\text{TOF} = \frac{jA}{4nF}$$

where $j$ is the current density (mA cm$^{-2}$) at an overpotential of 210 mV, $A$ is the geometric surface area of the Ni foam electrode (cm$^2$), number 4 means four electrons per mole of O$_2$, $F$ is the Faraday constant (96 485 C mol$^{-1}$), and $n$ is the number (mole) of active sites in the working electrode. Herein, the Ni species was only regarded as the active site, so the Zn and P atoms were ignored when calculating the TOF values of the solid NP MSs and yolk–shell NZP HMSs.

3. Results and discussion

3.1 Physicochemical and structural characteristics of yolk–shell NZP HMSs

In this work, a two-step synthetic strategy, i.e., a hydrothermal process followed by high-temperature phosphatization in a nitrogen atmosphere, is adopted, as described in Fig. 1a. Typically, the Ni-based benzotriacetic acid framework precursor (i.e., pre-NP) and Ni/Zn-MOF precursor (i.e., pre-NZP) are obtained via a surfactant-mediated hydrothermal treatment at 150 °C.\hspace{1cm} (29) Apparently, both precursors exist with a similar solid microspherical structure of size ~1 µm (Fig. S1, ESI†). During the subsequent calcination, three endothermic peaks, corresponding to the loss of adsorbed/bound water (P1, 100 °C), decomposition of PVP (P2, 420 °C) and sublimation of Zn (P3, 700 °C), respectively, are distinct in the thermogravimetric and differential scanning calorimetry (TG-DSC) curves of the pre-NP and pre-NZP products (Fig. S2, ESI†). The appropriate phosphatization temperature for the two precursors is preliminarily designed as 600 °C.

Fig. 1b comparatively displays the wide-angle X-ray diffraction (XRD) patterns of the NP MSs (the upper) and NZP HMSs (the lower) obtained at 600 °C for 2 h at a ramp rate of 3 °C min$^{-1}$ under a N$_2$ atmosphere. The discernable diffraction reflections of the NP MSs, regardless of the peak locations and intensities, match well with the standard spectrum of the

Fig. 1  (a) Schematic diagram of the synthesis procedure for the yolk–shell NZP HMSs and solid NP MSs. (b) XRD patterns of solid NP MSs and yolk–shell NZP HMSs. Crystallographic illustration of (c) hexagonal Ni$_2$P and (d) tetragonal ZnP$_2$. Typical XPS high-resolution elemental (e) Ni 2p, (f) Zn 2p and (g) P 2p spectra of the yolk–shell NZP HMSs.
hexagonal Ni$_2$P (JCPDS Card No. 03-0953) with a space group of $P62m$ (189), where elemental Ni occupies the tetrahedral sites and the center hole sites surrounded by the tetrahedral atoms (Fig. 1c). By contrast, as for the NZP HMSs, all the diffraction peaks can be unambiguously indexed to a mixture of hexagonal Ni$_2$P and tetragonal ZnP$_2$ (JCPDS Card No. 24-1464) with a space group of $P43212$ (96), in which the Zn and P occupy the center and vertex sites, respectively (Fig. 1d).

To further obtain the specific chemical states of Ni, Zn and P species on the surface of the NZP HMSs, X-ray photoelectron spectroscopy (XPS) analysis is conducted in detail, as depicted in Fig. 1e–g. Typical survey photoelectron spectrum shows the co-existence of Ni, Zn and P with a molar ratio of approximately 1:1:2.3 (Fig. S3, ESI†). The core level Ni 2p XPS spectra and the corresponding fitted data are illustrated in Fig. 1e. Evidently, the expected peaks of Ni-P bond are Ni 2p$_{3/2}$ ($\approx 853.4$ eV) and Ni 2p$_{1/2}$ ($\approx 870.6$ eV) along with two satellite (Sat.) peaks of $\approx 861.0$ and $\approx 880.0$ eV; another two peaks located at $\approx 856.8$ and $\approx 876.0$ eV are assigned to the Ni–O bond. 18,30 The high-resolution spectrum of Zn 2p (Fig. 1f) shows two peaks, corresponding to Zn 2P$_{3/2}$ and Zn 2p$_{1/2}$ located at binding energies (BEs) of $\approx 1021.7$ and $\approx 1044.7$ eV, respectively, and the BE gap of $\approx 23.0$ eV between the two peaks indicates the existence of the Zn–P bond. 31,32 As for the P 2p spectrum (Fig. 1g), the peaks centered at $\approx 129.5$ and $\approx 130.6$ eV are attributed to the P–M (M = Zn/Ni) bonds, confirming the presence of Ni$_2$P and ZnP$_2$, 33–36 and the peaks at BEs of $\approx 133.2$ and $\approx 134.0$ eV are assigned to typical P–O species from partially superficial oxidation. 

Fig. 2a and b show the representative field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the resultant NP MSs. Obviously, lots of solid MSs with a smooth surface, well inheriting the typical morphology of pre-NP (Fig. S1a and b, ESI†), are characterized. The NZP HMS specimen shows a representative spherical architecture, similar to pre-NZP, but with numerous discernible nanoparticles of size $\approx 10$ nm located on their surface, rendering a rough surface. To visualize the nanoparticles more clearly, we purposefully chose the yolk–shell NZP-5 HMSs for further investigation. Apparently, the nanoparticles increase up to $\approx 90$ nm in size (Fig. S4a and b, ESI†), and can be confirmed to be the ZnP$_2$ phase with distinct elemental (Ni, Zn and P) distributions, as presented in STEM and the corresponding EDS mapping images (Fig. S4c, ESI†). Anyway, the sizes of both NP MSs and NZP HMSs are basically consistent with those of their precursors, indicating no occurrence of the distinct calcination-induced shrinkage. More interestingly, the NZP HMSs, unlike the NP MSs, manifest a yolk–shell structure with an apparent void, as verified by the sharp color contrast in Fig. 2e. And the shell is $\approx 100$ nm in thickness, along with a yolk of $\approx 500$ nm diameter. The higher magnification TEM (HRTEM) images (Fig. 2f and g) further corroborate the existence of nanoparticles on the rough surface of NZP HMSs. Further HRTEM observation (the inset in panel g) visualizes the well-defined lattice fringes.
with a spacing of 0.223 nm, corresponding to the (111) crystal-
line plane of Ni$_2$P. Moreover, clear lattice fringes are evident in
two regions with spacings of 0.193 and 0.225 nm, well indexed to
the (210) plane of Ni$_2$P, and the (211) plane of ZnP$_2$, which
authenticates that the nano-domains of Ni$_2$P and ZnP$_2$ are
distributed perfectly throughout the whole yolk–shell
species are all distributed perfectly throughout the whole yolk–shell

Co$_2$P/ZnP$_2$ samples

authenticates that the nano-domains of Ni$_2$P and ZnP$_2$ are
shell sphere.

And the yolk–shell hollow spherical Co$_2$P/ZnP$_2$ samples

obtained by using the mixed solvent (i.e.,

i.e.

the yolk–shell NP HMSs (Fig. S7c and d, ESI†)

that elemental Zn plays a decisive role in the formation of

It is the unique yolk–shell hollow architecture with hetero-
interfaces at the nanoscale that will guarantee the large electro-
chemical active surface area (EASA) (i.e., electrocatalyst/electrolyte contact area), enhanced charge transfer, and lower
chemisorption free energies of OH$^-$/C$_0$.$^1$ As a result, appealing
electrocatalytic properties can be highly anticipated for the NZP HMS catalyst.

More interestingly, owing to the absence or introduction of
extra elemental Zn, two distinguished structures, i.e., solid NP
MSs and yolk–shell NZP HMSs, are presented, while other
synthetic parameters are always kept the same, as discussed
above. It is worth mentioning that the difference has no effect on the morphologies of their precursors, and both of them are
solid MSs with a similar size (Fig. S1, ESI†). Additionally, with
the huge increase in the Zn content, namely without the
addition of Ni species, the ZOP HMSs can be formed, rather
than the ZnP$_2$ phase (Fig. S6, ESI†). Conversely, with a slight
decrease in the Zn content, the solid NZP MSs can be surpris-
ingly formed (Fig. S7a and b, ESI†). It is therefore concluded
that elemental Zn plays a decisive role in the formation of yolk–shell HMSs over the annealing process. More appealingly,
the yolk–shell NP HMSs (Fig. S7c and d, ESI†) can also be
obtained by using the mixed solvent (i.e., 15 mL of DMF and
15 mL of absolute alcohol) instead of the single-component
DMF. And the yolk–shell hollow spherical Co$_2$P/ZnP$_2$ samples
(Fig. S8a and b, ESI†) are still formed just by replacing the Ni
species with elemental Co. Anyway, an in-depth exploration of
the intrinsic role or the underlying formation mechanism of
the yolk–shell hollow architecture is currently underway in
our lab.

3.3 Electrochemical evaluation of the OER

Considering the appealing structural merits, as mentioned
above, next, we mainly focus on the dependence of the OER performance of the resultant NZP HMS product upon their
specific structures and composition. Accordingly, the OER
catalytic activities of the yolk–shell NZP HMSs and solid NP
MSs are systematically investigated in 1 M KOH aqueous
solution as catalysts in a three-electrode cell. Remarkably, the
yolk–shell NZP HMSs, as observed from the linear sweep
voltammetry (LSV) curves (Fig. 3a), exhibit good catalytic per-
formance, requiring a low overpotential of ~210 mV to achieve
a current density of 10 mA cm$^{-2}$, while the required over-
potentials are ~240 and ~279 mV for the solid NP MSs and
commercial NF support, respectively, to render the same
current density. Considering that more ZnP$_2$ nanoparticles
are located on the surface of yolk–shell NZP-5 HMSs, the OER performance of the yolk–shell NZP-5 HMSs is investigated with
a low overpotential of ~220 mV at 10 mA cm$^{-2}$ (Fig. S9a, ESI†),
which suggests that the large nanoparticles will decrease the
OER properties, due to the increase in ZnP$_2$ content on the
surface. Meanwhile, the solid NZP MSs and yolk–shell NP HMSs
also present poor OER behaviors with low overpotentials of
~243 and ~263 mV at 10 mA cm$^{-2}$, respectively, although they
are both better than the ZOP HMSs (a high overpotential of
~398 mV at 2 mA cm$^{-2}$, Fig. S9a, ESI†). More encouragingly,
the overpotential of the yolk–shell NZP HMSs is much lower than those of other reported Ni-based phosphide electro-
catalysts (~240 to ~360 mV) (Table S1, ESI†). Furthermore,
the catalytic kinetics of the electrocatalysts are also evaluated by
the Tafel slopes, as plotted in Fig. 3b. In general, a lower Tafel
slope indicates higher electrocatalytic kinetics in the OER.$^{37}$
The Tafel slope of yolk–shell NZP HMSs, as displayed in Fig. 3b,
is fitted as ~57.8 mV dec$^{-1}$, which is much lower than those of the
solid NP MS catalyst (~191.7 mV dec$^{-1}$), NF (~183.7 mV dec$^{-1}$),

![Fig. 3](image-url)
yolk–shell NZP-5 HMSs (~94.7 mV dec⁻¹, Fig. S9b, ESI†), solid NZP MSs (~89.8 mV dec⁻¹) and yolk–shell NP HMSs (~93.4 mV dec⁻¹, Fig. S9b, ESI†), and even other retrieved Ni-based phosphides (~59–153 mV dec⁻¹) (Table S1, ESI†), revealing that the NZP HMS catalyst possesses a favorable reaction kinetics toward the OER. More remarkably, both the lower overpotential and Tafel slope of the NZP HMSs observed here, to a great extent, highlight their distinct merits of the yolk–shell hollow structure and hetero Ni₂P–ZnP₂ interface towards the OER, since ZnP₂ is a fully inert phase in the OER.³⁸ To further assess the intrinsic catalytic activity of solid NP MSs and NZP HMSs, the TOFs are further analyzed at an overpotential of 210 mV, assuming that all the Ni atoms are the catalytically active centers. The TOF of the NZP HMSs is calculated as ~0.08 s⁻¹, which is higher than those of the NP MSs (~0.02 s⁻¹) and the NZP-5 HMSs (~0.06 s⁻¹).

As well established, the EASA, which always can be quantified by the double layer capacitance (Cdl), is another significant parameter affecting the catalytic performance of any electrocatalyst.³⁹ According to the cyclic voltammetry (CV) profiles (Fig. S10, ESI†) and scanning rate dependence of the current densities (Fig. 3c), the Cdl values of the NZP HMSs, NP MSs and NF are estimated as ~6.77, ~3.98 and ~2.87 mF cm⁻², respectively, elucidating that the yolk–shell hollow NZP HMSs possess more active surface area (~112.8 cm²) compared with the NP MSs (~66.3 cm²) and NF (~47.8 cm²). The electrochemical impedance spectroscopy (EIS) plots of the NZP HMSs and NP MSs are depicted in Fig. 3d. And the NZP HMS catalyst exhibits a much smaller charge transfer resistance (Rct) compared to the NP MSs, suggesting a fast electron transfer rate in the yolk–shell HMSs towards a highly efficient OER.⁴⁰ Besides the contribution from hollow, porous and yolk–shell structural features, the ZnP₂ phase enhanced the EASA and smaller Rct observed in NZP HMSs cannot be ignored at all. Although ZnP₂ itself has no catalytic activity in the OER, it favors the enhancement of EASA, and rapid electronic transport owing to the rich hetero Ni₂P–ZnP₂ interfaces in the HMSs.

To identify the durability of the yolk–shell NZP HMS catalyst, continuous CV sweeps are performed from 1.2 to 1.6 V (vs. RHE) at a scanning rate of 100 mV s⁻¹ in 1 M KOH aqueous solution. Impressively, no obvious change between the first and 1000th cycle can be detected in the LSV plot (Fig. 3e). Surprisingly, the current density in consecutive chronoamperometric tests first
increases, and afterward turns out to be relatively steady over 71 h at an overpotential of 210 mV (Fig. 3f), which highlights the superb electrochemical durability of yolk–shell NZP HMSs for OER application. Unlike other Ni-based phosphide electrocatalysts reported previously, one abnormal phenomenon, that is the gradual increase in current density with testing, takes place in the yolk–shell NZP HMSs here, which suggests that something must have happened in the process.

To further understand the structural/compositional transformation of the NZP HMSs occurring over the long-term durability test in depth, XRD measurements are first conducted (Fig. 4a). Impressively, all the typical diffraction reflections of Ni$_2$P and ZnP$_2$ completely vanish, and new weak signals appear, suggesting the presence of Ni$^{3+}$ on the surface. Additional, the BEs for the Zn 2p$_{3/2}$ (1022.1 eV) and Zn 2p$_{1/2}$ (1045.1 eV) peaks in the Zn 2p region (Fig. 4d) are around 0.6 eV lower than those of yolk–shell NZP HMSs, and close to that of Zn(OH)$_2$. The corresponding O 1s spectrum is presented in Fig. 4e. The three fitted peaks at 529.9, 531.6 and 533.3 eV are attributed to the main metal (Ni/Zn)–oxygen component, the hydroxyls and surface-adsorbed water molecules. As for the P 2p spectrum (Fig. 4f), the representative peaks of the M–P (M = Ni/Zn) metal species disappear, and only those P–O species with higher valence are left, which indicates the formation of the soluble phosphorus oxides. As a result, the P content in the cycled NZP HMSs largely decreases. With the XRD and XPS analysis above, it is easy to conclude that the amorphous NiOOH is the real electroactive phase delivering electroactive surface area and rapid charge transport, thanks to the rich hetero Ni$_2$P–ZnP$_2$ interfaces in unique yolk–shell NZP HMSs. The as-fabricated yolk–shell NZP HMSs displayed more excellent OER properties in terms of overpotentials, catalytic kinetics, and stabilities than the solid Ni$_2$P microspheres in 1 M KOH, benefiting from their remarkable structural and compositional merits. Our contribution here may inspire a constructive way to synthesize other yolk–shell hollow transition metal phosphides with hetero-interfaces toward energy conversion applications and beyond.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors acknowledge the financial support from the National Natural Science Foundation of China (No. 51772127, 51772131), Taishan Scholars (No. ts201712050), the Major Program of Shandong Province Natural Science Foundation (ZR2018ZB0317) and the Collaborative Innovation Center of Technology and Equipment for Biological Diagnosis and Therapy in Universities of Shandong.

## References

Research Article

Materials Chemistry Frontiers

15 M. Ju, X. Wang, X. Long and S. Yang, Recent advances in transition metal based compound catalysts for water splitting from the perspective of crystal engineering, CrystEngComm, 2020, 22, 1531.
32 N. Kamarulzaman, M. F. Kasim and N. F. Chayed, Elucidation of the highest valence band and lowest conduction band shifts using XPS for ZnO and Zn0.99Cu0.01O band gap changes, Results Phys., 2016, 6, 217.
33 X. Cheng, Z. Pan, C. Lei, J. Y. Jin and Y. Hou, Strongly coupled 3D ternary Fe2O3@NiP2/Ni[PO3]3 hybrid for enhanced


