Hierarchically Phosphorus Doped Bimetallic Nitrides Arrays with Unique Interfaces for Efficient Water Splitting

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Graphical abstract

Surface and interface controlled twist braid structures hierarchical arrays P-NiMo₄N₅@Ni-1 exhibits remarkable water splitting catalytic activity.

Highlights

• Strategy for controlled design of different morphologies arrays of bimetallic nitride on nickel foam
• Controllable synthesis of catalysts with multi-interfaces facilitate the effective mass and electron transport
• The twist braid nanorod arrays electrode exhibits outstanding electrocatalytic activities for OER and electrolysis of water
• Synergistic combination of heteroatomic doping for enhanced electrochemical activity
• In-depth research of the chemical evolution at the surface of bimetallic nitride under OER reaction

Abstract

Engineering of nanomaterials with abundant interfaces are vital but remain challenges for the electrocatalysts of renewable energy conversion systems. Benefitting from the efficient synthetic approach, a high degree of controlled design can be attained for the first time in the synthesis of hierarchical catalysts P-NiMo₄N₅@Ni, in which different morphologies arrays on nickel foam (NF) were achieved via introducing polyoxometalates with the capability of controlling the nucleation and crystal growth. Especially, the optimized twist braid nitrides nanorod arrays electrode P-NiMo₄N₅@Ni-1 with high surface-to-volume ratio of energetic actives exhibited unprecedented activity as a bifunctional electrocatalyst for water splitting, approaching 50 and 100 mA cm⁻² at low cell voltages of 1.59 and 1.66 V, respectively, which is one of the best electrolytic water catalysts. The insights gained through this work may provide novel approach for designing other arrays derived from polyoxometalates with unique surfaces as versatile electrode and provide a design platform to prepare the invertible oxides catalysts from nitrides at high potential with enhanced catalytic performance.

Keywords: polyoxometalates; bimetallic nitride; electrocatalysis; electrolysis of water; stability

1. Introduction

Controllable synthesis of electrode surface and interface has sparked researcher’s intense interests due to the essential and effective function for optimizing the electrochemical activity of electrode materials [1-4]. Properly-defined surface and interface of electrode concentrated mainly on constructing the hierarchical and open structures, controlling the morphology of composites with high surface-to-volume ratio of actives for the effective mass and electron transport [5-7]. With respect to the water splitting driven by electricity with the sustainable production of inexhaustible hydrogen and oxygen in particular [8], the approach electrolysis of water with low
energy consumption and high electrical efficiency heavily relies on the innovative breakthroughs in design of outstanding electrocatalysts for the two half reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [9]. Especially, OER electrocatalysts are prerequisite of the formidable bottleneck of water splitting due to the sluggish multielectron transfer process [10, 11]. Great enthusiasm in exploring non-noble metal electrocatalysts has brought abundant achievements even surpassing the state-of-the-art catalysts Pt for HER and IrO$_2$ for OER [12, 13]. Multiple researches pointed to some promising catalysts such as phosphides [14, 15], sulfide [16, 17], selenides [18, 19] nitrides [20-22], oxides [23, 24], hydroxides [25, 26] for HER or OER, but it remained a grand challenge to controllably prepare bifunctional catalysts with high reaction activity and electron conductivity for both HER and OER. Furthermore, the traditional catalysts are inclined to aggregate during pyrolysis and require additional polymeric binders to coat on a conductive substrate (carbon paper (CP), carbon cloth (CC), Ni foam (NF), etc.), which is greatly incommodious for electron conductivity and bubbles release.

A tricky issue is how to monitor and design the microstructure of electrocatalysts for water splitting, in which the catalytic system presents a complex process evolving the three phase action between the electrode active actives, the electrolyte and the generated gas. As the surface active sites of catalysts are energetic in electrocatalytic reaction [27] the promising strategy is to rational design multilevel structures with high surface-to-volume ratio for a quantity of catalytically active sites on multi-interfaces [26, 28]. Notably, the controlled self-assembly of nanocomposites in the form of hierarchical superstructures such as nanosheets [29], nanowires [15], rodlike [30, 31] and other nanotubes [32] arrays with oriented arrangement in situ grew on conductive substrate and acted as electrode directly, which markedly exposed catalytic sites along with effective gas release, mass and electron diffusions, thereby resulting in elevated electrochemical performances [33,34]. However, exploration of effective routes to realize the controllable growth of nanoarrays catalysts in the form of one-dimensional (1D) nanorod and two-dimensional (2D) nano-foliated structure anchored on three-dimensional (3D) NF are rarely developed due to the complexity intermolecular interface controls. Moreover, surface roughening of catalysts has weak bubble adhesion at the nanoarray electrode for the weak surface tension by affording the superaerophobic interface under water [35], which gives us the inspiration to controllably synthesis of arrays for different morphologies with abundant interfaces in the nano-scale level design.
Here, we report an original fabrication of P doped crystalline arrays NiMo$_4$N$_5$ supported on the Ni foam (P-NiMo$_4$N$_5$@Ni) with controlled morphologies via a facile strategy adopting polymolybdic acid and nickel nitrate as metal sources. Notably, H$_5$PMo$_{12}$O$_{40}$ (PMo$_{12}$) as Keggin-type POM has good water solubility and acidic properties, which could moderately dissolve a small amount of nickel on the surface of NF to form a homogeneous solution favorable for uniform arrays growth in situ and simultaneously introduce the heteroatomic P to the system. As a result, the self-supported binder-free electrode with the tailored 3D hierarchically architecture can be directly used to catalyze the OER and HER. Especially for the self-assembly P-NiMo$_4$N$_5$@Ni-1 twist braid nanorod arrays electrode, it provided efficient electron conducting pathway and multiple interfaces exhibiting high bifunctional electrocatalytic activity toward HER and OER under alkaline conditions for the first time. Furthermore, our research discloses that NiMo-O@Ni on the surface of P-NiMo$_4$N$_5$@NF-1 serves as the active species for OER due to the oxidation in situ. When electrodes P-NiMo$_4$N$_5$@Ni-1 were directly assembled as both cathode and anode for the electrolyzer, it exhibited surprising catalytic performance along with the long-term electrocatalytic stability, superior to most reported bifunctional electrocatalysts.

2. Material and methods

2.1 Synthesis of P-NiMo$_4$N$_5$@Ni-1,2,3,4,5 and NiMo$_4$N$_5$@Ni

Ni foams (NF) were washed ultrasonically for 10 minutes with acetone, water and ethanol two times each, respectively, and dried in an oven at 50 °C for use. In a typical procedure, a mixture of 0.1 mmol of phosphomolybdic acid (H$_5$PMo$_{12}$O$_{40}$· xH$_2$O), 0.6 mmol of nickel nitrate hexahydrate (Ni(NO$_3$)$_2$· 6H$_2$O) (atomic ratio Mo: Ni=2:1) and 1 mmol urea (CO(NH$_2$)$_2$) were dissolved in water with continuous ultrasound for 20 min to obtain a clarified solution. Then the solution was transferred into Teflon-lined stainless-steel autoclave with a piece of preprocessed NF (1 cm × 2 cm) immersing it. The autoclave was maintained at 180 °C for 12 h and naturally cooled to room temperature. The resulting light yellow NF was washed with water and ethanol three times in turn and dried in an oven at 50 °C to obtain the nanorod arrays on NF as precursor. The amount of loading catalyst on NF was about 2.5 mg cm$^{-2}$. The precursor was subjected the ammoniated treatment at 500 °C for 4 h in NH$_3$ (150 ccm) reduction atmosphere to obtain the sample P-NiMo$_4$N$_5$/Ni-1, whose mass loading is about 2.5 mg/cm$^2$.

P-NiMo$_4$N$_5$@Ni-2,3 were obtained by the similar process with atomic ratio Mo:Ni (1:1) and
Mo:Ni (1:2), respectively. P-NiMo₄N₅@Ni-4.5 was also prepared similar with P-NiMo₄N₅/Ni-1 without CO(NH₂)₂ and nickel source addition in the hydrothermal process. NiMo₄N₅@Ni was gained by accepting molybdenum source NaMoO₄·2H₂O to replace H₃PMo₁₂O₄₁·xH₂O without P source.

2.2 Synthesis of Pt/C@Ni and IrO₂@Ni

Similarly, the Pt/C@Ni and IrO₂@Ni working electrode were prepared by the following process. Firstly 2.5 mg catalyst Pt/C or IrO₂ was dispersed in 950 μL ethanol and 50 μL Nafion (1 wt.%) solution under sonication for 30 min to form a homogeneous solution. Then, 100 μL solution was slowly loaded onto the preprocessed NFs and dried to obtain the working electrode Pt/C@Ni and IrO₂@Ni with the area loading 2.5 mg/cm².

2.3 Characterization

X-ray powder diffraction (XRD) measurements were characterized on a D/max 2500 VL/PC diffractometer equipped with graphite monochromatized Cu Kα radiation (λ= 1.54060 Å). Scanning electron microscopy (SEM) images and Energy dispersive X-ray spectroscopy (EDS) were conducted by a JSM-7600F apparatus with an acceleration voltage of 10 kV to character the morphology of samples. Transmission electron microscopy (TEM) images were recorded on JEOL-2100 F instrument with an acceleration voltage of 200 kV. High-resolution TEM (HRTEM) images, Energy dispersive X-ray spectroscopy (EDS) and corresponding elemental mapping were carried on JSM-5160LV-Vantage typed energy spectrometer. Fourier transform infrared spectroscopy (FTIR) was conducted on a Mattson Alpha-Centauri spectrometer. X-ray photoelectron spectroscopy (XPS) was recorded on scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) employing Al kα radiation and C1s peak at 284.8 eV as an internal standard.

2.4 Electrochemical Measurements

All electrochemical measurements were conducted on the autolab workstation (Biologic) in a typical three-electrode configuration at room temperature. The as-prepared samples were directly used as working electrode with Ag/AgCl (saturated potassium chloride) and graphite rod as reference and counter electrodes, respectively.

Linear sweep voltammetry (LSV) scans for HER and OER were conducted at a scan rate of 5 mV s⁻¹ in 1 M KOH between 0.1 to -0.8 V and 1 to 2 V vs. RHE, respectively. All the LSV data were acquired till the stable polarization curves were obtained after several CV cycles.
The durability for HER and OER was executed by the chronoamperometry at the corresponding overpotential to the current density of 10 mA cm\(^{-2}\) for HER and 50 mA cm\(^{-2}\) for OER up to 24 h. The durability for water splitting was also performed by the chronoamperometry at the corresponding potential to the current density for 24 h.

Electrochemical double layer capacitance evaluations were carried out via CV method at non-faradaic potentials range from 1.2 to 1.3 V vs RHE with different scan rates: 20, 40, 60, 80, 100, 120, 140 mV s\(^{-1}\). By plotting the ΔJ at the potential of 1.25 V vs RHE against the scan rate, the linear slope Cdl is used to represent the ECSA.

The overall water splitting was conducted in a two-electrode system, comprising of P-NiMo\(_4\)N\(_5\)/Ni-1 as both anode and cathode electrode. The polarization curves were obtained by linear sweep voltammetry in the potential range of 1 to 2 V vs RHE at a scan rate of 5 mV s\(^{-1}\) in 1 M KOH. Faradic efficiency was performed by adopting the electrolysis in a sealed electrochemical H-type cell at the corresponding potential to the current density of 50 mA cm\(^{-2}\).

The gaseous generated by water electrolysis was detected by a gas chromatography (GC-7920), \(\text{H}_2\) and \(\text{O}_2\) was monitored by the thermal conductivity detector (TCD) with nitrogen as the carrier gas. The calculation of Faradaic efficiency

\[
FE = \alpha \times \frac{n \times F}{Q} \times 100\%
\]

where \(\alpha\) is the electron transfer number, \(n\) is the moles of the generated gas and \(F\) is the Faraday constant, \(Q\) represents the corresponding electric quantity.

### 3. Results and discussion

#### 3.1 Structural and morphological characterization

The synthesis of the electrocatalyst was illustrated in Figure 1 with two-step procedure. First, Ni–Mo oxide precursor slippy nanorod arrays were prepared via a hydrothermal reaction by a mixed solution containing PMo\(_{12}\), Ni(NO\(_3\))\(_2\) with atom ratio 1:2 of nickel and molybdenum, urea (0.01 mol) and a piece of Ni foam (NF, 1*2 cm\(^2\)) at 180 °C for 12 h. Owing to the action of PMo\(_{12}\), the soluble small amount of Ni\(^{2+}\) ions from NF tend to concentrate at the substract surfaces where the reaction prefers to obtain the nanorod arrays perpendicularly grown on the NF. Second, when the as-synthesized precursors were calcined in the NH\(_3\) atmosphere at 700 °C for 4 h, the formed twist braid nanorod arrays NiMo\(_4\)N\(_5\) directly vertically aligned on NF and recorded as P-NiMo\(_4\)N\(_5\)@Ni-1. Some controlled samples were prepared for comparison. To clarify the effect
of different compositions on electrochemical performances, the as-synthesized samples were also prepared and denoted as P-NiMo$_4$N$_5$@Ni-2 (n$_{Ni}$ : n$_{Mo}$ =1:1), P-NiMo$_4$N$_5$@Ni-3 (n$_{Ni}$ : n$_{Mo}$ =2:1) and P-NiMo$_4$N$_5$@Ni-4 (n$_{Ni}$ : n$_{Mo}$ =1:2 without urea) after the nitriding process. We also tried to use NF as both Ni source and self-supported 3D integrated skeletons, whose nitrides denoted as P-NiMo$_4$N$_5$@Ni-5. In order to further get insight into the influence of molybdenum source to the electrochemical properties, sodium molybdate was applied as the precursor instead of PMo$_{12}$ and the corresponding nitrides was noted as NiMo$_4$N$_5$@Ni.

First, X-ray diffraction (XRD; Figure 2a) of the composite Ni-Mo oxide precursor gave signals for the crystalline NiMoO$_4$·xH$_2$O (JCPDS no. 13-128) and Ni$_2$O$_3$H (JCPDS no. 40-1139). Then we carried out ICP-AES on the pure oxide, which were carefully mechanically removed from the Ni foam, which gave a Ni/Mo ratio of 5.2:1.8 (Table S1), resulting in that the composition of NiMoO$_4$·xH$_2$O and Ni$_2$O$_3$H is close to 1:1. Scanning electron microscopy (SEM) (Figure 2b, Figure 2c) and transmission electron microscopy (TEM) images (Figure 2d) scrutinized that oxide precursor was constructed of oriented nanorod arrays with smooth surface, diameters ranging between 100-120 nm and lengths about 5-10 μm uniformly aligned on NF. Furthermore, the element mapping of the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in Figure 2e manifested the uniform distribution of elements in nanorods prepared by hydrothermal method.

The crystalline structures of different nitride samples were also identified by XRD, Figure 3a and Figure S1 in the Supporting Information). Results reveal the as-obtained peaks resulting from the crystalline NiMo$_4$N$_5$ (JCPDS no. 65-9385) and Ni (JCPDS no. 1-1258). Interesting, the original morphology of nanorod arrays was well maintained (Figure 3b), but the surface changed to form twist braid nanorods with unique interfaces shown by SEM (Figure 3c, Figure 3d) and TEM (Figure 3e) images after annealing in a reduction ammonia atmosphere for 4 h, which may attribute that most oxygen atoms in arrays were near the surface and could be easily replaced by nitrogen atoms for a thermodynamically stable structure in the ammonia reduction environments [35]. Besides, the twist braid nanorod array morphology was further proofed by linear scanning of Energy dispersive X-ray spectrometry (EDS, Figure 3g) with special zigzag graphics. High-resolution TEM (HRTEM) image in Figure 3f clearly showed the lattice spacing of 0.246 nm, corresponding to the (100) plane of NiMo$_4$N$_5$(JCPDS no. 65-9385). Interestingly, the precursors of
P-NiMo$_2$N$_2$@Ni-2 and P-NiMo$_2$N$_3$@Ni-3 exhibited layers laminated of nanoflower arrays (Figure 4a, 4b) and tremella-like thin nanosheet arrays (Figure 4c, 4d), respectively, which may ascribe that high concentrations of Ni source significantly facilitate the growth of crystal nucleation along the flakes. Their corresponding morphologies changed little after the ammoniation treatment (Figure S2a and S3a). The element mapping measurements were also executed out on the nanorod or nanosheet peeled from P-NiMo$_2$N$_2$@Ni-1 (Figure 3h), P-NiMo$_2$N$_3$@Ni-2 (Figure S2c) and P-NiMo$_2$N$_3$@Ni-3 (Figure S3c) manifesting P, N, Ni and Mo elements are all homogeneously distributed in line with the Energy dispersive X-ray spectrometry (EDS, Figure S4) and embodying the uniformity of different arrays by hydrothermal method. In the control experiment of P-NiMo$_2$N$_5$@Ni-1, irregular nanorod arrays shape (Figure S5a) were obtained in P-NiMo$_2$N$_5$@Ni-4 when there is no urea adding while irregular bulk shape (Figure S5c) in P-NiMo$_2$N$_5$@Ni-5 were achieved when NF acted as the nickel source in the precursor preparation. There is no obvious change in the corresponding morphology after ammoniation treatment (Figure S5b, 5d). When sodium molybdate was used as the molybdenum source, acicular arrays of NiMo$_2$N$_5$@Ni were irregularly distributed on NF in Figure S5e. Worse still, some samples were removed from the skeleton after ammoniation treatment (Figure S5f).

3.2 Electro catalytic activity

3.2.1 HER performance of catalysts

The catalytic activity of P-NiMo$_2$N$_2$@Ni-1 for HER was evaluated employing a three-electrode configuration in 1 M KOH and was compared to Pt/C@Ni and bare NF (Figure 5a). Notably, all the curves were demonstrated without iR correction including the real resistive loss in the catalytic process. The polarization curve of P-NiMo$_2$N$_2$@Ni-1 delivered a relatively low overpotential of 118 mV at the current density of 10 mA cm$^{-2}$ ($\eta_{10}$), which greatly outperformed that of NF (296 mV) even better than Pt/C@NF at relatively high potentials giving large current densities. The superior activity may due to the fact that nitrogen atoms modulated d-band density of positively charged Ni and Mo atoms contributing the similar electronic structures with noble metals of group VIII [36]. Tafel plots were constructed from the polarization curves to evaluate the catalytic activity from a kinetic viewpoint. As expected, P-NiMo$_2$N$_3$@Ni-1 manifested a small Tafel slope of 125 mV dec$^{-1}$ higher than Pt/C@Ni (39 mV dec$^{-1}$) but evidently lower than bare Ni foam (296 mV dec$^{-1}$) in Figure 5b. To further give sight in the effect of ammoniated treatment on the activity
of catalyst, we compared the performance of precursor of P-NiMo4N5@Ni-1 and P-NiMo4N5@Ni-1 in Figure S6a and S6b. As can be seen, precursor of P-NiMo4N5@Ni-1 have inferior property, which manifested the favourable performance for the nitrides adjusting the density of metal d-band to realize vacancy defect and thus improving the ability to supply electrons for electrolytic water. The electrocatalytic activity of different nickel and molybdenum element molar ratio for nitrides toward HER was evaluated in Figure 6a. The corresponding overpotentials required for $\eta_{10}$ are 123 and 156 mV for P-NiMo4N5@Ni-2 and P-NiMo4N5@Ni-3 (Figure 6b), respectively. The results showed that the HER activity decreased with the decreasing level of molybdenum source, which may ascribe that nickel–molybdenum based composites combined two non-noble metals from an ascending branch with weaker Ni–H bonds and a descending branch with stronger Mo–H bonds of volcano curve generating enhanced activity for HER [37-39]. We also tested the HER polar curves and corresponding Tafel plot of P-NiMo4N5@Ni-4,5 constructed by different precursors (Figure S7a, S7b). Obviously, the performance of P-NiMo4N5@Ni-4 and P-NiMo4N5@Ni-5 for HER was influenced by the irregular nanorods and bulk morphology, which greatly decreased the specific surface area for contacting the electrolyte and thus weakened the corresponding performance. NiMo4N5@Ni obtained inferior catalytic performance for HER acquiring high overpotential of 221 mV at $\eta_{10}$ and Tafel plot of 172 mV dec$^{-1}$, which manifested the effect of P doping and regular morphology on electrochemical performance. Comparatively, P-NiMo4N5@Ni-1 obtained superior performance attributing to two aspects. On the one hand, P doping modified the electronic properties of nitrides and created more active sites. On the other hand, P-NiMo4N5@Ni-1 had uniformly twist braid nanorod morphology with large specific surface to immerse the electrolyte and thus improved its electrocatalytic activity [40].

3.2.2 OER performance of catalysts

The OER as the bottle-neck reaction in many energy devices hinders the development of energy storage and conversation due to its multistep proton-coupled sluggish electron transfer processes. The OER activity of P-NiMo4N5@Ni-1 was also estimated by a three electrode device in 1.0 M KOH and compared to precious metal catalysts IrO$_2$@Ni and bare NF. The polarization curves in Figure 5c manifested the well-known oxidation peak of NiOOH from Ni(OH)$_2$ at about 1.38 V and the performance of P-NiMo4N5@Ni-1 exhibited a fairly higher activity than that of IrO$_2$@Ni and
bare NF. Specifically, the 3D hierarchical electrode achieved the current densities of 100 mA cm\(^{-2}\) (\(\eta_{100}\)) requiring the overpotential of 297 mV and even superior to the most highly catalytic activity of non-noble metal OER catalysts (Table S2). In contrast, state of the art IrO\(_2\)@Ni and bare NF electrodes exhibited poor performance with the overpotentials of 554 and 625 mV at \(\eta_{100}\), respectively. Furthermore, the P-NiMo\(_4\)N\(_5\)@Ni-1 electrode showed a fairly small Tafel slope among the catalysts (Figure 5d). In stark contrast, the particular low Tafel slope value of 33.6 mV dec\(^{-1}\) for P-NiMo\(_4\)N\(_5\)@Ni-1 indicated fast kinetics of \(O_2\) evolution representing the inherent OER activity. The catalytic activities achieved by bimetallic composites P-NiMo\(_4\)N\(_5\)@Ni-1 are tremendous, which may due to different metal species modulation of gas adsorption energy and improvement of electronic conductivity [13, 41]. For comparison, precursor of P-NiMo\(_4\)N\(_5\)@Ni-1 was carried out for OER approaching the overpotential of 435 mV at \(\eta_{100}\) and Tafel slope of 65 mV dec\(^{-1}\) (Figure S6c and Figure S 6d), and further indicated the superiority of nitride P-NiMo\(_4\)N\(_5\)@Ni-1. Control sample P-NiMo\(_4\)N\(_5\)@Ni-2,3 were also used for OER with the overpotential of 370 and 420 mV at \(\eta_{100}\), and Tafel slope of 44.1 and 59.9 mV dec\(^{-1}\)(Figure 6c, 6d), respectively. Their inferior catalysts activity may ascribe that the congregated nanoflowers and nanosheets of P-NiMo\(_4\)N\(_5\) easily folded and stacked during the high temperature processing (Figure S2a and Figure S3a) providing less accessible catalytic sites. Furthermore, unstable morphologies also hindered its performance, which was verified by the SEM images of post-OER P-NiMo\(_4\)N\(_5\)@Ni-2,3(Figure S7a and Figure S7b). Similarly, P-NiMo\(_4\)N\(_5\)@Ni-4,5 and P-NiMo\(_4\)N\(_5\)@Ni obtained poor performance with the overpotential of 403, 426 and 498 mV at \(\eta_{100}\), and Tafel slope of 49.4, 53.6 and 58.2 mV dec\(^{-1}\)(Figure S8c, 8d), respectively, illustrating the positive effect of uniform morphology and P doping.

To investigate the effective electrochemically active surface area (ECSA) of various morphologies during OER catalysis, cyclic voltammetry (CV) with different scan rates was carried out to estimate the double-layer capacitance (Cdl). The comparison of Cdl values (Figure 7) indicates that the active surface area of P-NiMo\(_4\)N\(_5\)@Ni-1 is higher than that of P-NiMo\(_4\)N\(_5\)@Ni-2, P-NiMo\(_4\)N\(_5\)@Ni-3. The high surface area attributed to the controlled nanorod arrays and subsequent unique twist braid nanorod structure with more interfaces after the annealing processes, whose hierarchical structure was favorable for the intimate accessibility of electrolyte, exposed more active sites for electrochemical reactions and thus promoted the electrochemical activity in
alkaline medium.

Electrochemical impedance spectroscopy (EIS) was carried out to provide essential insights into the electrode kinetics during electrochemical catalysis process in Figure S9. The as-prepared vertical P-NiMo4N5@Ni-1 retained a vast interconnected structure on NF providing greater electrochemically active surface area to expose abundant reaction sites than that of the accumulated P-NiMo4N5@Ni-2 and P-NiMo4N5@Ni-3, which was more benefit for the transfer of electrons and protons, thus decreased the electrochemical impedance.

3.2.3 Stability of electrode P-NiMo4N5@Ni-1

High durability of catalysts are also crucial issues for electrochemical reaction due to the corrosive potential. Expectedly, the P-NiMo4N5@Ni-1 also show good durability for HER and OER proved by the chronoamperometric measurements (Figure 10a), in which negligible current decay is detected upon the 24 h operation with the corresponding overpotential of η10 and η50. Furthermore, the morphology of P-NiMo4N5@Ni-1 still remains as nanorod arrays after the HER and OER measurement (Figure 8b, 8c, 8d), demonstrating the structural integrity of 3D nanorods can still be maintained during the process of repeated bubbles aggregation and release. Then we carried out the XRD characterization of P-NiMo4N5@Ni-1 after the electrochemical tests (Figure 8a). Obviously, The XRD pattern of post-HER P-NiMo4N5@Ni-1 have no changes in the characteristic peaks. While, the intensity of characteristic peaks in post-OER P-NiMo4N5@Ni-1 may due to the formation of new composite on the surface. To confirm the compositional element change, EDX elemental mapping of P-NiMo4N5@Ni-1 after the electrochemical test for OER was conducted on the pure nanorods which were mechanically removed from the Ni foam (Figure 8e). There are a small amount of N and P elements on the surface of the nanorods, but also a small amount of O elements, which further indicates that the composition changes during the catalytic process.

As recent studies showed that transition metal nitrides may undergo unconspicuous component changes and convert into the corresponding metal hydroxides/oxides at high voltage for OER [42]. So some surface structure sensitive characterizations were performed to give some insight in the changes of the catalytic active species P-NiMo4N5@Ni-1 after OER. We carried out the X-ray photoelectron spectroscopy (XPS) to trace the elemental composition and valence changes of surface elements in the P-NiMo4N5@Ni-1 before and after the oxidation process (Figure 9). As can been seen, N, P, Ni and Mo elements existed in the as prepared sample P-NiMo4N5@Ni-1
before the OER reaction. The high-resolution N 1s spectra were fitted into two peaks at 395.02 and 397.82 eV revealing the existence of Mo-N and Ni-N [43]. The P 2p spectrum deconvoluted into two peaks with binding energy of 129.8 and 133.8 eV assigning to phosphide and phosphate signals [44]. The peaks in high-resolution XPS spectra of Ni 2p located at 852.4 and 869.5 eV attributing to Ni⁰, the others at 855.6 and 873.3 eV accompanied by two satellite peaks corresponded to Ni²⁺ [25]. In the Mo 3d spectrum, two characteristic peaks at 232.5 and 229.2 eV are ascribed to Mo⁴⁺ and the other pair of peaks at 235.9 and 233.2 eV confirmed the presence of the Mo⁶⁺ assigning to the surface oxidation of Mo [43]. After the OER, the spectrum of Ni 2p is positively shifted displaying four peaks of Ni²⁺ (856.6 and 874.9 eV) and NiOOH (855.7 and 873.1 eV) [45], respectively, and signifying the coexistence of Ni²⁺ and Ni³⁺ species after the oxidation. Similarly, the peaks around 234.4, 230.9, 235.6 and 232.1 eV for Mo 2p were attributed to Mo⁵⁺ and Mo⁶⁺ after the OER [46]. Fourier transform infrared spectra (FT-IR) further affirmed the presence of MoOₓ in Figure S10 for the characteristic peaks at ~ 1385, ~ 824 and ~ 634 cm⁻¹.

Based on the above analysis, the resulting active sites on the surface of the electrode for OER may be the oxidized catalyst MoNi-O-@Ni derived from the P-NiMo₅N₅@Ni-1. The conversion is so fast that there is no obvious current change in the durability test (Figure 10a).

3.2.4 The performance of the electrolysis water of symmetric electrode P-NiMo₅N₅@Ni-1

Inspired by the superior bifunctional electrocatalytic performance of P-NiMo₅N₅@Ni-1 towards HER and OER, we fabricated an electrolyzer to evaluate the overall water splitting performance, comprising P-NiMo₅N₅@Ni-1 electrode as both the cathode and anode. For comparison, control electrolyzer was also assembled by using the state of the art Pt/C and IrO₂ catalysts both combined on NF (IrO₂@Ni||Pt/C@Ni) with the same loading of P-NiMo₅N₅@Ni-1 as cathode and anode. As shown in Figure 10b, the P-NiMo₅N₅@Ni-1||P-NiMo₅N₅@Ni-1 electrode can achieve η₁₀₀ at the voltage of 1.66 V which are better than that of IrO₂@Ni||Pt/C@Ni electrode and most of nonprecious metal catalysts (Table S3). Furthermore, P-NiMo₅N₅@Ni-1 also has a good durability for water electrolysis at a fixed current density of 50 mA cm⁻² (Figure 10a), which meets the requirements of practical application. The moles of released hydrogen and oxygen bubbles was plotted with the coincidence of theoretically calculated value in Figure 10c. Correspondingly, nearly 100 % of faradaic efficiency in Figure 10d was obtained by comparing the amount of gas generated experimentally with theoretical value, manifesting the electrolysis has almost no side
effects.

Such remarkable catalytic activity of the P-NiMo₄N₅@Ni-1 could be due to the following factors: (1) The hierarchical architecture of 1D highly active nanorod arrays vertically grew on 3D conductive substrate NF ensures good electrical contacts without additional binders benefiting for the efficient mass and electron transfer. (2) The unique twist braid structures with plentiful interfaces facilitate small bubbles generation and detaching from the electrode. (3) P-NiMo₄N₅@Ni-1 have high intrinsically catalytic activities for HER and their surface can be easily transformed into NiMo-O@Ni active species for the OER. The above synergistic electronic interactions of bimetallic nitrides and oxides together may make a big contribution for water electrolysis performance.

4. Conclusions

In conclusion, the confined NiMo₄N₅@Ni arrays with controllable morphologies were achieved by introducing the polyoxometalates into array synthesis for the first time and the following simple ammoniation process, in which the exposed large specific surface area endowed these architectures with richness activity. Especially, the as-synthesized P-NiMo₄N₅@Ni-1 possesses twist braid hierarchical structure with multiple interfaces featuring the avoidable active sites aggregation, large specific surface area and high electronic conduction beneficial for energy conversion. The unique morphology coupled with intrinsic catalytic activity of P doping bimetallic nitride NiMo₄N₅ resulted the outstanding performance for electrolysis of water far exceeding most of electrocatalysts and long-term electrocatalytic stability for at least 24 h. This work sets a refined method to explore other multi-interface electrocatalysts in nanoscale for water splitting and give the fundamental investigation of the transition of nitrides catalysts at high potential catalysis. Furthermore, in view of the simple preparation and remarkable catalytic performance, the integrated electrode P-NiMo₄N₅@Ni-1 advance the practical research for alkaline electrolyzers.

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**Figures**
Figure 1. Schematic illustration of the synthetic process of twist braid nanorod arrays P-NiMo$_4$N$_5$@Ni-1 composite.

Figure 2. Characterization of Ni-Mo oxide precursor of P-NiMo$_4$N$_5$-1. (a) XRD patterns of the precursor. (b) and (c) SEM images of precursor under different magnifications. (d) TEM image and (e) EDX elemental mapping of Ni-Mo oxide precursor of P-NiMo$_4$N$_5$-1.
**Figure 3.** Characterization of P-NiMo₄N₅@Ni-1. (a) XRD patterns of the composite P-NiMo₄N₅@Ni-1. (b), (c) and (d) SEM images of P-NiMo₄N₅@Ni-1 under different magnifications. (e) TEM and (f) HRTEM images of P-NiMo₄N₅@Ni-1. EDX elemental mapping of (g) linear scan and (h) plane sweep of N, P, Mo and Ni for P-NiMo₄N₅@Ni-1.
Figure 4. SEM images of (a) precursor of P-NiMo$_4$N$_5$@Ni-2 and (b) under different magnifications, (c) precursor of P-NiMo$_4$N$_5$@Ni-3 and (d) under different magnifications.

Figure 5. Electrochemical performances of electrocatalysts. (a) Polarization curves of catalysts for HER and (b) corresponding Tafel plots. (c) Polarization curves of catalysts for OER and (d) corresponding Tafel plots. All the experiments were conducted in 1 M KOH at room temperature.
Figure 6. Electrochemical performances of electrocatalysts. (a) Polarization curves of catalysts with different atom ratio of nickel and molybdenum for HER and (b) corresponding Tafel plots. (c) Polarization curves of catalysts with different atom ratio of nickel and molybdenum for OER and (d) corresponding Tafel plots.
Figure 7. Electrochemical activity specific surface area of different catalysts. (a), (c) and (e) CV of P-NiMo$_2$N$_2$@Ni-1,2,3 with different rates from 20 to 140 mV s$^{-1}$. (b), (d) and (f) $\Delta J$ of catalysts P-NiMo$_2$N$_2$@Ni-1,2,3 plotted against scan rates at the potential of 1.25 V vs RHE. The slopes were used to denote the ECSA.
Figure 8. Characterization of P-NiMo₅N₅@Ni-1 after electrochemical tests. (a) XRD patterns of P-NiMo₅N₅@Ni-1 after tests, (b) SEM of P-NiMo₅N₅@Ni-1 after electrochemical test for HER, (c) SEM, (d) TEM and (e) EDX elemental mapping of P-NiMo₅N₅@Ni-1 after the electrochemical test for OER.
Figure 9. XPS spectrum of electrode P-NiMo$_4$N$_5$@Ni-1. XPS high-resolution scans of (a) N 1s, (b) P 2P, (d) Mo 2P, (e) Ni 2P before the chronoamperometric test for OER. XPS high-resolution scans of (e) Mo 2P, (f) Ni 2P after the chronoamperometric test for OER.
Figure 10. Long term catalytic stability and overall water splitting performance of P-NiMo₅N₅@Ni-1. (a) Chronoamperometric curves of P-NiMo₅N₅@Ni-1 for HER, OER and water splitting corresponding to the potential of 0.118, 1.47 and 1.59 V vs RHE. (b) Polarization curves of the two electrode P-NiMo₅N₅@Ni-1||P-NiMo₅N₅@Ni-1 electrolyzer. (c) Gas yield of H₂ and O₂ generated for water splitting and (d) corresponding faraday efficiency.