

A charge-mediated cooperative assembly strategy toward phase-tunable mesoporous nickel phosphides for efficient alkaline hydrogen evolution

Ye Wang^{1,§}, Lu Liu^{1,§}, Ling Zhang²(✉), Zhen-An Qiao¹(✉)

¹ State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

² State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China

[§] Ye Wang and Lu Liu contributed equally to this work.

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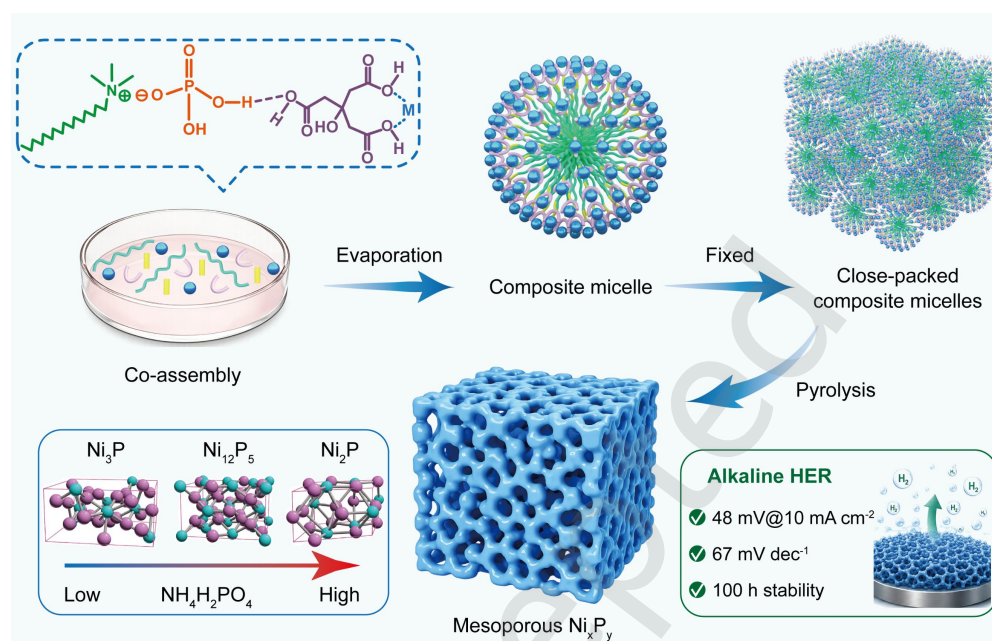
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We report a charge-mediated cooperative assembly strategy that enables the one-pot synthesis of phase-tunable mesoporous Ni_xP_y . Benefiting from the favorable Ni_2P phase, accessible mesoporosity, and efficient interfacial charge transfer, the optimized mesoporous Ni_2P -1.0 exhibits excellent alkaline HER activity and long-term operational stability.

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[§] Ye Wang and Lu Liu contributed equally to this work.

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 Address correspondence to Ling Zhang, zhanglingchem@jlu.edu.cn; Zhen-An Qiao, qiaozhenan@jlu.edu.cn

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ABSTRACT: Phase-tunable mesoporous nickel phosphides are promising electrocatalysts for alkaline hydrogen evolution. Their catalytic behavior can be regulated by Ni/P stoichiometry and accessible mesoporous architectures. However, simultaneously controlling phosphide phase evolution while maintaining an open mesoporous framework remains challenging, as high-temperature phosphidation often causes framework shrinkage, pore collapse, and uncontrolled phase transformation. Herein, we report a charge-mediated cooperative assembly strategy for the one-pot synthesis of mesoporous Ni_xP_y with tunable crystalline phases. In this system, CTAC-derived CTA^+ micelles, phosphate species, and Ni-citrate complexes cooperatively assemble into inorganic-organic composite micelle precursors through electrostatic interactions and hydrogen bonding. Dynamic light scattering, zeta-potential analysis, and Fourier transform infrared spectroscopy support an $\text{S}^+ \text{X}^-$ I-type cooperative assembly pathway, in which CTA^+ micelles, phosphate species, and Ni-citrate complexes act as structure-directing agents, charge-mediating/hydrogen-bonding linkers, and inorganic precursor units, respectively. By regulating the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage, the effective phosphorus supply can be precisely adjusted, enabling a stepwise phase evolution from Ni_3P to Ni_{12}P_5 and ultimately to Ni_2P while preserving the well-defined mesoporous framework. The optimized mesoporous Ni_2P -1.0 catalyst requires an overpotential of 48 mV to reach 10 mA cm^{-2} , exhibits a Tafel slope of 67 mV dec^{-1} , and maintains stable operation for 100 h in 1.0 M KOH. These findings establish a practical route for coupling phase regulation with mesostructure engineering in transition-metal phosphides and offer guidance for designing efficient noble-metal-free electrocatalysts toward alkaline hydrogen evolution.

KEYWORDS: mesoporous materials, nickel phosphides, charge-mediated cooperative assembly, phase regulation, alkaline hydrogen evolution.

1 Introduction

The growing demand for sustainable energy technologies has stimulated extensive efforts to develop efficient and scalable approaches for clean hydrogen production. Hydrogen, with its high gravimetric energy density and carbon-free utilization, is widely regarded as a promising energy carrier for future low-carbon energy systems [1–3]. Electrochemical water splitting powered by renewable electricity offers a viable route for sustainable hydrogen generation. However, its practical implementation is still limited by the sluggish kinetics of the hydrogen evolution reaction (HER), especially in alkaline media, where water dissociation and hydrogen-intermediate conversion introduce additional kinetic barriers [4–6]. Although Pt-based materials remain the benchmark HER catalysts, their scarcity and high cost have motivated the exploration of earth-abundant alternatives with high activity and durability. Among various noble-metal-free HER catalysts, nickel phosphides (Ni_xP_y) have attracted considerable attention, because their catalytic properties can be regulated by

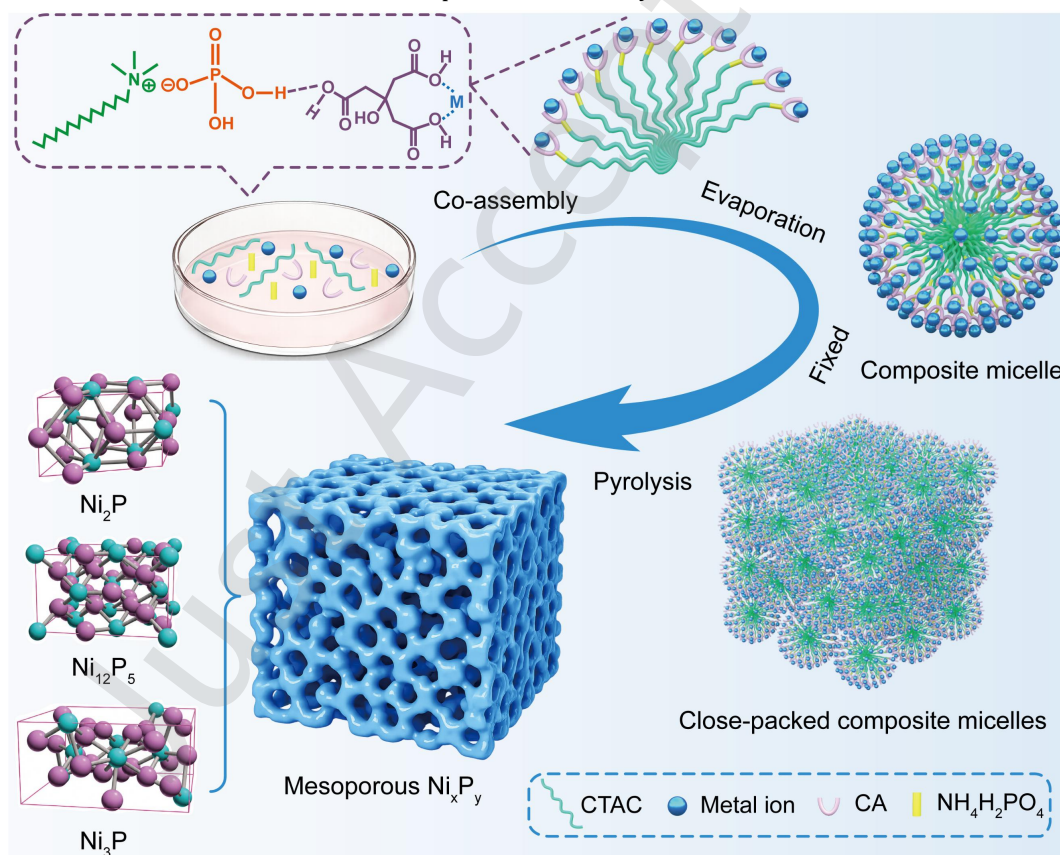
tailoring their crystalline phase and Ni/P stoichiometry. Within the Ni_xP_y family, different Ni/P ratios can modulate the electronic interaction between electropositive Ni sites and electronegative P sites, thereby influencing water activation, hydrogen adsorption, and hydrogen desorption processes [7–9]. This phase-dependent electronic regulation provides an effective strategy for tuning the Volmer, Heyrovsky, and Tafel steps in alkaline HER. However, conventional synthetic methods, such as solid-state phosphidation, hydrothermal synthesis, and post-phosphidation conversion, often yield dense particles or irregular aggregates [10–15]. These structures generally suffer from limited exposure of active sites, long ion/electron transport pathways, and inefficient hydrogen-bubble release, which restrict the catalytic advantages derived from phase regulation.

Constructing mesoporous metal phosphides provides a promising strategy to address these limitations. A well-defined mesoporous framework can expose abundant electrochemically accessible sites, enhance electrolyte

penetration, shorten mass- and charge-transport distances, and facilitate hydrogen-bubble release, all of which are beneficial for alkaline HER [16–18]. Despite these advantages, the synthesis of phase-tunable mesoporous metal phosphides remains challenging for three main reasons: (i) the cooperative assembly between inorganic precursors and organic templates is difficult to control, which hinders the formation of stable mesostructured precursors; (ii) the high-temperature treatment required for phosphide formation can damage thermally sensitive mesoporous frameworks, causing structural shrinkage or pore collapse; and (iii) phase evolution during phosphidation is often coupled with mesostructural reconstruction, making it difficult to tune the crystalline phase while preserving a well-defined pore architecture. Therefore, the development of a feasible synthetic strategy that simultaneously enables phase regulation and mesostructure preservation is highly desirable.

Herein, we develop a charge-mediated cooperative assembly strategy for the one-pot synthesis of phase-tunable mesoporous Ni_xP_y (Scheme 1). In this approach, citric acid (CA) coordinates with Ni^{2+} to form Ni-citrate complexes,

$\text{NH}_4\text{H}_2\text{PO}_4$ provides phosphate species for both precursor assembly and phosphide formation, and CTAC-derived CTA^+ micelles direct mesostructure construction. Driven by electrostatic interactions and hydrogen bonding, these components cooperatively assemble into inorganic-organic composite micelle precursors, which are subsequently converted into mesoporous nickel phosphides through in situ thermal phosphidation. Mechanistic investigations based on dynamic light scattering, zeta-potential analysis, and FT-IR spectroscopy reveal an $\text{S}^+\text{X}^-\text{I}$ -type cooperative assembly pathway and clarify the interactions among the precursor components. By adjusting the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage, the crystalline phase can be tuned from Ni_3P to Ni_{12}P_5 and finally to Ni_2P while preserving the well-defined mesoporous architecture. Furthermore, the extension of this strategy to Co-, Fe-, and Cu-based phosphides demonstrates its potential applicability for constructing mesoporous phosphide materials. Benefiting from the favorable Ni_2P phase, accessible mesoporosity, and rapid interfacial charge transfer, the optimized mesoporous Ni_2P -1.0 exhibits excellent alkaline HER activity and long-term operational stability.



Scheme 1 Schematic illustration of the charge-mediated cooperative assembly strategy for the synthesis of phase-tunable mesoporous nickel phosphides.

2 Results and discussion

2.1 Mesostructural Evolution of Mesoporous Ni_2P Framework

The phase-tunable mesoporous Ni_xP_y series catalysts were synthesized via a charge-mediated cooperative assembly strategy using CTAC as the structure-directing agent, phosphate species as charge-mediating/hydrogen-

bonding linkers, and Ni-citrate complexes as inorganic precursor units. Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CA and a selected amount of $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in CTAC-containing deionized water to obtain a uniform precursor solution. The solution was then cast into Petri dishes and allowed to evaporate and solidify to yield composite micelle precursors. Finally, the mesoporous Ni_xP_y series catalysts were obtained by thermal treatment of the precursors at 600°C under a 10 vol% H_2/N_2 atmosphere (Fig. S1 in the ESM).

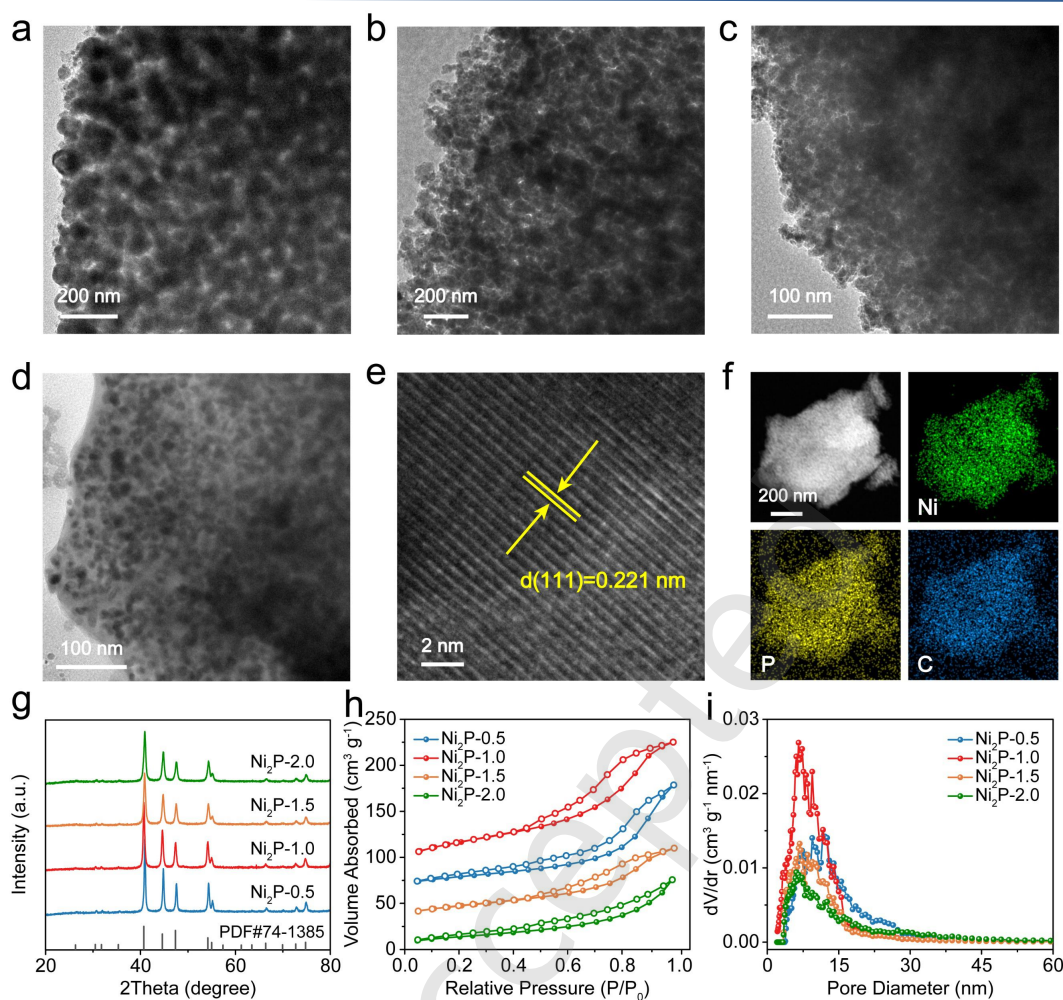


Figure 1 Mesoporous evolution of mesoporous Ni_2P frameworks. TEM images of (a) Ni_2P -0.5, (b) Ni_2P -1.0, (c) Ni_2P -1.5, and (d) Ni_2P -2.0. (e) HRTEM image and (f) EDS elemental mapping of mesoporous Ni_2P -1.0. (g) XRD patterns, (h) N_2 adsorption-desorption isotherms, and (i) pore-size distributions for the mesoporous Ni_2P -z series.

To clarify the structure-directing role of cetyltrimethylammonium chloride (CTAC) in the formation of mesoporous Ni_2P , a series of mesoporous Ni_2P -z samples, where z represents the CTAC amount in mmol, was synthesized by varying the CTAC dosage while keeping the other synthetic parameters unchanged. The morphology and mesoporous evolution of the obtained samples were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images (Fig. S2(a) – (d) in the ESM) show that all samples consist of densely packed nanocrystalline aggregates, with no obvious variation in the overall particle morphology observed upon increasing the CTAC dosage. TEM characterization was further performed to examine the internal pore structure. As shown in Fig. 1(a) – (d), mesoporous Ni_2P -0.5, prepared with a relatively low CTAC dosage of 0.5 mmol, displays a loosely connected network composed of aggregated nanocrystals. When the CTAC dosage is increased to 1.0 mmol, the resulting mesoporous Ni_2P -1.0 sample exhibits a well-defined mesoporous framework with abundant interconnected pore channels. The pore walls are constructed from ultrasmall Ni_2P nanocrystals with an average size of ~ 13 nm. Further increasing the CTAC dosage to 1.5 and 2.0 mmol leads to the formation of an amorphous carbonaceous layer on the nanocrystal surfaces, which likely

originates from the carbonization of excess CTAC species during thermal conversion. In contrast, the sample prepared without CTAC exhibits dense bulk particles without discernible mesoporosity (Fig. S3 in the ESM). These observations indicate that CTAC is essential for constructing the mesoporous Ni_2P framework, while an appropriate CTAC dosage is required to avoid excessive carbonaceous residues.

The mesoporous evolution can be understood by considering the competition between micelle-mediated framework organization and CTAC-derived carbon accumulation during thermal conversion. At an insufficient CTAC concentration, the limited number of CTA^+ micelles cannot effectively organize the inorganic precursor species or stabilize the developing mesoporous framework against shrinkage and nanocrystal coalescence, resulting in poorly developed mesoporosity. At the optimized CTAC dosage, the CTA^+ micelles provide sufficient soft-templating capability for cooperative assembly, thereby facilitating the formation of interconnected mesopore channels while suppressing severe nanocrystal aggregation. However, excessive CTAC increases the organic fraction in the precursor and promotes the formation of residual carbonaceous species during thermal treatment. These carbonaceous residues can coat the Ni_2P nanocrystals, narrow the mesopore channels, and reduce the accessibility

of active sites. Thermogravimetric (TG) analysis further supports the decomposition of organic components and the formation of residual carbon during thermal conversion (Fig. S4 in the ESM). CHN elemental analysis shows that the residual carbon content progressively increases from 6.3 to 15.8 wt% as the CTAC dosage increases from 0.5 to 2.0 mmol (Table S1 in the ESM). Therefore, 1.0 mmol CTAC represents an optimal dosage that balances mesostructure development, nanocrystal dispersion, and the suppression of excessive carbon accumulation.

The optimized mesoporous Ni₂P-1.0 sample was further characterized to evaluate its crystallinity and elemental distribution. The high-resolution TEM (HRTEM) image in Fig. 1(e) shows distinct lattice fringes with a d-spacing of 0.221 nm, which can be indexed to the (111) plane of hexagonal Ni₂P. This result confirms the formation of Ni₂P nanocrystals within the mesoporous framework. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Fig. 1(f)) further reveals a uniform spatial distribution of Ni, P, and C throughout the architecture. X-ray diffraction (XRD) analysis was performed to examine the crystalline phases of the mesoporous Ni₂P-z series. As presented in Fig. 1(g), all samples exhibit diffraction peaks at $2\theta = 40.71^\circ$, 44.61° , 47.36° , 54.20° , and 55.00° , which can be assigned to the (111), (201), (210), (300), and (211) planes of hexagonal Ni₂P, respectively [JCPDS No. 74-1385] [19, 20]. No additional diffraction peaks are detected, indicating that varying the CTAC dosage does not alter the crystalline phase of Ni₂P. The porous characteristics of the mesoporous Ni₂P-z series were further investigated by N₂ adsorption-desorption measurements. As displayed in Fig. 1(h), all samples exhibit type-IV isotherms with H3-type hysteresis loops at $P/P_0 = 0.4$ – 0.8 , suggesting the presence of interparticle mesopores within the aggregated nanocrystalline frameworks [21, 22]. The Brunauer-Emmett-Teller (BET) specific surface areas and total pore volumes fall within the ranges of 43 – $111 \text{ m}^2 \text{ g}^{-1}$ and 0.114 – $0.218 \text{ cm}^3 \text{ g}^{-1}$, respectively, with detailed textural data listed in Table S2 in the ESM.

2.2 NH₄H₂PO₄-Dosage-Regulated Phase Evolution of Mesoporous Ni_xP_y Frameworks

After identifying 1.0 mmol CTAC as the optimal dosage for constructing a well-defined mesoporous framework, the effect of NH₄H₂PO₄ dosage on the phase composition of nickel phosphides was systematically investigated. A series of mesoporous Ni_xP_y-1.0 samples was synthesized by varying the NH₄H₂PO₄ dosage from 0.1 to 0.5 mmol while keeping the other synthetic parameters unchanged. XRD analysis was first performed to monitor the NH₄H₂PO₄-dosage-dependent phase evolution. As shown in Fig. 2(a), the sample prepared with 0.1 mmol NH₄H₂PO₄ exhibits diffraction peaks that can be indexed to Ni₃P [JCPDS No. 74-1384] [23, 24], indicating the preferential formation of a Ni-rich phosphide phase under phosphorus-deficient conditions. When the NH₄H₂PO₄ dosage is increased to 0.2 mmol, diffraction peaks corresponding to both Ni₃P and Ni₁₂P₅ are observed, suggesting the formation of an intermediate biphasic composition. Further increasing the dosage to 0.3 mmol results in Ni₁₂P₅ becoming the dominant crystalline phase, as evidenced by the characteristic

reflections of Ni₁₂P₅ [JCPDS No. 74-1381] [25, 26]. At 0.4 mmol NH₄H₂PO₄, a second biphasic composition consisting of Ni₁₂P₅ and Ni₂P is obtained. When the NH₄H₂PO₄ dosage is increased to 0.5 mmol, the diffraction peaks can be assigned to hexagonal Ni₂P. Further increasing the NH₄H₂PO₄ dosage to 1.0–2.0 mmol does not change the dominant Ni₂P phase (Fig. S5 in the ESM). These results demonstrate a stepwise phase evolution from Ni₃P to Ni₁₂P₅ and finally to Ni₂P, indicating that increasing the NH₄H₂PO₄ dosage progressively shifts the nickel phosphide system from Ni-rich phases toward more P-rich compositions.

To determine whether this NH₄H₂PO₄-regulated phase evolution can be achieved without compromising the mesoporous architecture, representative samples in the phase-evolution series were further characterized by SEM, TEM, and HRTEM. SEM and TEM images (Fig. S6(a) – (d) in the ESM and Fig. 2(b) – (e)) show that the interconnected mesoporous channels are preserved throughout the series, suggesting that the NH₄H₂PO₄ dosage mainly regulates the crystalline phase rather than disrupting the mesostructure. For the sample prepared with 0.1 mmol NH₄H₂PO₄, clear lattice fringes with a d-spacing of 0.216 nm are observed (inset of Fig. 2(b)), which can be assigned to the Ni₃P (321) plane. The 0.2 mmol sample shows two sets of lattice fringes with d-spacings of 0.216 and 0.186 nm (inset of Fig. 2(c)), corresponding to the Ni₃P (321) and Ni₁₂P₅ (312) planes, respectively, supporting the coexistence of the two phases. For the 0.3 mmol sample, the observed 0.186 nm fringe (inset of Fig. 2(d)) can be indexed to the Ni₁₂P₅ (312) plane, indicating the formation of Ni₁₂P₅ as the dominant phase. At 0.4 mmol NH₄H₂PO₄, two sets of lattice fringes with d-spacings of 0.186 and 0.221 nm are simultaneously observed (inset of Fig. 2(e)), assignable to the Ni₁₂P₅ (312) and Ni₂P (111) planes, respectively, suggesting the coexistence of Ni₁₂P₅ and Ni₂P. For the 0.5 mmol sample, the 0.221 nm fringe corresponding to the Ni₂P (111) plane is observed in the HRTEM image of Ni₂P-1.0 (Fig. 1(e)). These HRTEM observations, together with the XRD results, collectively confirm a stepwise phase evolution from Ni₃P to Ni₁₂P₅ and ultimately to Ni₂P with increasing NH₄H₂PO₄ dosage.

The NH₄H₂PO₄-dosage-regulated phase evolution can be understood in terms of the effective phosphorus supply during thermal conversion. Under a low NH₄H₂PO₄ dosage, the limited phosphorus availability favors the formation of Ni-rich Ni₃P. As the NH₄H₂PO₄ dosage increases, the enhanced phosphorus supply promotes a higher degree of phosphidation of the nickel precursor, thereby stabilizing progressively P-rich nickel phosphide phases. The appearance of biphasic Ni₃P/Ni₁₂P₅ and Ni₁₂P₅/Ni₂P intermediates suggests that the phase transformation proceeds through a stepwise phosphidation process rather than an abrupt phase transition. This transformation pathway is chemically reasonable and agrees with the reported formation sequences of nickel phosphides under increasingly phosphorus-rich conditions [27–29].

The textural properties of the phase-regulated mesoporous Ni_xP_y samples were further evaluated by N₂ adsorption-desorption measurements. As presented in Fig. 2(f), all samples exhibit type-IV isotherms with distinct capillary condensation behavior, confirming the

preservation of mesoporosity after phosphidation. The BET surface areas of mesoporous Ni_3P -1.0, $\text{Ni}_3\text{P}/\text{Ni}_{12}\text{P}_5$ -1.0, Ni_{12}P_5 -1.0, $\text{Ni}_{12}\text{P}_5/\text{Ni}_2\text{P}$ -1.0, and Ni_2P -1.0 are 76, 78, 105, 89, and $111 \text{ m}^2 \text{ g}^{-1}$, respectively. Their average pore sizes, derived from the desorption branches using the Barrett-Joyner-Halenda (BJH) method, are 9.4, 9.4, 8.2, 9.4, and 6.6

nm, respectively. In addition, CHN results show that these phase-regulated Ni_xP_y -1.0 samples possess comparable carbon contents of 7.1–7.7 wt% (Table S1 in the ESM), indicating that the residual carbon content remains nearly unchanged during $\text{NH}_4\text{H}_2\text{PO}_4$ -dosage-regulated phase evolution.

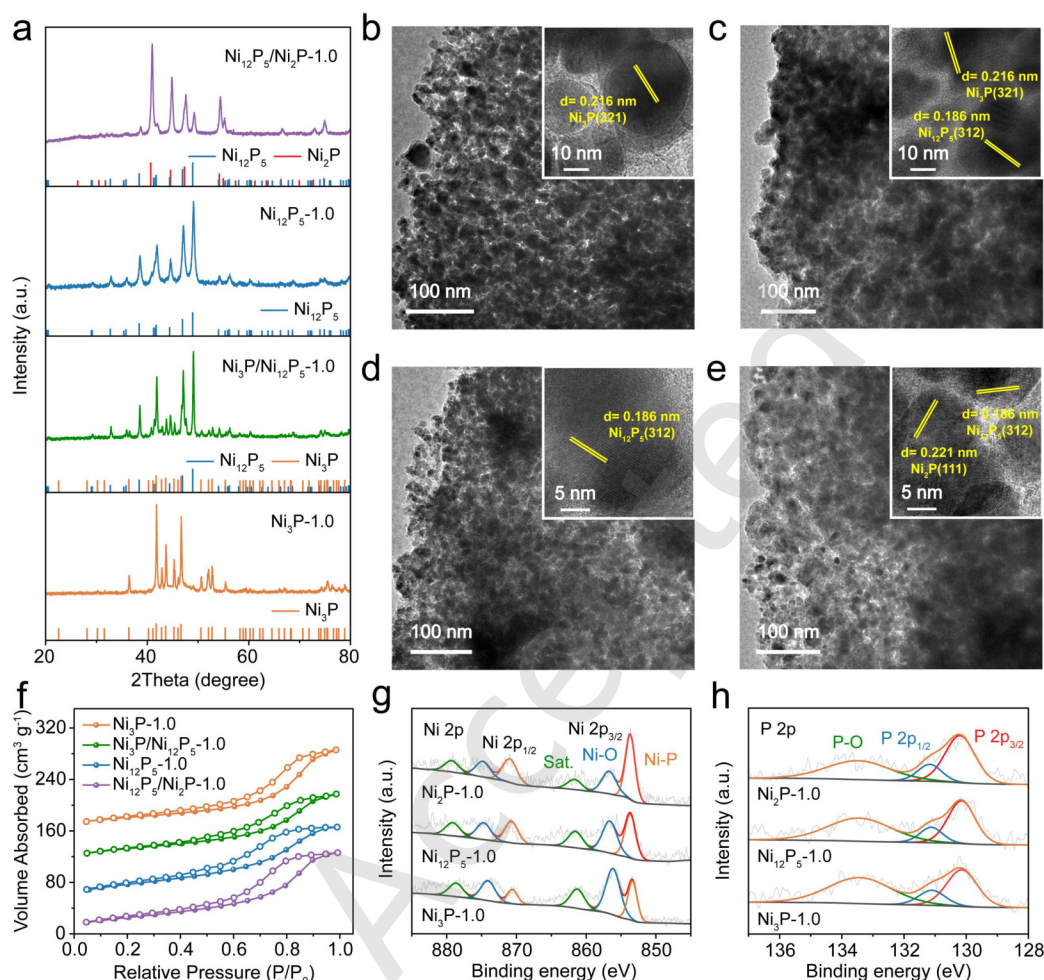


Figure 2 $\text{NH}_4\text{H}_2\text{PO}_4$ -dosage-regulated phase evolution of the mesoporous Ni_xP_y -1.0 series. (a) XRD patterns of the mesoporous Ni_xP_y -1.0 series. TEM images of (b) Ni_3P -1.0, (c) $\text{Ni}_3\text{P}/\text{Ni}_{12}\text{P}_5$ -1.0, (d) Ni_{12}P_5 -1.0, and (e) $\text{Ni}_{12}\text{P}_5/\text{Ni}_2\text{P}$ -1.0. (f) N_2 adsorption-desorption isotherms, (g) high-resolution Ni 2p spectra, and (h) high-resolution P 2p spectra of the mesoporous Ni_xP_y -1.0 series.

The surface chemical compositions and valence states of the mesoporous Ni_xP_y -1.0 series were investigated by X-ray photoelectron spectroscopy (XPS). The survey spectra (Fig. S7 in the ESM) show the presence of Ni and P signals in all samples, confirming the successful incorporation of Ni and P elements in the obtained samples. The high-resolution Ni 2p spectra provide further insight into the surface Ni species. As displayed in Fig. 2(g), the deconvoluted peaks at ~ 853.6 and 870.9 eV can be assigned to the $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ components associated with Ni-P bonding, respectively, while the broad features centered at ~ 861.6 and 879.2 eV correspond to satellite peaks in the Ni 2p region. Additional peaks at ~ 856.7 and 874.8 eV are attributed to oxidized Ni species, most likely arising from superficial oxidation upon exposure to air [30–32]. Notably, the relative contribution of the Ni-P component shows an increasing tendency from mesoporous Ni_3P -1.0 to mesoporous Ni_{12}P_5 -1.0 and then to mesoporous Ni_2P -1.0, whereas the oxidized Ni-related contribution becomes less pronounced. This trend indicates a gradual enrichment of phosphide-bonded Ni species at the

surface, consistent with an enhanced degree of surface phosphidation as the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage increases. The high-resolution P 2p spectra show a similar evolution in the surface phosphorus environment. As shown in Fig. 2(h), the characteristic doublet at ~ 129.9 and 130.9 eV can be assigned to the $\text{P } 2p_{3/2}$ and $\text{P } 2p_{1/2}$ components of lattice phosphide species, respectively. The higher-binding-energy component centered at $\sim 133.5 \text{ eV}$ is attributed to oxidized phosphorus species formed by superficial oxidation [33–35]. Notably, with the phase evolution from mesoporous Ni_3P -1.0 to mesoporous Ni_{12}P_5 -1.0 and finally to mesoporous Ni_2P -1.0, the relative contribution of lattice phosphide P gradually increases, while that of oxidized P decreases. Among these samples, mesoporous Ni_2P -1.0 exhibits the highest relative contribution of phosphide P and the lowest contribution of oxidized P, suggesting a more highly phosphidized and P-rich surface environment. Furthermore, the relative contents of Ni-P and lattice phosphide P species were quantified based on the integrated fitted peak areas of the high-resolution XPS spectra. As summarized in Table S3 in the

ESM, both the Ni-P/Ni-total and phosphide P/P-total ratios progressively increase with the phase evolution from Ni_3P to Ni_{12}P_5 and finally to Ni_2P , quantitatively supporting the gradual enrichment of phosphide-related surface species with increasing $\text{NH}_4\text{H}_2\text{PO}_4$ dosage. These results agree with the bulk phase evolution revealed by XRD, confirming that increasing the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage not only drives the formation of more P-rich crystalline phases but also modulates the surface bonding configuration.

Raman spectra were further collected to probe the surface bonding environment of the mesoporous Ni_xP_y samples. As shown in Fig. S8 in the ESM, the weak band at $\sim 550\text{ cm}^{-1}$ can be associated with Ni-O-related stretching

vibrations, while the broad feature in the $900\text{--}1100\text{ cm}^{-1}$ region is related to P-O-related vibrational modes [36, 37]. Notably, the P-O-related feature becomes more pronounced from mesoporous Ni_3P -1.0 to mesoporous Ni_{12}P_5 -1.0 and finally to mesoporous Ni_2P -1.0. This evolution indicates more detectable P-O-related surface species in the increasingly P-rich phosphide frameworks. Together with the XPS results, these Raman data support the evolution of the surface chemical environment from relatively Ni-rich toward more P-rich character with increasing $\text{NH}_4\text{H}_2\text{PO}_4$ content.

2.3 Mechanistic Insight into the Charge-Mediated Cooperative Assembly Strategy

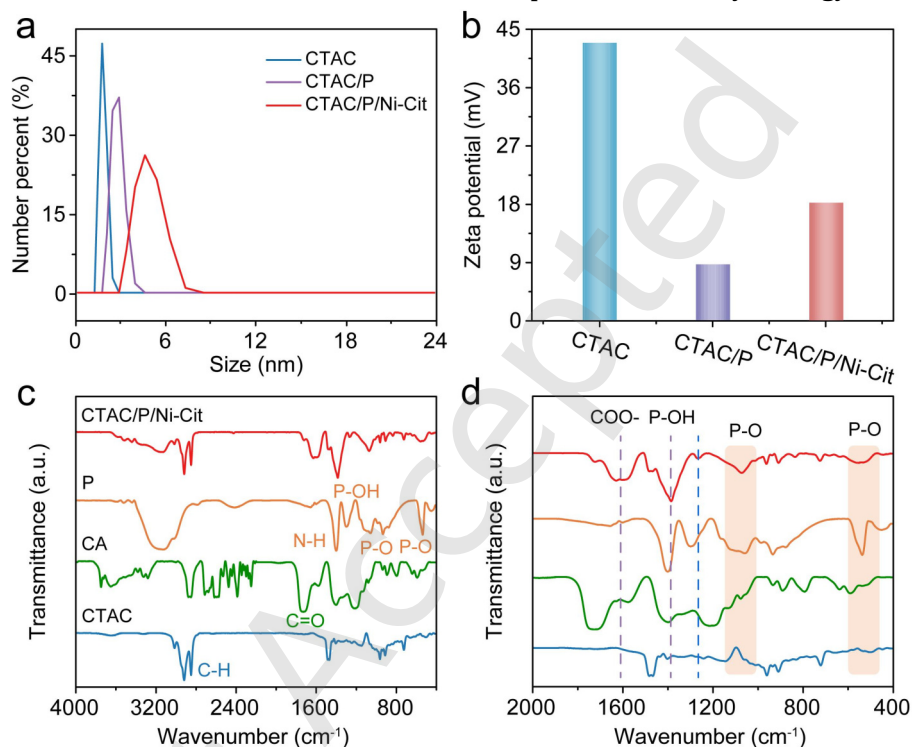


Figure 3 (a) DLS size distributions and (b) zeta potentials of CTAC, CTAC/P, and CTAC/P/Ni-Cit solutions. (c) FT-IR spectra of different precursor species and (d) the corresponding enlarged FT-IR spectra in the selected wavenumber region. P and Ni-Cit denote $\text{NH}_4\text{H}_2\text{PO}_4$ and Ni-citrate complexes, respectively.

Building on the above analyses, CTAC is identified as a key structure-directing agent for constructing the mesoporous framework, while the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage plays an important role in regulating the phase evolution of the mesoporous Ni_xP_y series. These observations raise two important questions: how the organic and inorganic precursor species are organized in solution and how this organization contributes to the subsequent formation of mesoporous nickel phosphides with tunable phase compositions. To address these issues, dynamic light scattering (DLS) measurements were first performed to probe the assembly behavior of the precursor species in solution. As shown in Fig. 3(a), the pure CTAC solution exhibits an average hydrodynamic diameter of 2.0 nm, which can be associated with the formation of CTA^+ micelles in aqueous solution. After the addition of $\text{NH}_4\text{H}_2\text{PO}_4$, the hydrodynamic diameter increases to 3.1 nm, suggesting interactions between CTA^+ micelles and phosphate species. Upon further introduction of Ni-citrate complexes into the

system, the hydrodynamic diameter further increases to 4.8 nm, which is larger than those of pure CTAC and the CTAC/ $\text{NH}_4\text{H}_2\text{PO}_4$ system. This progressive increase in hydrodynamic diameter suggests the gradual association of CTA^+ micelles with phosphate species and Ni-citrate complexes, thereby promoting the formation of composite micelle assemblies. Zeta-potential measurements were further conducted to probe the interfacial charge evolution during precursor assembly. As shown in Fig. 3(b), the pure CTAC solution displays a highly positive zeta potential of +42.7 mV, consistent with the cationic nature of CTA^+ micelles. After the addition of $\text{NH}_4\text{H}_2\text{PO}_4$, the zeta potential decreases markedly to +8.6 mV, suggesting partial charge compensation between cationic CTA^+ micelles and negatively charged phosphate species. Upon further addition of Ni-citrate complexes, the zeta potential increases to an intermediate positive value of +18.1 mV, indicating further redistribution of interfacial charge after the incorporation of Ni-citrate complexes. The combined changes in

hydrodynamic diameter and zeta potential support a cooperative assembly process involving CTA⁺ micelles, phosphate species, and Ni-citrate complexes. Moreover, the lower zeta potential of the complete precursor solution compared with that of pure CTAC further supports the presence of partial charge compensation and electrostatic interactions among these species.

Fourier transform infrared (FT-IR) spectroscopy was further used to probe the molecular-level interactions among the precursor components. As shown in Fig. 3(c), (d), pure CA exhibits an intense band at $\sim 1750\text{ cm}^{-1}$, which can be assigned to the C=O stretching vibration of carboxylic acid groups [38]. In the complete precursor spectrum, this band is markedly weakened, accompanied by the emergence of carboxylate-related bands in the $1600\text{--}1400\text{ cm}^{-1}$ region. These changes indicate the deprotonation of CA and coordination between carboxylate groups and Ni²⁺, leading to the formation of Ni-citrate complexes [39, 40]. For pure NH₄H₂PO₄, the bands at ~ 1280 and 900 cm^{-1} are associated with P-OH-related and P-O-related stretching vibrations, respectively, while the band near 1400 cm^{-1} can be attributed to N-H-related vibrations [41, 42]. In the complete precursor spectrum, the P-OH-related band shifts to a lower wavenumber, and the P-O-related features become broader and less resolved than those of pure NH₄H₂PO₄. These changes suggest that the hydrogen-bonding and electrostatic environments of phosphate species are altered in the mixed precursor system, which is consistent with their interactions with Ni-citrate complexes and CTA⁺ micelles. In contrast, the characteristic C-H stretching vibrations of CTAC at ~ 2920 and 2850 cm^{-1}

remain essentially unchanged [43], indicating that CTAC does not undergo an obvious chemical transformation during precursor formation and mainly participates in the assembly process through noncovalent interactions.

On the basis of these results, a charge-mediated cooperative assembly mechanism is proposed for the synthesis of phase-tunable mesoporous Ni_xP_y. As illustrated in Scheme 1, Ni(NO₃)₂·6H₂O, CTAC, CA, and NH₄H₂PO₄ are dissolved in deionized water to form a homogeneous precursor solution. In this system, CA coordinates with Ni²⁺ through its carboxylate groups to form Ni-citrate complexes, which serve as the main inorganic precursor units. NH₄H₂PO₄ provides phosphate species that function not only as the phosphorus source for subsequent phosphidation but also as charge-mediating and hydrogen-bonding linkers between cationic CTA⁺ micelles and Ni-citrate complexes. Meanwhile, CTAC self-assembles into cationic CTA⁺ micelles in aqueous solution. Driven by electrostatic interactions and hydrogen bonding, CTA⁺ micelles, phosphate species, and Ni-citrate complexes cooperatively assemble into inorganic-organic composite micelles. During solvent evaporation, these composite micelles are progressively concentrated and fixed into a close-packed mesostructured precursor framework, thereby enabling controlled precursor organization rather than uncontrolled aggregation. Subsequent thermal treatment under an H₂/N₂ atmosphere decomposes the organic components, promotes phosphidation, and consolidates the inorganic framework, ultimately yielding mesoporous Ni_xP_y with a well-defined pore architecture and tunable phase composition.

2.4 Generality of the Synthetic Strategy

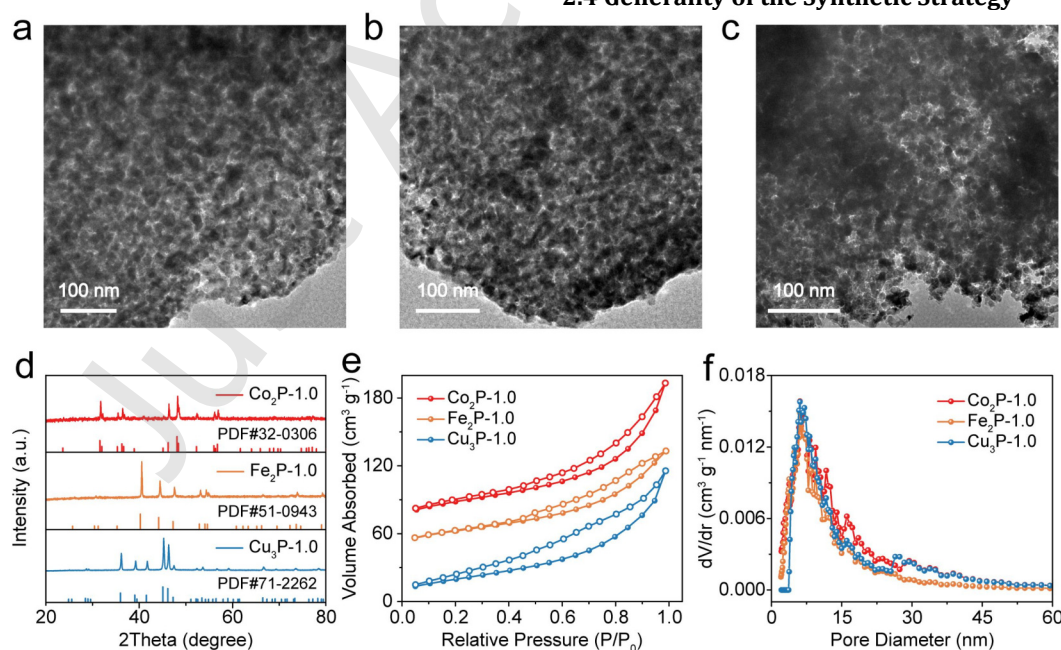


Figure 4 Generality of the charge-mediated cooperative assembly strategy. TEM images of mesoporous (a) Co₂P-1.0, (b) Fe₂P-1.0, and (c) Cu₃P-1.0. (d) XRD patterns, (e) N₂ adsorption-desorption isotherms, and (f) pore-size distributions for mesoporous Co₂P-1.0, Fe₂P-1.0, and Cu₃P-1.0.

To evaluate the broader applicability of the charge-mediated cooperative assembly strategy, the synthetic route was extended to other metal phosphide systems by replacing the nickel precursor with Fe, Co, or Cu salts under similar synthetic conditions. Using this approach, a series of mesoporous metal phosphides, including Co₂P-1.0, Fe₂P-1.0,

and Cu₃P-1.0, were obtained. SEM and TEM images (Fig. S9(a) – (c) in the ESM and Fig. 4(a) – (c)) show that the obtained samples possess well-defined mesoporous architectures with interconnected pore channels. The crystalline phase compositions were further verified by XRD. As presented in Fig. 4(d), the diffraction peaks of Co₂P-1.0, Fe₂P-1.0, and

Cu₃P-1.0 can be well indexed to their corresponding standard phosphide phases. The N₂ adsorption-desorption isotherms in Fig. 4(e) show that all samples exhibit typical mesoporous adsorption-desorption behavior, consistent with the TEM observations. The BET surface areas are 88 m²

g⁻¹ for Co₂P-1.0, 68 m² g⁻¹ for Fe₂P-1.0, and 64 m² g⁻¹ for Cu₃P-1.0, with corresponding total pore volumes of 0.200, 0.139, and 0.173 cm³ g⁻¹, respectively.

2.5 Electrocatalytic HER Performance

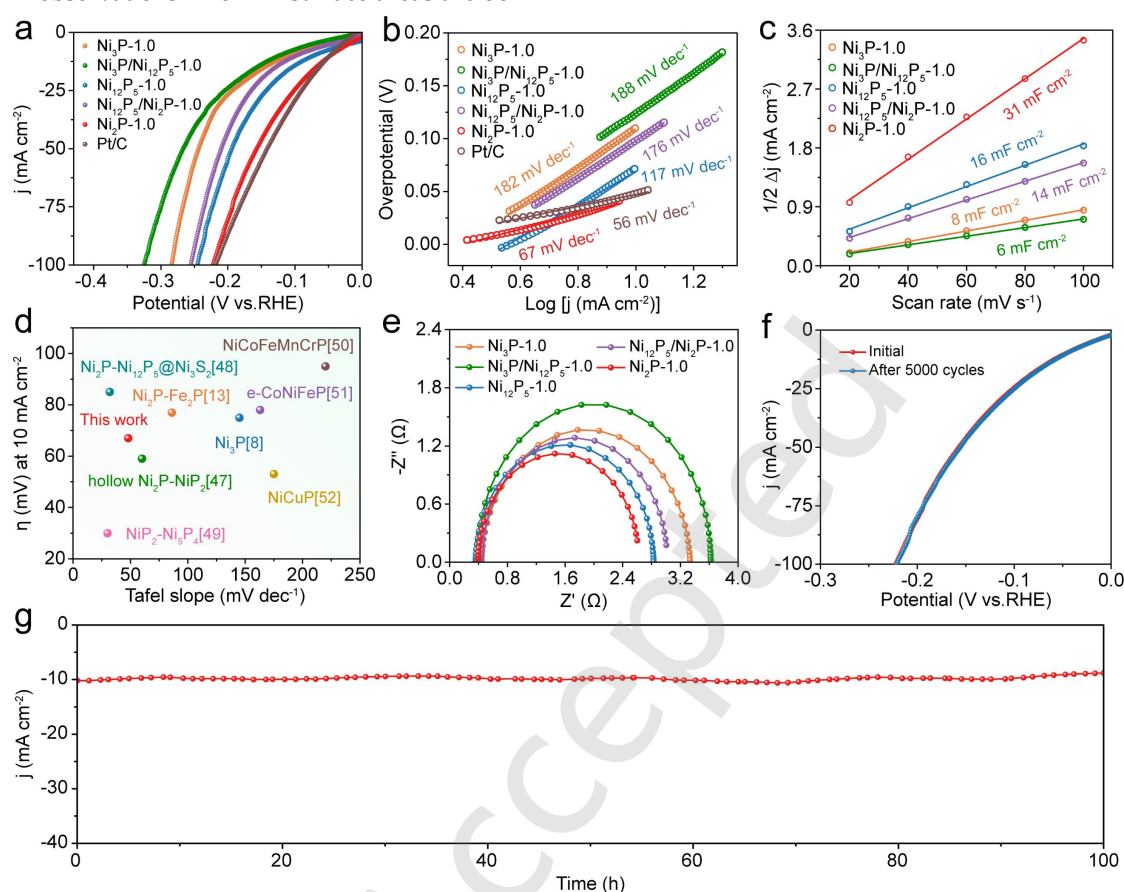


Figure 5 Electrocatalytic HER performance of the mesoporous Ni_xP_y-1.0 series in 1.0 M KOH. (a) LSV curves recorded at 5 mV s⁻¹. (b) Tafel plots. (c) Measured capacitive current density as a function of scan rate for the catalyst-loaded carbon cloth electrodes. (d) Comparison of the HER activity at 10 mA cm⁻². (e) Nyquist plots. (f) LSV curves of mesoporous Ni₂P-1.0 before and after 5000 CV cycles. (g) Long-term stability test of mesoporous Ni₂P-1.0 at a constant overpotential of 48 mV.

The development of highly active and durable hydrogen evolution reaction (HER) electrocatalysts is essential for practical alkaline water electrolysis [44–46]. The as-prepared mesoporous Ni_xP_y series, featuring tunable phase compositions and well-defined mesoporous architectures, provides a suitable platform for investigating the influence of phase composition and mesostructure on alkaline HER performance. The electrocatalytic HER activity of the mesoporous Ni_xP_y-1.0 series was evaluated in 1.0 M KOH using a standard three-electrode configuration. All polarization curves were recorded with 90% iR compensation to reduce the contribution of solution resistance. As displayed in Fig. 5(a), the overpotentials required to reach a current density of 10 mA cm⁻² are 111, 124, 72, 98, and 48 mV for mesoporous Ni₃P-1.0, Ni₃P/Ni₁₂P₅-1.0, Ni₁₂P₅-1.0, Ni₁₂P₅/Ni₂P-1.0, and Ni₂P-1.0, respectively. Among these catalysts, mesoporous Ni₂P-1.0 exhibits the lowest overpotential, indicating its highest HER activity within the investigated Ni_xP_y series. This result suggests that phase composition plays an important role in modulating the alkaline HER behavior of mesoporous nickel phosphides. To gain insight into the reaction kinetics, Tafel analysis was performed based on the corresponding

polarization curves. As presented in Fig. 5(b), mesoporous Ni₂P-1.0 delivers a Tafel slope of 67 mV dec⁻¹, which is much lower than those of Ni₃P-1.0 (182 mV dec⁻¹), Ni₃P/Ni₁₂P₅-1.0 (188 mV dec⁻¹), Ni₁₂P₅-1.0 (117 mV dec⁻¹), and Ni₁₂P₅/Ni₂P-1.0 (176 mV dec⁻¹). The relatively low Tafel slope of 67 mV dec⁻¹ lies between the typical values generally associated with Volmer- and Heyrovsky-dominated kinetics, suggesting that alkaline HER over mesoporous Ni₂P-1.0 most likely follows a Volmer–Heyrovsky pathway involving coupled water dissociation and electrochemical hydrogen desorption. This behavior may be associated with the more highly phosphidized and P-rich Ni₂P surface, whose abundant polar Ni–P bonding configurations are expected to facilitate water activation and optimize H⁺ adsorption/desorption during alkaline HER. The contribution of the mesoporous architecture was further verified using a bulk Ni₂P control sample prepared without CTAC. As presented in Fig. S10 in the ESM, bulk Ni₂P requires a much higher overpotential of 182 mV at 10 mA cm⁻² and shows a larger Tafel slope of 169 mV dec⁻¹ than mesoporous Ni₂P-1.0, confirming the important role of the interconnected mesoporous framework in enhancing HER activity and kinetics. The reproducibility of mesoporous Ni₂P-1.0 was also evaluated

using three independently prepared electrodes, and the corresponding polarization curves are highly consistent, with an average η_{10} value of 47 ± 1 mV (Fig. S11 in the ESM).

To further understand the origin of the enhanced activity, double-layer capacitance (C_{dl}) was determined from cyclic voltammetry (CV) curves collected in the non-Faradaic region to compare electrochemical accessibility (Fig. S12 in the ESM). As shown in Fig. 5(c), the measured C_{dl} values obtained from the catalyst-loaded carbon cloth electrodes are 8, 6, 16, 14, and 31 mF cm⁻² for mesoporous Ni₃P-1.0, Ni₃P/Ni₁₂P₅-1.0, Ni₁₂P₅-1.0, Ni₁₂P₅/Ni₂P-1.0, and Ni₂P-1.0, respectively. To clarify the contribution from the carbon cloth substrate, a blank carbon cloth electrode prepared without catalyst was measured under identical conditions, and its C_{dl} value was subtracted from the measured C_{dl} values of the catalyst-loaded electrodes. The measured and background-corrected C_{dl} values are summarized in Table S4 in the ESM. Notably, mesoporous Ni₂P-1.0 still exhibits the largest background-corrected C_{dl} value among the series, suggesting the highest electrochemical accessibility, which is beneficial for exposing more catalytically available sites during HER. The catalytic performance of mesoporous Ni₂P-1.0 was further benchmarked against representative phosphide-based HER electrocatalysts reported in the literature [8, 13, 47–52]. As shown in Fig. 5(d), mesoporous Ni₂P-1.0 combines an overpotential of 48 mV at 10 mA cm⁻² with a Tafel slope of 67 mV dec⁻¹, placing it among competitive nickel phosphide-based and multicomponent phosphide catalysts for alkaline HER. This comparison supports the effectiveness of coupling phase regulation with mesostructure engineering to improve HER performance. Electrochemical impedance spectroscopy (EIS) was conducted to evaluate the interfacial charge-transfer behavior of the mesoporous Ni_xP_y catalysts. The Nyquist plots were fitted using an equivalent circuit model (Fig. 5(e) and Fig. S13 in the ESM). The fitted charge-transfer resistance (R_{ct}) values are 2.90, 3.24, 2.46, 2.57, and 2.22 Ω for mesoporous Ni₃P-1.0, Ni₃P/Ni₁₂P₅-1.0, Ni₁₂P₅-1.0, Ni₁₂P₅/Ni₂P-1.0, and Ni₂P-1.0, respectively. The lowest R_{ct} value of mesoporous Ni₂P-1.0 indicates more favorable interfacial charge-transfer kinetics among the investigated phase series.

Durability is another important parameter for evaluating practical alkaline HER electrocatalysts. The stability of mesoporous Ni₂P-1.0 was assessed by accelerated cyclic voltammetry and long-term chronoamperometry. As shown in Fig. 5(f), after 5000 consecutive CV cycles, the polarization curve shows a negligible change in overpotential, indicating good cycling stability. In addition, mesoporous Ni₂P-1.0 maintains 87.3% of its initial current density after 100 h of continuous operation at a constant overpotential of 48 mV in 1.0 M KOH (Fig. 5(g)). The moderate current decay may be associated with hydrogen-bubble accumulation, partial blockage of accessible active sites, or possible surface changes during prolonged HER operation. Post-stability characterizations were performed to examine the structural stability of mesoporous Ni₂P-1.0 after electrochemical testing. As displayed in Fig. S14 in the ESM, the XRD pattern collected after the 100 h HER test shows no detectable phase

transformation, indicating that the crystalline Ni₂P phase is retained during electrolysis. Meanwhile, the TEM image reveals that the mesoporous framework remains largely preserved without obvious aggregation or collapse. These results demonstrate that mesoporous Ni₂P-1.0 maintains both crystallographic stability and mesostructural integrity under alkaline HER conditions.

Overall, the superior HER activity of mesoporous Ni₂P-1.0 within the investigated series arises from the combined advantages of favorable phase composition, accessible mesoporosity, efficient charge transfer, and structural robustness. Compared with the Ni-rich Ni₃P phase and the intermediate Ni₁₂P₅ phase, the Ni₂P phase possesses a more highly phosphidized and P-rich surface environment, which provides abundant Ni–P bonding configurations and is expected to modulate the electronic states of active sites, thereby facilitating water activation and optimizing hydrogen-intermediate adsorption/desorption during alkaline HER. Meanwhile, the interconnected mesoporous framework exposes abundant accessible sites and facilitates electrolyte penetration. Moreover, the low charge-transfer resistance promotes rapid interfacial electron transfer, while the stable crystalline and porous architecture ensures durable operation during prolonged electrolysis. These combined advantages account for the superior activity and durability of mesoporous Ni₂P-1.0.

3 Conclusion

In summary, we have developed a charge-mediated cooperative assembly strategy for the one-pot synthesis of phase-tunable mesoporous nickel phosphides. This approach integrates precursor assembly, mesostructure construction, and phase regulation into a single synthetic process, avoiding separate template removal or post-phosphidation steps. Experimental results indicate that CTAC-derived CTA⁺ micelles play a key role in directing the formation of a well-defined mesoporous framework, while the NH₄H₂PO₄ dosage regulates the effective phosphorus supply and thereby controls the phase evolution across the Ni_xP_y series. By adjusting the NH₄H₂PO₄ dosage, the crystalline phase can be tuned from Ni₃P to Ni₁₂P₅ and finally to Ni₂P while preserving the well-defined mesoporous architecture. Moreover, the successful extension of this strategy to other mesoporous metal phosphides demonstrates its synthetic versatility. Among the as-prepared catalysts, mesoporous Ni₂P-1.0 exhibits the highest alkaline HER activity and excellent long-term operational stability. The enhanced catalytic performance arises from the combined advantages of the favorable Ni₂P phase, high electrochemical accessibility, efficient charge-transfer capability, and robust mesoporous framework. This work provides a feasible strategy for integrating phase regulation with mesostructure design and offers insights into the development of phosphide-based electrocatalysts.

Electronic Supplementary Material: Supplementary material (additional experimental details and data, XRD patterns, SEM and TEM images, TG curves, XPS and Raman spectra, LSV and Tafel plots, reproducibility tests, CV curves, EIS fitting model, post-stability characterizations, CHN elemental analysis, structural parameters, quantitative XPS fitting results, and electrocatalytic HER activity parameters)

is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909002>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. W. and Z.-A. Q. conceptualized and designed the experiments. Y. W. and L. L. performed the experiments and collected the data. L. Z. and Z.-A. Q. supervised the project. Y. W. and Z.-A. Q. authored the initial manuscript draft. All the authors have approved the final manuscript.

Informed consent

Not applicable

Ethics statement

Not applicable

Use of AI statement

None.

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A charge-mediated cooperative assembly strategy toward phase-tunable mesoporous nickel phosphides for efficient alkaline hydrogen evolution

Ye Wang^{1,§}, Lu Liu^{1,§}, Ling Zhang²  , and Zhen-An Qiao¹  

¹ State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

² State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China

[§] Ye Wang and Lu Liu contributed equally to this work.

 Address correspondence to Ling Zhang, zhanglingchem@jlu.edu.cn; Zhen-An Qiao, qiaozhenan@jlu.edu.cn

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Experimental Section

Materials

Cetyltrimethylammonium chloride (CTAC, 97%) was purchased from Aladdin Industrial Corporation (China). Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 99%), and absolute ethanol (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 99%) and copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%) were supplied by Guangzhou Xilong Chemical Factory. Nafion solution (5 wt%) was purchased from Sigma-Aldrich. Deionized water with a resistivity of 18.2 M Ω cm was produced using a PALL PURELAB Plus water purification system. All chemicals were used as received without further purification.

Synthesis of Mesoporous Nickel Phosphides

In a typical synthesis, 1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mmol of citric acid monohydrate were dissolved in 20 mL of deionized water. Then, a certain amount of $\text{NH}_4\text{H}_2\text{PO}_4$ (0.1, 0.2, 0.3, 0.4, or 0.5 mmol) was added under continuous magnetic stirring, followed by the introduction of a controlled dosage of CTAC (0.5, 1.0, 1.5, or 2.0 mmol). The mixture was stirred continuously until a homogeneous transparent green solution was obtained. The resulting solution was transferred to a 90 mm Petri dish, maintained at 40 °C for 12 h to allow solvent evaporation, and then aged at 100 °C for 12 h to yield a uniform green gel membrane. The resulting membrane was gently ground into a fine powder, loaded into a porcelain boat, and thermally treated at 600 °C for 6 h under a 10 vol% H_2/N_2 flow with a heating rate of 5 °C min⁻¹. By varying the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage, a series of mesoporous Ni_xP_y -1.0 samples with tunable phase compositions was obtained. The samples prepared with 0.1, 0.2, 0.3, 0.4, and 0.5 mmol $\text{NH}_4\text{H}_2\text{PO}_4$ are denoted as mesoporous Ni_3P -1.0, $\text{Ni}_3\text{P}/\text{Ni}_{12}\text{P}_5$ -1.0, Ni_{12}P_5 -1.0, $\text{Ni}_{12}\text{P}_5/\text{Ni}_2\text{P}$ -1.0, and Ni_2P -1.0, respectively. Additional control samples based on the Ni_2P -1.0 synthesis were prepared by varying the thermal-treatment temperature (450, 500, 550, or 600 °C) or increasing the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage to 1.0, 1.5, or 2.0 mmol. The sample prepared without adding CTAC was denoted as bulk Ni_2P and used as a control sample for structural and electrochemical comparison.

Synthesis of Other Mesoporous Metal Phosphides

Other mesoporous metal phosphides were synthesized by a similar procedure, with the metal precursor, $\text{NH}_4\text{H}_2\text{PO}_4$ dosage, and thermal-treatment temperature adjusted according to the target phase.

For mesoporous Co_2P , 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mmol of citric acid monohydrate were dissolved in 20 mL of deionized water. Then, 0.5 mmol ammonium dihydrogen phosphate and 1.0 mmol CTAC were added. The mixture was stirred continuously until a homogeneous transparent pink solution was obtained. The resulting solution was transferred to a 90 mm Petri dish, maintained at 40 °C for 12 h to allow solvent evaporation, and then aged at 100 °C for 12 h to yield a uniform blue-violet gel membrane. The resulting membrane was gently ground into a fine powder, loaded into a porcelain boat, and subsequently thermally treated at 650 °C for 6 h under a 10 vol% H_2/N_2 flow with a heating rate of 5 °C min⁻¹.

For mesoporous Fe_2P , 1 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1 mmol of citric acid monohydrate were dissolved in 20 mL of deionized water. Then, 0.5 mmol ammonium dihydrogen phosphate and 1.0 mmol CTAC were added. The mixture was stirred continuously until a homogeneous yellow solution was obtained. The resulting solution was transferred to a 90 mm Petri dish, maintained at 40 °C for 12 h to allow solvent evaporation, and then aged at 100 °C for 12 h to yield a uniform yellow gel membrane. The resulting membrane was

gently ground into a fine powder, loaded into a porcelain boat, and subsequently thermally treated at 650 °C for 6 h under a 10 vol% H₂/N₂ flow with a heating rate of 5 °C min⁻¹.

For mesoporous Cu₃P, 1 mmol Cu(NO₃)₂·3H₂O and 1 mmol of citric acid monohydrate were dissolved in 20 mL of deionized water. Then, 0.2 mmol ammonium dihydrogen phosphate and 1.0 mmol CTAC were added. The mixture was stirred continuously until a homogeneous transparent blue solution was obtained. The resulting solution was transferred to a 90 mm Petri dish, maintained at 40 °C for 12 h to allow solvent evaporation, and then aged at 100 °C for 12 h to yield a uniform blue gel membrane. The resulting membrane was gently ground into a fine powder, loaded into a porcelain boat, and subsequently thermally treated at 400 °C for 6 h under a 10 vol% H₂/N₂ flow with a heating rate of 5 °C min⁻¹.

Characterizations

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D2 Advance diffractometer using Cu K α radiation (λ = 0.15418 nm, 30 kV, 15 mA). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a JEOL JSM-6700F field-emission scanning electron microscope operated at 15 kV. Transmission electron microscopy (TEM) was carried out on a Philips-FEI Tecnai G2S-Twin microscope equipped with a 200 kV field-emission gun.

N₂ adsorption-desorption isotherms were recorded at 77 K on a Quanta 4200e surface area analyzer. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were derived from the desorption branch using the Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared (FT-IR) spectra were collected on an IFS-66 V/S infrared spectrophotometer. Dynamic light scattering (DLS) measurements and zeta-potential analyses were performed on a Malvern Zetasizer Nano ZS90 instrument. Carbon contents were determined using an Elementar Vario MACRO cube CHNS analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 X-ray photoelectron spectrometer using Al K α radiation ($h\nu$ = 1486.8 eV) as the excitation source. Thermogravimetric (TG) analysis was conducted on a TA Instruments Q50 thermogravimeter under a nitrogen atmosphere from 60 to 800 °C with a heating rate of 10 °C min⁻¹.

Electrochemical Measurements

Electrochemical measurements were conducted in 1.0 M KOH using a standard three-electrode configuration on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Company). To prepare the working electrode, 5 mg of electrocatalyst was dispersed in a mixture of 375 μ L deionized water, 125 μ L ethanol, and 20 μ L Nafion solution (5 wt%), followed by sonication for 1.5 h to form a homogeneous catalyst ink. Subsequently, 50 μ L of the ink was uniformly drop-cast onto a cleaned carbon cloth substrate (0.4 cm $\times$ 0.4 cm) and dried at 65 °C, corresponding to a catalyst loading of approximately 3 mg cm⁻². Current densities were normalized to the geometric electrode area, and the same loading and substrate were used for all catalysts unless otherwise stated.

A graphite rod and an Hg/HgO electrode were used as the counter and reference electrodes, respectively. All measured potentials were converted to the reversible hydrogen electrode (RHE) using the Eq 1:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{ V} + 0.0591 \times \text{pH} \quad (1)$$

(pH = 13.6 for 1.0 M KOH at 25 °C)

Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV s⁻¹ with 90% iR correction to compensate for electrolyte resistance.

Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range of 10⁵ to 0.1 Hz at an overpotential of 48 mV vs. RHE to evaluate charge-transfer resistance. The EIS Nyquist plots were fitted using an equivalent circuit consisting of solution resistance (R_s), charge-transfer resistance (R_{ct}), and a constant phase element (CPE). The same fitting model was applied to all investigated samples.

Cyclic voltammetry (CV) curves were collected in the non-Faradaic potential range of -0.10 to 0 V vs. Hg/HgO at scan rates of 20, 40, 60, 80, and 100 mV s⁻¹ to determine the double-layer capacitance (C_{dl}).

The reproducibility of mesoporous Ni₂P-1.0 was evaluated using three independently prepared electrodes fabricated and tested under identical electrochemical conditions, and the corresponding η_{10} values are reported as mean $\pm$ standard deviation.

Long-term stability was evaluated via chronoamperometric (i - t) measurements at a constant overpotential of 48 mV vs. RHE for 100 h.

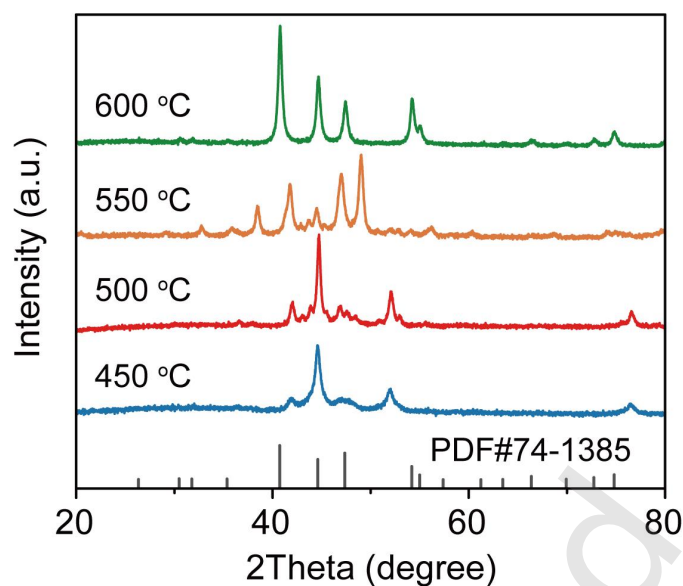


Figure S1. XRD patterns of samples prepared using the $\text{Ni}_2\text{P-1.0}$ precursor composition at different thermal-treatment temperatures under a 10 vol% H_2/N_2 atmosphere for 6 h.

As shown in Figure S1, the thermal-treatment temperature has a clear influence on the phase formation of nickel phosphides. At relatively low treatment temperatures of 450–500 °C, only weak and broad diffraction peaks are observed, indicating insufficient crystallization and incomplete conversion of the precursor. When the temperature is increased to 550 °C, several additional diffraction peaks appear, suggesting the formation of mixed or intermediate nickel phosphide phases during the phosphidation process. In contrast, the sample treated at 600 °C shows sharper and better-resolved diffraction peaks that can be well indexed to hexagonal Ni_2P , without obvious crystalline impurity peaks. These results indicate that 600 °C is an appropriate thermal-treatment temperature for obtaining well-crystallized $\text{Ni}_2\text{P-1.0}$ under the present synthetic conditions.

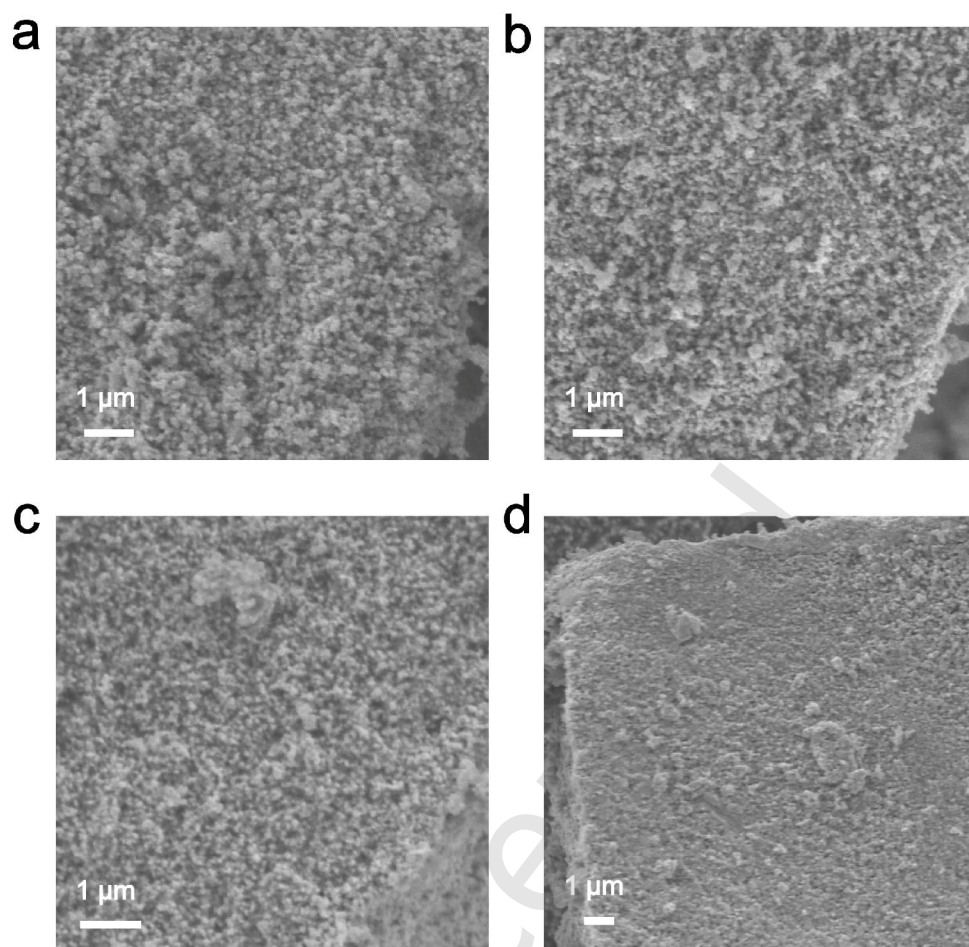


Figure S2. SEM images of (a) Ni₂P-0.5, (b) Ni₂P-1.0, (c) Ni₂P-1.5, and (d) Ni₂P-2.0.

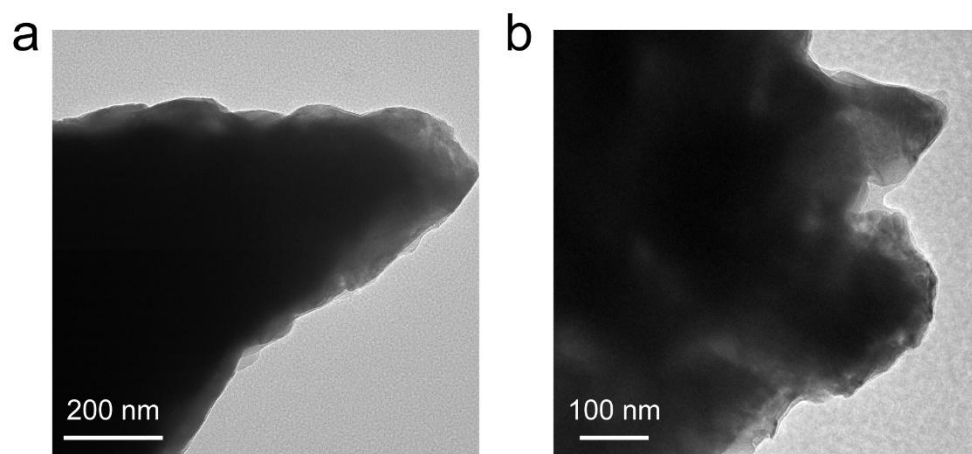


Figure S3. (a, b) TEM images of bulk Ni_2P sample prepared without adding CTAC.

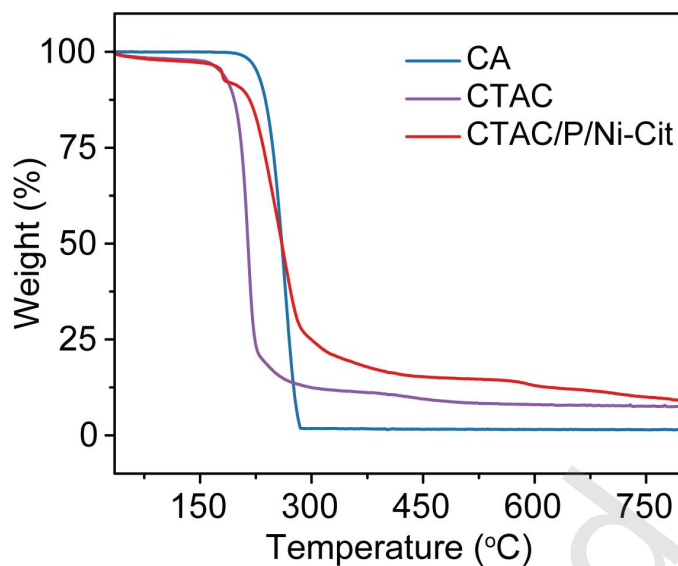


Figure S4. TG curves of CA, CTAC, and the CTAC/P/Ni-Cit composite precursor measured under a nitrogen atmosphere.

As shown in Figure S4, CA and CTAC exhibit pronounced weight loss below 300 °C, which can be attributed to the decomposition of organic species. In comparison, the CTAC/P/Ni-Cit composite precursor shows a multi-stage weight-loss behavior. The slight weight loss at low temperature is associated with the removal of physically adsorbed water and residual solvent. The major weight-loss stage is mainly related to the decomposition of CTAC and citrate-related organic components, possibly accompanied by the evolution of phosphate- and Ni-containing species. This process may also involve partial carbonization of organic species, which is consistent with the residual carbon detected in the final products. Above approximately 600 °C, the weight loss becomes much slower, indicating that the main decomposition and precursor-conversion processes have largely occurred. These results provide useful information on the thermal behavior of the precursor system.

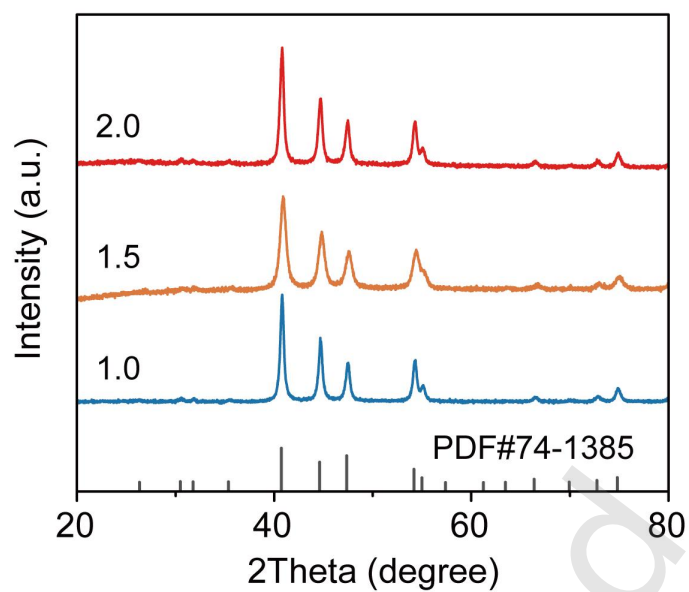


Figure S5. XRD patterns of the samples prepared with increased $\text{NH}_4\text{H}_2\text{PO}_4$ dosages under identical synthetic conditions. The numbers 1.0, 1.5, and 2.0 denote the $\text{NH}_4\text{H}_2\text{PO}_4$ dosage in mmol.

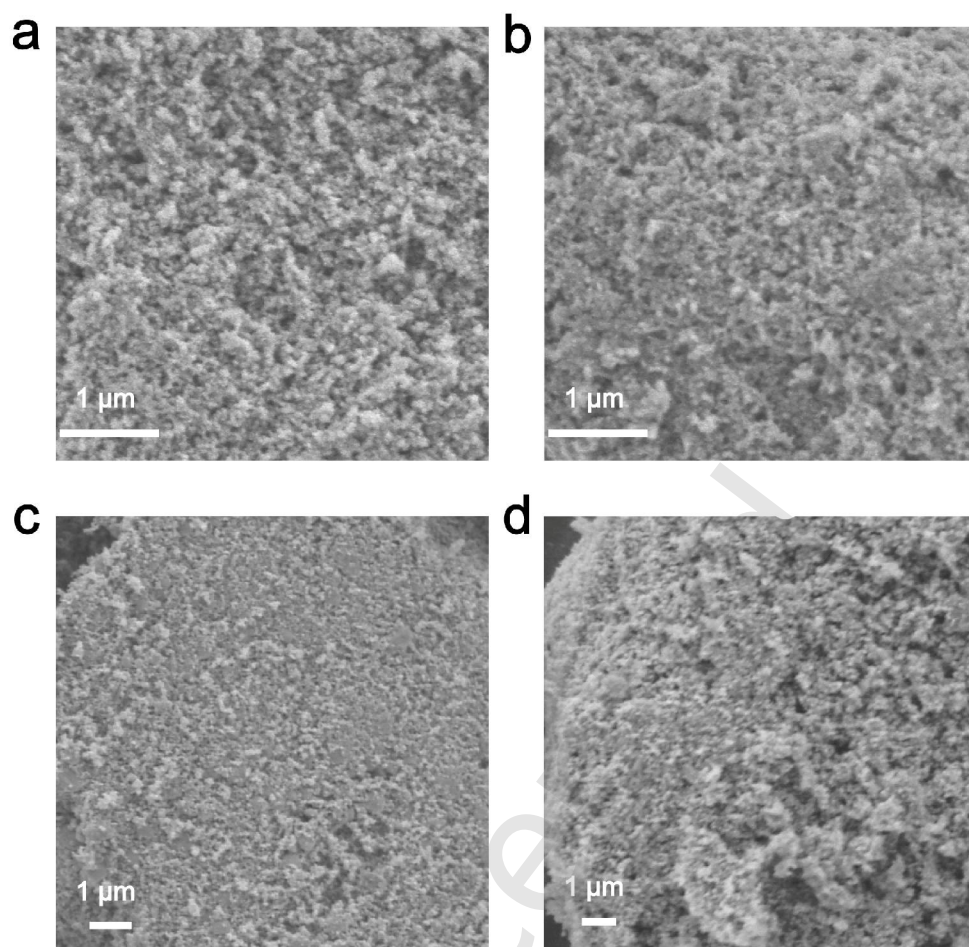


Figure S6. SEM images of (a) mesoporous Ni_3P -1.0, (b) mesoporous $\text{Ni}_3\text{P}/\text{Ni}_{12}\text{P}_5$ -1.0, (c) mesoporous Ni_{12}P_5 -1.0, and (d) mesoporous $\text{Ni}_{12}\text{P}_5/\text{Ni}_2\text{P}$ -1.0.

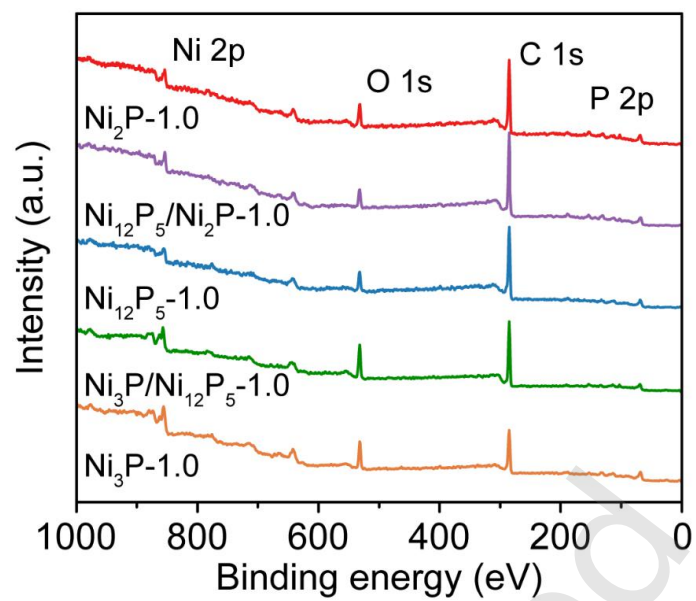


Figure S7. XPS survey spectra of the mesoporous $\text{Ni}_x\text{P}_y-1.0$ series.

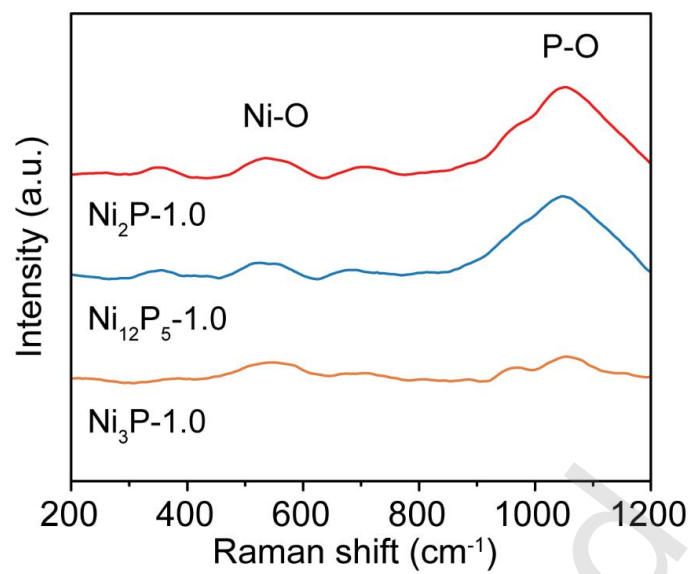


Figure S8. Raman spectra of the mesoporous $\text{Ni}_x\text{P}_y-1.0$ series.

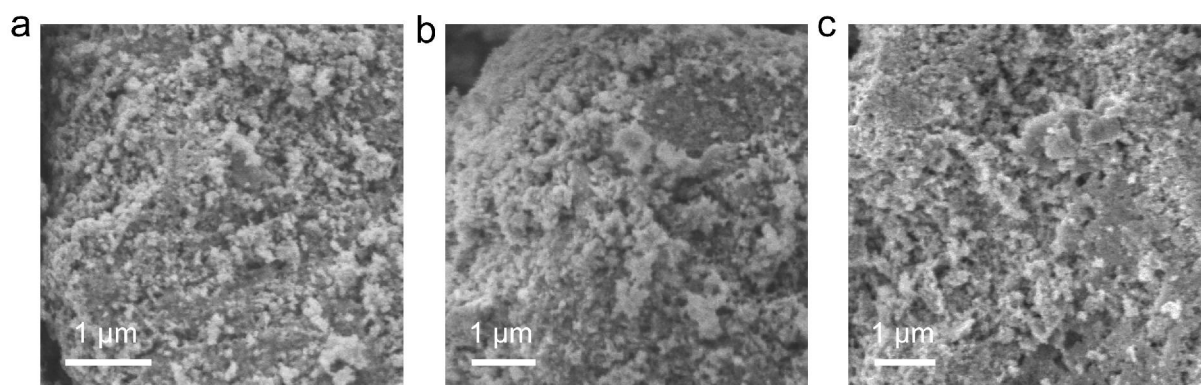


Figure S9. SEM images of (a) mesoporous $\text{Co}_2\text{P-1.0}$, (b) mesoporous $\text{Fe}_2\text{P-1.0}$, and (c) mesoporous $\text{Cu}_3\text{P-1.0}$.

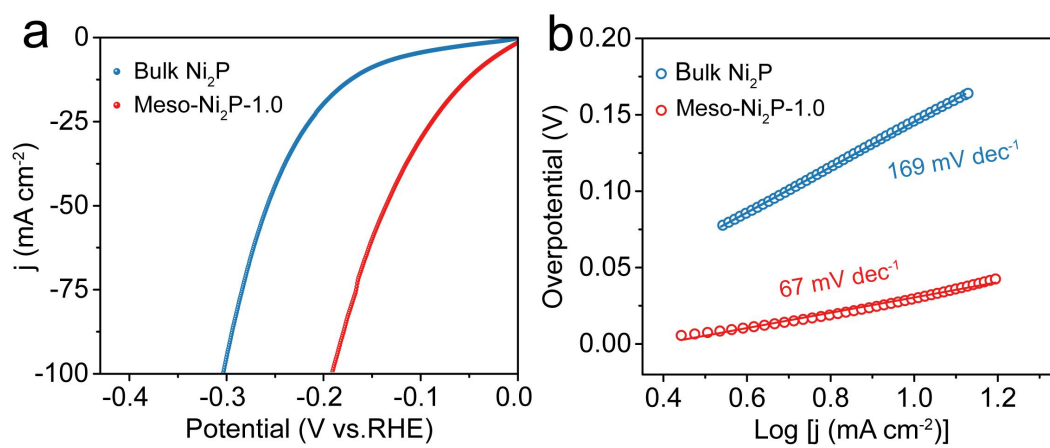


Figure S10. (a) LSV curves and (b) Tafel plots of bulk Ni_2P and mesoporous Ni_2P -1.0 measured in 1.0 M KOH.

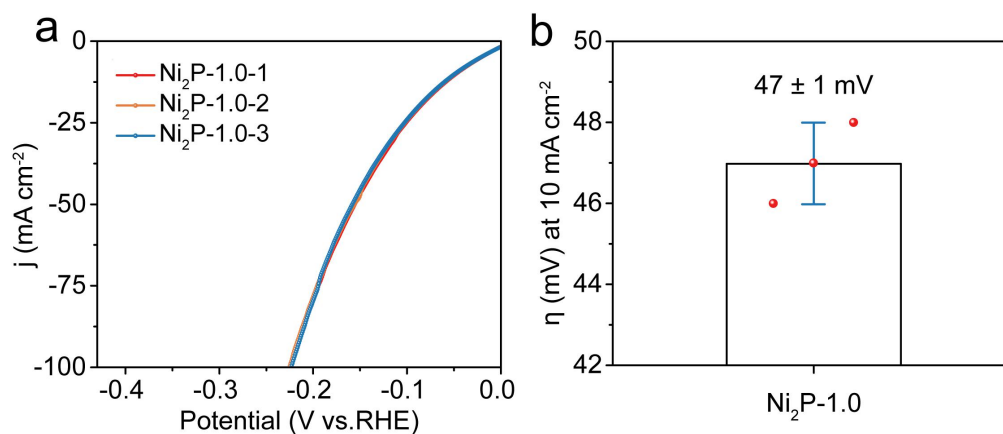


Figure S11. Reproducibility evaluation of mesoporous $\text{Ni}_2\text{P-1.0}$. (a) HER polarization curves of three independently prepared $\text{Ni}_2\text{P-1.0}$ electrodes measured in 1.0 M KOH at a scan rate of 5 mV s^{-1} . (b) Corresponding η_{10} values presented as mean $\pm$ SD based on three independently prepared electrodes.

As shown in Figure S11(a), the HER polarization curves of the three independently prepared electrodes are highly consistent. The overpotentials required to reach 10 mA cm^{-2} are 46, 47, and 48 mV, respectively, giving an average η_{10} value of 47 ± 1 mV. In addition, the corresponding η_{10} values are summarized as mean $\pm$ SD in Figure S11(b). These results demonstrate the good reproducibility and reliability of the HER performance of mesoporous $\text{Ni}_2\text{P-1.0}$ under the present testing conditions.

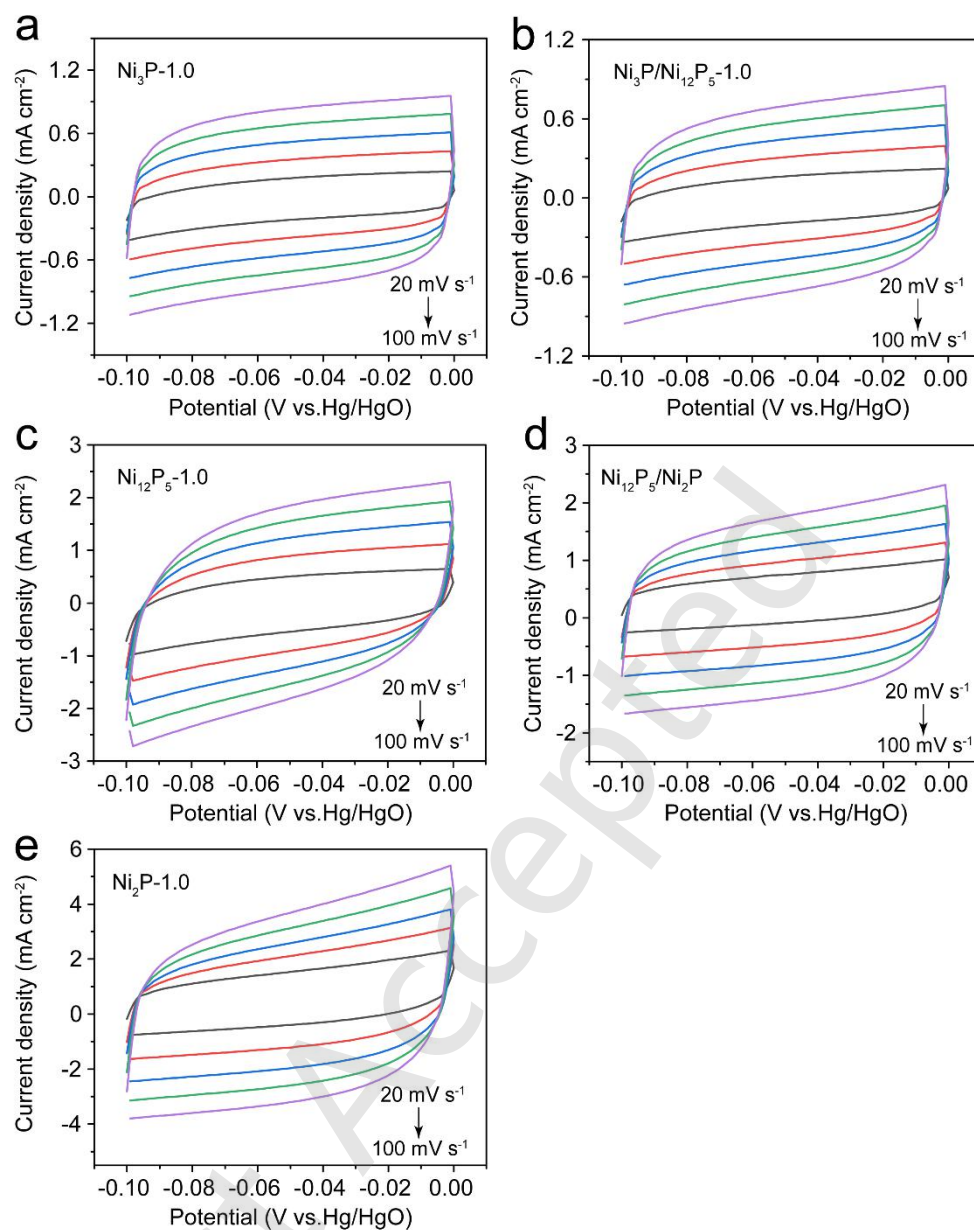


Figure S12. CV curves of (a) mesoporous Ni₃P-1.0, (b) mesoporous Ni₃P/Ni₁₂P₅-1.0, (c) mesoporous Ni₁₂P₅-1.0, (d) mesoporous Ni₁₂P₅/Ni₂P-1.0, and (e) mesoporous Ni₂P-1.0 measured at different scan rates in the non-Faradaic region.

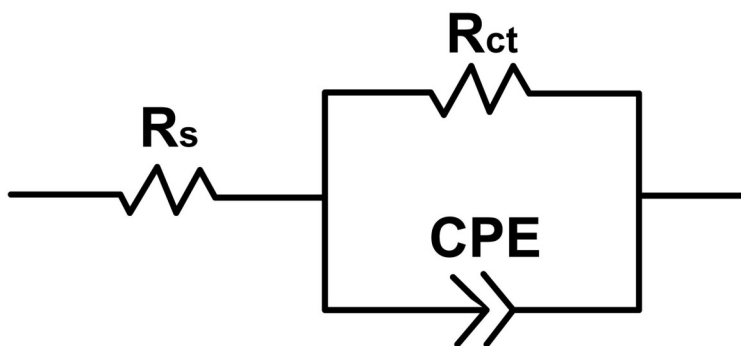


Figure S13. Equivalent circuit model used for fitting the EIS Nyquist plots of the mesoporous Ni_xP_y catalysts.

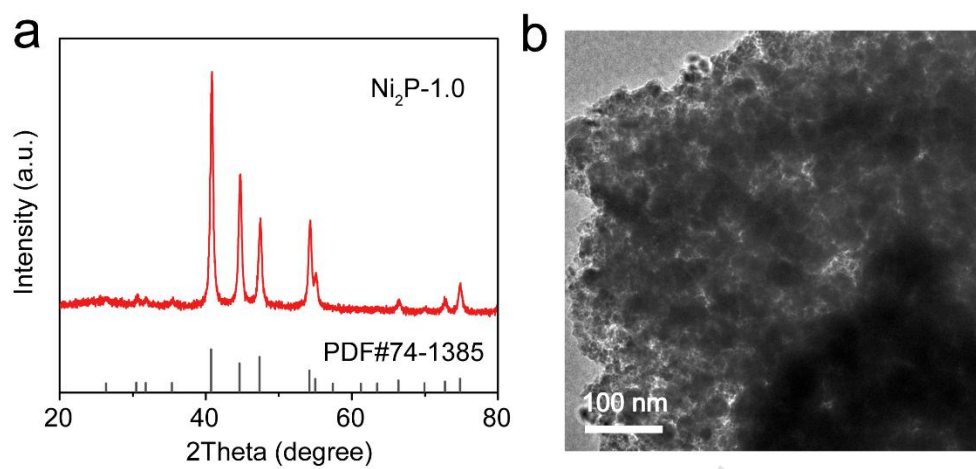


Figure S14. (a) XRD pattern and (b) TEM image of mesoporous $\text{Ni}_2\text{P-1.0}$ after the 100 h HER stability test.

Table S1. Carbon contents obtained by CHN elemental analysis.

Sample	Carbon content (wt%)
Ni ₂ P-0.5	6.3
Ni ₂ P-1.0	7.4
Ni ₂ P-1.5	10.3
Ni ₂ P-2.0	15.8
Ni ₃ P-1.0	7.1
Ni ₃ P/Ni ₁₂ P ₅ -1.0	7.7
Ni ₁₂ P ₅ -1.0	7.3
Ni ₁₂ P ₅ /Ni ₂ P-1.0	7.5

Table S2. Structural properties of mesoporous Ni_xP_y-z and other mesoporous metal phosphide samples.

Sample	$T^{[a]}$ [°C]	$S_{\text{BET}}^{[b]}$ [m ² g ⁻¹]	$d^{[c]}$ [nm]	$V_{\text{T}}^{[d]}$ [cm ³ g ⁻¹]
Ni ₂ P-0.5	600	61	11.7	0.178
Ni ₂ P-1.0	600	111	6.6	0.218
Ni ₂ P-1.5	600	54	6.8	0.120
Ni ₂ P-2.0	600	43	6.1	0.114
Ni ₃ P-1.0	600	76	9.4	0.194
Ni ₃ P/Ni ₁₂ P ₅ -1.0	600	78	9.4	0.166
Ni ₁₂ P ₅ -1.0	600	105	8.2	0.185
Ni ₁₂ P ₅ /Ni ₂ P-1.0	600	89	9.4	0.195
Co ₂ P-1.0	650	88	6.1	0.200
Fe ₂ P-1.0	650	68	6.1	0.139
Cu ₃ P-1.0	400	64	6.1	0.173

[a] T , [b] S_{BET} , [c] d , and [d] V_{T} denote the thermal-treatment temperature, BET surface area, pore size, and total pore volume, respectively.

Table S3. Quantitative analysis of phosphide-related surface species based on XPS fitting.

Sample	Ni-P/Ni-total (%)	Phosphide P/P-total (%)
Ni ₃ P-1.0	44.86	47.94
Ni ₁₂ P ₅ -1.0	52.29	50.59
Ni ₂ P-1.0	63.89	60.22

The quantitative ratios were calculated from the fitted peak areas rather than from the raw peak intensities. For each chemical state, the areas of the corresponding spin-orbit doublet were summed, and the same fitting procedure and constraints were applied consistently to all samples. The satellite peaks in the Ni 2p spectra were excluded from the chemical-state ratios because they are shake-up features rather than independent Ni species.

The Ni-P/Ni-total ratio was calculated using the Eq. 2:

$$\frac{\text{Ni-P}}{\text{Ni-total}} = \frac{A(\text{Ni-P})}{A(\text{Ni-P}) + A(\text{oxidized Ni})} \times 100\% \quad (2)$$

where A(Ni-P) and A(oxidized Ni) represent the summed integrated areas of the corresponding fitted Ni 2p doublets.

The phosphide P/P-total ratio was calculated using the Eq. 3:

$$\frac{\text{Phosphide P}}{\text{P-total}} = \frac{A(\text{Phosphide P})}{A(\text{Phosphide P}) + A(\text{oxidized P})} \times 100\% \quad (3)$$

where A(phosphide P) represents the summed integrated area of the fitted lattice phosphide P doublet, and A(oxidized P) represents the integrated area of the oxidized P component.

Table S4. Electrocatalytic HER activity parameters of the as-prepared catalysts and commercial Pt/C.

Sample	η_{10} mV	Tafel slope mV dec ⁻¹	$C_{dl, \text{measured}}$ mF cm ⁻²	$C_{dl, \text{corrected}}$ mF cm ⁻²	R_{ct} Ω
Ni ₃ P-1.0	111	182	8	7.997	2.90
Ni ₃ P/Ni ₁₂ P ₅ -1.0	124	188	6	5.997	3.24
Ni ₁₂ P ₅ -1.0	72	117	16	15.997	2.46
Ni ₁₂ P ₅ /Ni ₂ P-1.0	98	176	14	13.997	2.57
Ni ₂ P-1.0	48	67	31	30.997	2.22
Pt/C	48	56	—	—	—
Blank carbon cloth	—	—	0.003	—	—

[a] η_{10} , [b] C_{dl} , and [c] R_{ct} represent the overpotential at 10 mA cm⁻², double-layer capacitance, and charge-transfer resistance, respectively.

The background-corrected C_{dl} values were calculated by subtracting the blank carbon cloth contribution from the measured C_{dl} values of the catalyst-loaded electrodes according to the Eq. 4:

$$C_{dl, \text{corrected}} = C_{dl, \text{measured}} - C_{dl, \text{blank carbon cloth}} \quad (4)$$