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A porous nickel cyclotetraphosphate nanosheet as a new acid-stable electrocatalyst for efficient hydrogen evolution[†]

Xiong Liu,‡ Bo Wen,‡ Ruiting Guo,‡ Jiashen Meng, Ziang Liu, Wei Yang, Chaojiang Niu, Qi Li* and Liqiang Mai 💿 *

The stability of non-precious metal-based electrocatalysts for the acidic hydrogen evolution reaction (HER) is of great importance. Here, we have used nickel cyclotetraphosphate (Ni₂P₄O₁₂) nanosheet arrays as a HER electrocatalyst for the first time. The Ni₂P₄O₁₂ arrays were obtained through a facile low-temperature phosphorylation process and possess superior HER catalytic activities and stability in acid. The Ni₂P₄O₁₂ delivers a small overpotential of 131.8 mV at -10 mA cm⁻² and a low Tafel slope of 47.8 mV dec⁻¹ in 0.5 M H₂SO₄, comparable to most of the non-precious metal-based catalysts. Importantly, the Ni₂P₄O₁₂ shows a negligible potential change (6.5 mV) over 80 000 s continuous testing in acid. The inductive effect of P₄O₁₂⁴⁻ and its polymer-like structure, promoting it as a potential acid-stable HER electrocatalyst.

Increasing energy demands and the accompanying environment crisis have triggered the development of clean energy and high-efficiency energy conversion techniques in recent years.^{1,2} Hydrogen is an ideal energy carrier for future energy supply by virtue of its low cost and environmental friendliness.²⁻⁴ The hydrogen evolution reaction (HER), a half reaction of electrochemical water splitting, is considered as an effective strategy to produce pure hydrogen.⁴⁻⁶ Traditionally, platinum-based materials are regarded as the best electrocatalysts to accelerate the HER kinetics with a near zero overpotential. However, their large-scale applications are greatly impeded by their scarcity, exorbitant cost, and unsatisfactory long-term durability.^{7,8} As the electrocatalytic HER kinetics in acidic media are generally faster than those in alkaline media,⁹ much research has been focused on the development

E-mail: qi.li@whut.edu.cn, mlq518@whut.edu.cn

of inexpensive, acid-stable and high-efficiency Earth-abundant electrocatalysts as alternatives, such as transition metal chalcogenides, phosphides, and carbides as well as newly developed non-metal based catalysts.¹⁰⁻¹⁸

Despite the great progress achieved recently, most non-precious metal-based HER electrocatalysts can only be used in the alkaline media.¹⁹⁻²¹ Transition-metal phosphides (TMPs, M = Fe, Co, Ni, Cu, Mo, and W) with the metalloid characteristics have recently been utilized to catalyze the HER in acid.3,22-29 Though the theoretical and experimental studies have demonstrated these TMPs to be potential alternatives for HER electrocatalysts, the role of the oxidized species or phosphates that always exist on the surface of TMPs (Table S1[†]) cannot be neglected. Sundaram et al. reported that much less soluble phosphate which was formed on the nickel phosphide surface by oxidation could effectively protect the TMPs from dissolution,^{2,30} which means the possible existence of acid-stable phosphates. Li et al. demonstrated that the introduction of oxygen atoms into the TMPs not only activated catalytic sites via the elongation of the M-P bond, but also resulted in a much higher density of states (DOS) across the Fermi level and so enhanced the intrinsic conductivity of TMPs.31 Metal phosphosulfides and O-incorporated phosphides have also been reported to show better acidic HER or hydrogenation activity and stability than their simplex metal phosphides or sulfides.^{11,32-34} Therefore, metal phosphates or catalysts containing metal, oxygen and phosphorus elements, such as Ni-based phosphates, are expected to be promising electrocatalysts for boosting efficient and acid-stable HER. This is because a small Ni \rightarrow X (X = O, S and P) charge transfer occurs and thus Ni catalytic sites are activated.35 To the best of our knowledge, metal cyclotetraphosphates as efficient electrocatalysts for hydrogen evolution have not been reported, with only a few reports investigating the OER performance of metal cyclotetraphosphates.³⁶⁻³⁹ As reported, the phosphates in the OER electrocatalysts can serve as proton acceptors^{40,41} and also contribute to a favorable water adsorption and adjusting catalyst wettability.^{36,37,42} Therefore, it would be a great advance if metal cyclotetraphosphates can be used as high-efficiency HER electrocatalysts.



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State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, 430070 Hubei, China.

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[‡] These authors contributed equally to this work.

Herein, we report a novel and acid-stable HER electrocatalyst composed of nickel cyclotetraphosphate $(Ni_2P_4O_{12})$ nanosheet arrays which are grown on carbon cloth $(Ni_2P_4O_{12}/CC)$ through a low-temperature phosphorylation process under an argon atmosphere. The obtained $Ni_2P_4O_{12}/CC$ can catalyze the HER with a small overpotential and exhibit an excellent catalytic stability in acid. On the basis of experimental analyses, we demonstrate that the enhanced proton adsorption capacity and the porous structure enable $Ni_2P_4O_{12}$ with fast HER kinetics and its polymer-like structure contributes to the superior acid resistance. This newly developed HER electrocatalyst represents a promising candidate for high-efficiency non-precious metal-based electrocatalysts.

The detailed synthesis procedure of the Ni₂P₄O₁₂ nanosheet arrays grown on carbon cloth (Ni₂P₄O₁₂/CC) is presented (Fig. S1, ESI†). Uniformly hydrated nickel hydroxide nanosheet arrays were prepared *via* a facile wet-chemical method (Fig. S2, ESI†), followed by calcination in air to obtain NiO (Fig. S3, ESI†) and then phosphorylation in argon to form Ni₂P₄O₁₂. Only a few hours of phosphorylation are needed, much shorter than the reported molten-pyrolysis method which lasts for seven days with the morphology not well-retained.⁴³ During the phosphorylation process, the sodium hypophosphite $(NaH_2PO_2 \cdot H_2O)$ is used to generate the PH₃ and H₂O gases,^{36,44} and the Na₅P₃O₁₀ is the residue after a thermal decomposition of NaH₂PO₂·H₂O (Fig. S4, ESI[†]). Finally, the generated gases react with NiO to form Ni₂P₄O₁₂.

The crystal structure of Ni₂P₄O₁₂ is presented in Fig. 1a. It shows a three-dimensional (3D) framework with NiO₆ polyhedra connecting with P₄O₁₂ rings by Ni–O–P. As the basic structure unit is centrosymmetric, the vibrational mode is considered to be made up of P₄O₁₂^{4–} anions.⁴⁵ The Ni₂P₄O₁₂ belongs to a kind of cyclic phosphate and possesses a polymer-like structure⁴⁶ which may promote its acid resistance. The X-ray diffraction (XRD) peaks of the obtained Ni₂P₄O₁₂/CC can be well-indexed to the pure phase of the monoclinic Ni₂P₄O₁₂ phase (JCPDS no. 76-1557) and the peaks for phosphides cannot be detected (Fig. 1b). The broad peak at ~26° comes from the carbon cloth.

As shown in the scanning electron microscopy (SEM) images (Fig. 1c and d), the nanosheet arrays are well-retained after the phosphorylation process. The surface of the $Ni_2P_4O_{12}$ nanosheets is rough and the thickness is around 120 nm determined by the atomic force microscopy (AFM) measure-



Fig. 1 (a) Crystal structure of nickel cyclotetraphosphate (Ni₂P₄O₁₂). (b) XRD pattern of the obtained Ni₂P₄O₁₂ nanosheet arrays. (c and d) SEM images of Ni₂P₄O₁₂/CC. (e) HAADF-STEM image with elemental mapping of Ni₂P₄O₁₂ and (f) the corresponding EDX spectrum. (g and h) HRTEM images and (i) SAED pattern of Ni₂P₄O₁₂.

ment (Fig. S5, ESI[†]). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images with the corresponding energy-dispersive X-ray (EDX) mappings show that the Ni, P and O elements are distributed homogeneously (Fig. 1e). The corresponding EDX spectrum further demonstrates the existence of Ni, P, and O elements (Fig. 1f). According to the high-resolution transmission electron microscopy (HRTEM) images, the lattice fringes of 0.203 and 0.284 nm are indexed to the ($\bar{3}33$) and ($\bar{3}13$) planes of Ni₂P₄O₁₂, respectively (Fig. 1g and h). The selected-area electron diffraction (SAED) pattern of the Ni₂P₄O₁₂ nanosheet (Fig. 1i) displays diffraction rings which are well indexed to ($\bar{1}11$), ($\bar{2}22$), ($\bar{3}33$), ($\bar{4}44$), ($\bar{5}55$), ($\bar{1}12$), ($\bar{3}13$), ($\bar{1}33$) and (041) planes of Ni₂P₄O₁₂, in good agreement with the above-mentioned XRD result.

The Fourier-transform infrared (FTIR) spectra demonstrate different structures at the molecular level between Ni₂P₄O₁₂ and NiO (Fig. 2a). After phosphorylation, the various P–O bonds representing characteristic bonds of cyclotetraphosphates⁴⁷ in the frequency range of 400–1800 cm⁻¹ were observed for Ni₂P₄O₁₂. The bonds of Ni₂P₄O₁₂ in the ranges of 1260–1410, 1020–1190, 880–1020, and 640–785 cm⁻¹ can be well assigned to ν_{as} (PO₂), ν_{s} (PO₂), ν_{as} (POP), and ν_{s} (POP) stretching vibrations, respectively. The bonds below 610 cm⁻¹ belong to the bending motion of the tetrahedral group with the external bonding.^{48,49} X-ray photoelectron spectroscopy



Fig. 2 (a) FTIR spectra of $Ni_2P_4O_{12}$ and NiO. XPS spectra of $Ni_2P_4O_{12}$ and NiO: (b) survey scan, (c) Ni 2p, (d) P 2p and (e) O 1s. XPS spectra of $Ni_2P_4O_{12}$ and Ni: (f) Ni 2p.

(XPS) measurements were further carried out to obtain a deep insight into the difference of surface elemental composition between Ni₂P₄O₁₂ and NiO with the C 1s peak calibrated. First, the XPS survey spectra reveal the presence of Ni (10.66%), P (20.48%), and O (68.86%) in the Ni₂P₄O₁₂ and Ni (48.5%) and O (51.5%) in NiO (Fig. 2b), which are well in accordance with their stoichiometric ratios, respectively. In the range of 120-225 cm⁻¹, the bonds at 134 and 191 eV for the Ni₂P₄O₁₂ sample represent the P 2p and P 2s bonds. For the Ni 2p spectra (Fig. 2c), the Ni 2p_{1/2} and Ni 2p_{3/2} peaks of Ni₂P₄O₁₂ show a positive shift compared to those of NiO, which is similar to the reported $Mn_3(PO_4)_2 \cdot 3H_2O$ catalyst.⁵⁰ In this work, Jin *et al.* reported that the Mn 2p1/2 peak of Mn3(PO4)2·3H2O was positively shifted compared to that of MnO, which results from the inductive effect of phosphate anions. Therefore, in our as-prepared Ni₂P₄O₁₂ sample, the strong P–O bonds in P₄O₁₂^{4–} can induce the lattice distortion (Fig. S6, ESI[†]) and strong polarization of O²⁻, thus making the Ni 2p peaks more positive. Moreover, the P 2p core level spectrum of Ni₂P₄O₁₂ displays a sole peak at 134.1 eV which is not observed in NiO, indicating the formation of phosphate bonding in Ni₂P₄O₁₂ (Fig. 2d).³⁶ For O 1s in Fig. 2e, the peaks at 529.8 and 531.3 eV in NiO suggest the existence of Ni–OH and metal–oxygen bonds, respectively.^{51,52} For Ni₂P₄O₁₂, the peaks at 531.3 and 532.7 eV are ascribed to the P-O-Ni and P-O bonds from PO₃^{-.36,39} Furthermore, in the Ni 2p spectra, Ni⁰ species are not detected for Ni₂P₄O₁₂, suggesting the absence of phosphides (Fig. 2f).

A three-electrode system was carried out to evaluate the electrocatalytic activities of Ni₂P₄O₁₂/CC and NiO/CC towards the HER in 0.5 M H₂SO₄. According to the linear sweep voltammetry (LSV) results (Fig. 3a), the bare carbon cloth has a negligible HER activity. To achieve a cathodic current density of -10 mA cm⁻², the Ni₂P₄O₁₂/CC only requires a small overpotential (η_{10}) of 131.8 mV, which is much lower than NiO/CC (461.6 mV). The HER activity of Ni₂P₄O₁₂/CC was also measured by the steady-state measurement with a dwell time of 5 min, and the η_{10} value is very close to the value measured by the LSV measurement (Fig. S8, ESI[†]). To elucidate the HER mechanism of the catalysts, the Tafel plots of the Ni₂P₄O₁₂ and NiO catalysts are fitted (Fig. 3b). The Ni₂P₄O₁₂/CC possesses a small Tafel slope of 47.8 mV dec⁻¹, which indicates a combination of the Volmer-Heyrovsky mechanism according to the HER mechanism under acidic conditions.⁴ This value is much lower than that of NiO/CC (259.2 mV dec⁻¹), which suggests the higher HER kinetics and catalytic activities of Ni₂P₄O₁₂/CC. The overpotential and the Tafel slope values for our as-prepared Ni₂P₄O₁₂/CC are comparable to those of most of the previously reported non-precious metal-based HER electrocatalysts in acid (Table S2[†]), indicating excellent HER catalytic activities of Ni₂P₄O₁₂ as the potential high-performance catalyst in acid.

To gain further insights into the excellent electrocatalytic activity of Ni₂P₄O₁₂/CC, the electrochemical impedance spectroscopy (EIS) measurement was conducted at -0.3 V vs. SCE (Fig. 3c). The Nyquist plots reveal a low charge transfer resistance (R_{ct}) of 32.6 Ω in 0.5 M H₂SO₄ for Ni₂P₄O₁₂/CC, which is



Fig. 3 (a) LSV polarization curves of Ni₂P₄O₁₂/CC, NiO/CC, bare carbon cloth and the commercial Pt/C for the HER. (b) Tafel plots of Ni₂P₄O₁₂/CC and NiO/CC. (c) EIS Nyquist plots of Ni₂P₄O₁₂/CC and NiO/CC measured at -0.3 V vs. SCE. (d) Capacitive currents at 0.13 V against the scan rate and corresponding C_{dl} values estimated through the linear fitting of the plots. (e) The dependence of the amount of adsorbed H⁺ on the Ni₂P₄O₁₂ and NiO catalysts in 5 mM HCl aqueous solution on the adsorption time. (f) Schematic illustration of Ni₂P₄O₁₂/CC as a high-efficiency HER electrocatalyst.

much smaller than that for NiO/CC (148.2 Ω), indicating a faster faradaic process and superior HER kinetics of Ni₂P₄O₁₂/ CC.⁵³ Generally, the electrochemical double-layer capacitance $(C_{\rm dl})$ is used to approximately estimate the surface active area.⁵⁴ The C_{dl} value of Ni₂P₄O₁₂/CC (42.3 mF cm⁻²) is much higher than that of NiO/CC (5.5 mF cm^{-2}), which could result in a better HER activity for Ni₂P₄O₁₂/CC (Fig. 3d and S9, ESI[†]). In addition, from the reported proton adsorption experiments⁵⁵ (Fig. 3e), the adsorbed H^+ amount on the Ni₂P₄O₁₂ powder (based on the quality of HCl) reaches 54.5 mg g^{-1} , which is larger than that on the NiO powder (22.0 mg g^{-1}) under the same experimental conditions. This result indicates that the abundant protons can accumulate on the surface of the Ni₂P₄O₁₂ catalyst and thus promote its hydrogen adsorption process. Moreover, due to the inductive effect of phosphate anions, the Mn atoms in the reported $Mn_3(PO_4)_2 \cdot 3H_2O$ catalyst have more nucleophilic character than those in MnO.⁵⁰ Similarly, the more nucleophilic nature of Ni atoms in Ni₂P₄O₁₂ may activate the catalytic sites and enhance its HER activity. In addition, the nitrogen adsorption/desorption isotherms were used to investigate the Brunauer-Emmett-Teller (BET) surface area and the porosity of the NiO and Ni₂P₄O₁₂ nanosheets (Fig. S10, ESI[†]). The surface area and the pore volume of the Ni₂P₄O₁₂ nanosheets are 43.2 m² g⁻¹ and 0.091 cm³ g⁻¹, respectively, much higher than those of the NiO nanosheets (10.9 m² g⁻¹ and 0.008 cm³ g⁻¹). The porous feature of Ni₂P₄O₁₂ nanosheets enables the exposure of more catalytic sites and thus enhances the catalytic activities of catalysts. Therefore, we have demonstrated the Ni₂P₄O₁₂ nanosheet arrays as a high-efficiency HER electrocatalyst (Fig. 3f).

To estimate the faradaic efficiency, a gas-tight electrochemical cell coupled to a gas burette was carried out to measure the volume of gas evolved during the catalytic reaction of the Ni₂P₄O₁₂/CC with a constant potential of -0.6 V vs. SCE applied. As shown in Fig. S11,† a 97.2% faradaic efficiency is estimated based on the observed gas volume and the theoretical gas volume calculated by the charge passed through the electrode. The 2.8% loss may be ascribed to the attached bubbles on the electrode surface and the dissolved gas in solution.^{56,57}

The long-term stability is also critical for the HER electrocatalysts in acid, and can be measured by the galvanostatic/ potentiostatic electrolysis. The durability tests of $Ni_2P_4O_{12}/CC$ and NiO/CC were conducted in 0.5 M H₂SO₄ by the chronopotentiometry method (Fig. 4a). After an 80 000 s continuous



Fig. 4 (a) Chronopotentiometry curves of Ni₂P₄O₁₂/CC and NiO/CC in 0.5 M H₂SO₄. (b) LSV polarization curves of Ni₂P₄O₁₂/CC and NiO/CC before and after an 80 000 s test in 0.5 M H₂SO₄ at a scan rate of 5 mV s⁻¹. (c) SEM image of Ni₂P₄O₁₂/CC after HER testing in 0.5 M H₂SO₄ for 80 000 s. (d) XRD patterns of Ni₂P₄O₁₂/CC before and after the stability testing in 0.5 M H₂SO₄ for 36 h. (e) Ni²⁺ concentration in the supernatant for the Ni₂P₄O₁₂ and NiO powders after soaking in 0.5 M H₂SO₄ for various time periods. Inset: A digital photograph comparison of the Ni₂P₄O₁₂ (right) and NiO (left) powders after soaking in 0.5 M H₂SO₄ for 36 h.

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testing, the potential difference $\Delta V (\Delta V = V_{80,000,s} - V_{1,6,s})$ of $Ni_2P_4O_{12}/CC$ (only 6.5 mV) is much lower than that of NiO/CC (273.9 mV), indicating an outstanding catalytic stability of Ni₂P₄O₁₂/CC. This result can also be reflected by comparing the LSV polarization curves of catalysts before and after the stability testing. The overlapped polarization curves of $Ni_2P_4O_{12}/CC$ suggest its stable catalytic performance (Fig. 4b). After testing in 0.5 M H₂SO₄ for 80 000 s, the nanosheet structure of Ni₂P₄O₁₂ is well-retained and the planes do not show changes (Fig. 4c, Fig. S12, ESI[†]), proving the superior catalytic stability of Ni₂P₄O₁₂ in acid. XPS measurements of Ni₂P₄O₁₂ before and after HER testing further demonstrate the catalytic stability of Ni₂P₄O₁₂ in acid (Fig. S13, ESI[†]). Moreover, the XRD pattern of Ni₂P₄O₁₂/CC after testing in 0.5 M H₂SO₄ for 36 h is similar to that of the initial one (Fig. 4d), further suggesting the acid-stable properties of Ni₂P₄O₁₂. In addition, the acidic stability was investigated by analyzing the Ni²⁺ concentration in the supernatant via inductively coupled plasma MS (ICP-MS) after soaking the solid catalysts (Ni₂P₄O₁₂ or NiO) in 0.5 M H₂SO₄ for 6, 12, 24 and 36 h, respectively. As shown in Fig. 4e, the much higher concentration of Ni^{2+} in the supernatant for the NiO sample indicates its easy dissolution in acid. According to the digital photograph (inset in Fig. 4e), the NiO powder disappears after soaking for 36 h. However, for the Ni₂P₄O₁₂ powder, the black catalyst is still visible after the same soaking time.

Based on the above-mentioned experimental results, it can be concluded that the excellent HER electrocatalytic performances of $Ni_2P_4O_{12}$ are attributed to (1) good proton adsorption capacity, (2) inductive effect of $P_4O_{12}^{4-}$ in $Ni_2P_4O_{12}$ to activate catalytic sites, (3) low charge transfer resistance, (4) porous nanosheet structure to enhance the exposed area of the catalyst and (5) polymer-like structure to enable $Ni_2P_4O_{12}$ with an excellent resistance to acid. Therefore, we have demonstrated a new electrocatalyst which can catalyze the acidic HER with high-efficiency.

Conclusions

In summary, we have prepared a new acid-stable HER electrocatalyst of nickel cyclotetraphosphate nanosheet arrays which were grown on carbon cloth (Ni₂P₄O₁₂/CC) *via* a low-temperature phosphorylation strategy. This new electrocatalyst exhibits excellent HER activities in acid (overpotential of 131.8 mV at -10 mA cm⁻² and a Tafel slope of 47.8 mV dec⁻¹) and superior long-term acid resistance according to an 80 000 s stability test. Our newly synthesized nickel cyclotetraphosphate electrocatalyst represents a promising candidate for high-efficiency and acid-stable HER electrocatalysis.

Conflicts of interest

There are no conflicts to declare.

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