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

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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 remarkable catalytic performances of Ni2P4O12 are mainly attributed to the inductive effect of P4O12 4− 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 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 simple 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 → 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 acceptors40,41 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.
Herein, we report a novel and acid-stable HER electrocatalyst composed of nickel cyclotetraphosphate (Ni$_2$P$_4$O$_{12}$) nanosheet arrays which are grown on carbon cloth (Ni$_2$P$_4$O$_{12}$/CC) through a low-temperature phosphorylation process under an argon atmosphere. The obtained Ni$_2$P$_4$O$_{12}$/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$_2$P$_4$O$_{12}$ 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 Ni$_2$P$_4$O$_{12}$ nanosheet arrays grown on carbon cloth (Ni$_2$P$_4$O$_{12}$/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 Ni$_2$P$_4$O$_{12}$. 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. During the phosphorylation process, the sodium hypophosphite (NaH$_2$PO$_2$·H$_2$O) is used to generate the PH$_3$ and H$_2$O gases, and the Na$_5$P$_3$O$_{10}$ is the residue after a thermal decomposition of NaH$_2$PO$_2$·H$_2$O (Fig. S4, ESI†). Finally, the generated gases react with NiO to form Ni$_2$P$_4$O$_{12}$.

The crystal structure of Ni$_2$P$_4$O$_{12}$ is presented in Fig. 1a. It shows a three-dimensional (3D) framework with NiO$_6$ polyhedra connecting with P$_4$O$_{12}$ rings by Ni–O–P. As the basic structure unit is centrosymmetric, the vibrational mode is considered to be made up of P$_4$O$_{12}$$^{4-}$ anions. The Ni$_2$P$_4$O$_{12}$ belongs to a kind of cyclic phosphate and possesses a polymer-like structure which may promote its acid resistance. The X-ray diffraction (XRD) peaks of the obtained Ni$_2$P$_4$O$_{12}$/CC can be well-indexed to the pure phase of the monoclinic Ni$_2$P$_4$O$_{12}$ 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$_2$P$_4$O$_{12}$ nanosheets is rough and the thickness is around 120 nm determined by the atomic force microscopy (AFM) measure-
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 (333) and (313) planes of Ni$_2$P$_4$O$_{12}$, respectively (Fig. 1g and h). The selected-area electron diffraction (SAED) pattern of the Ni$_2$P$_4$O$_{12}$ nanosheet (Fig. 1i) displays diffraction rings which are well indexed to (111), (222), (333), (444), (555), (112), (313), (133) and (041) planes of Ni$_2$P$_4$O$_{12}$, in good agreement with the above-mentioned XRD result.

The Fourier-transform infrared (FTIR) spectra demonstrate different structures at the molecular level between Ni$_2$P$_4$O$_{12}$ and NiO (Fig. 2a). After phosphorylation, the various P–O bonds representing characteristic bonds of cyclotetraphosphate can be well assigned to ν$_{as}$ (PO$_3$), ν$_s$ (PO$_2$), 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.

- **Ni 2p ($\nu$O)**
- **P 2p ($\nu$O)**
- **O 1s ($\nu$O)**

(XPS) measurements were further carried out to obtain a deep insight into the difference of surface elemental composition between Ni$_2$P$_4$O$_{12}$ 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 Ni$_2$P$_4$O$_{12}$ 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 Ni$_2$P$_4$O$_{12}$ sample represent the P 2p and P 2s bonds. For the Ni 2p spectra (Fig. 2c), the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks of Ni$_2$P$_4$O$_{12}$ show a positive shift compared to those of NiO, which is similar to the reported Mn$_3$(PO$_4$)$_2$·3H$_2$O catalyst. In this work, Jin et al. reported that the Mn 2p$_{3/2}$ peak of Mn$_3$(PO$_4$)$_2$·3H$_2$O was positively shifted compared to that of MnO, which results from the inductive effect of phosphate anions. Therefore, in our as-prepared Ni$_2$P$_4$O$_{12}$ sample, the strong P–O bonds in P$_2$O$_5$ can induce the lattice distortion (Fig. S6, ESI†) and strong polarization of O$^-$, thus making the Ni 2p peaks more positive. Moreover, the P 2p core level spectrum of Ni$_2$P$_4$O$_{12}$ displays a sole peak at 134.1 eV which is not observed in NiO, indicating the formation of phosphate bonding in Ni$_2$P$_4$O$_{12}$ (Fig. 2d). 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. For Ni$_2$P$_4$O$_{12}$, the peaks at 531.3 and 532.7 eV are ascribed to the P–O–Ni and P–O bonds from PO$_3^-$, respectively. Furthermore, in the Ni 2p spectra, Ni$^0$ species are not detected for Ni$_2$P$_4$O$_{12}$, suggesting the absence of phosphides (Fig. 2f).

A three-electrode system was carried out to evaluate the electrocatalytic activities of Ni$_2$P$_4$O$_{12}$/CC and NiO/CC towards the HER in 0.5 M H$_2$SO$_4$. 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 Ni$_2$P$_4$O$_{12}$/CC only requires a small overpotential ($\eta_{10}$) of 131.8 mV, which is much lower than NiO/CC (461.6 mV). The HER activity of Ni$_2$P$_4$O$_{12}$/CC was also measured by the steady-state measurement with a dwell time of 5 min, and the $\eta_{10}$ 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 Ni$_2$P$_4$O$_{12}$ and NiO catalysts are fitted (Fig. 3b). The Ni$_2$P$_4$O$_{12}$/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. 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 Ni$_2$P$_4$O$_{12}$/CC. The overpotential and the Tafel slope values for our as-prepared Ni$_2$P$_4$O$_{12}$/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 Ni$_2$P$_4$O$_{12}$ as the potential high-performance catalyst in acid.

To gain further insights into the excellent electrocatalytic activity of Ni$_2$P$_4$O$_{12}$/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 ($R_c$) of 32.6 Ω in 0.5 M H$_2$SO$_4$ for Ni$_2$P$_4$O$_{12}$/CC, which is...
much smaller than that for NiO/CC (148.2 \( \Omega \)), indicating a faster faradaic process and superior HER kinetics of Ni2P4O12/CC.53 Generally, the electrochemical double-layer capacitance (\( C_{dl} \)) 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 Mn3(PO4)2·3H2O 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 m\(^2\) g\(^{-1}\) and 0.091 cm\(^3\) g\(^{-1}\), respectively, much higher than those of the NiO nanosheets (10.9 m\(^2\) g\(^{-1}\) and 0.008 cm\(^3\) 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 Ni2P4O12/CC and NiO/CC were conducted in 0.5 M H2SO4 by the chronopotentiometry method (Fig. 4a). After an 80 000 s continuous...
testing, the potential difference $\Delta V$ ($\Delta V = V_{80\,000 \text{ s}} - V_{1.6 \text{ s}}$) of Ni$_2$P$_4$O$_{12}$/CC (only 6.5 mV) is much lower than that of NiO/CC (273.9 mV), indicating an outstanding catalytic stability of Ni$_2$P$_4$O$_{12}$/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$_2$P$_4$O$_{12}$/CC suggest its stable catalytic performance (Fig. 4b). After testing in 0.5 M H$_2$SO$_4$ for 80 000 s, the nanosheet structure of Ni$_2$P$_4$O$_{12}$ is well-retained and the planes do not show changes (Fig. 4c, Fig. S12, ESI†), proving the superior catalytic stability of Ni$_2$P$_4$O$_{12}$ in acid. XPS measurements of Ni$_2$P$_4$O$_{12}$ before and after HER testing further demonstrate the catalytic stability of Ni$_2$P$_4$O$_{12}$ in acid (Fig. S13, ESI†). Moreover, the XRD pattern of Ni$_2$P$_4$O$_{12}$/CC after testing in 0.5 M H$_2$SO$_4$ for 36 h is similar to that of the initial one (Fig. 4d), further suggesting the acid-stable properties of Ni$_2$P$_4$O$_{12}$. In addition, the acidic stability was investigated by analyzing the Ni$^{2+}$ concentration in the supernatant via inductively coupled plasma MS (ICP-MS) after soaking the solid catalysts (Ni$_2$P$_4$O$_{12}$ or NiO) in 0.5 M H$_2$SO$_4$ 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 Ni$_2$P$_4$O$_{12}$ 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$_2$P$_4$O$_{12}$ are attributed to (1) good proton adsorption capacity, (2) inductive effect of P$_4$O$_{12}^{4-}$ in Ni$_2$P$_4$O$_{12}$ 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$_2$P$_4$O$_{12}$ 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 (Ni$_2$P$_4$O$_{12}$/CC) via a low-temperature phosphorylation strategy. This new electrocatalyst exhibits excellent HER activities in acid (overpotential of 131.8 mV at $\sim$10 mA cm$^{-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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**Notes and references**