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A powerful solid-phase hot-pressing method was applied to grow POMOFs and the derived phosphides on carbon cloth rapidly and uniformly.
Solid-Phase Hot-Pressing Synthesis of POMOFs on Carbon Cloth and Derived Phosphides for All pH Values Hydrogen Evolution

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Designing an all pH values hydrogen evolution reaction (HER) electrocatalyst with low-cost and high activity is urgent for the future energy storage and conversion system. Metal-organic frameworks (MOFs) with well-defined pore structures and various metal sources provide feasible platforms for the design of efficient electrocatalysts. However, MOFs as crystalline materials are mostly in crystal or powder form, which would hinder their practical applications. Herein, polyoxometalates-based MOFs (POMOFs) were synthesized on carbon cloth (CC) through a facile and general solid-phase hot-pressing method for the first time. Thus-obtained POMOFs/CC can be converted into three phases bimetallic phosphides coated by porous carbon on CC through a phosphidation process and show high electrocatalytic stability over a wide pH range (pH, 0-14) and possess excellent HER performance with low overpotential (e.g., 90.5 mV at 10 mA cm$^{-2}$ in 1 M KOH). Moreover, POMOFs/CC derived phosphides present high selectivity for H$_2$ production (nearly 100% faradic efficiency) and ultra-low charge-transfer resistance (0.96 Ω) in alkaline medium, which hold promise in practical applications. This work provides a powerful strategy for the facile production of the fast nucleating MOFs-derived electrodes for potential industrial-scale applications in energy storage and conversion.

Introduction

Electrochemical water splitting, comprising hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), is a promising method to produce the renewable energy sources for the eco-friendly energy conversion and storage technologies. Although the commercial Pt/C and IrO$_2$ can serve as the efficient HER and OER electrocatalysts with low overpotential and large current density, the high-cost and rareness still hinder their further industrialization. Non-noble metal-based catalysts with low-cost and high abundant are desperately needed to replace the noble benchmark catalysts. Up to date, large amounts of non-noble metal-based catalysts such as sulfides, carbides, phosphides, oxides or their hybrid structures have been investigated. However, most reported non-noble metal-based materials only show significant HER performance in acidic, neutral or alkaline electrolytes. Such pH-restricted HER catalysts might have drawbacks in the practical usage over a wide pH range and their applications in overall water splitting system are limited. Therefore, the demand of ultra-stable electrocatalysts to satisfy the practical applications for HER catalysis at all pH values is urgent while largely unmet.

Recently, transition metal phosphides (TMPs, M$_2$P$_x$, M = Mo, W, Fe, Co, etc.) have been studied as the inspiring all pH values HER electrocatalysts. Among them, molybdenum phosphide (MoP) or tungsten phosphide (WP) has showed promise as HER electrocatalysts in various electrolytes. For example, Sun et al. reported that MoP nanosheet array on carbon cloth (CC) was used as the HER cathode in acid, basic and neutral media with the low overpotentials at 10 mA cm$^{-2}$ Moreover, another report demonstrated the WP nanorod arrays on CC as the pH-universal 3D HER cathode, which shown small overpotentials at 10 mA cm$^{-2}$ and long-term stability. Generally, TMPs particles are mixed with additives (i.e., Nafion) to cast onto glassy carbon electrodes for HER catalysis. In the process, there are some drawbacks like the dispersity of TMPs particles or the connection between TMPs particles and substrates, which might have problems in long-term catalysis. Powerful methods that can directly fabricate uniformly dispersed TMPs particles on conductive substrates are highly desirable. Besides, it remains a challenge for TMPs particles to be directly used in harsh conditions. Some works reported that the combination of TMPs particles with carbon-based materials could increase the stability and further enhance their electrocatalytic efficiency. In this work, we intend to explore powerful methods that can in-situ produce carbon-coated TMPs materials on conductive substrates to impart this system with high conductivity, dispersity and stability for efficient HER electrocatalysis.
As a class of porous materials, metal-organic-frameworks (MOFs) consist of rich metal ions and functional ligands to form the regular porous structures and periodic pores. Polyoxometalates (POMs) are composed by anionic metal oxide clusters with diverse structures and abundant high-valent transition metals (Mo, W, V, etc.). Polyoxometalates-based MOFs (POMOFs) are a kind of novel crystal materials that POMs can be the part of MOFs frameworks or within the cavities to form the intriguing novel crystal materials that POMs can be the part of MOFs frameworks or within the cavities to form the intriguing structures. As precursors, POMOFs can be pyrolyzed to produce porous-carbon-coated nano-sized transition-metal (Mo, W, V from POMs) oxides or carbides. These derivatives can serve as the promising electrocatalysts with advantages like: 1) after carbonization, the obtained composites contain bimetallic components with high specific surface areas and hierarchical pores for efficient mass transfer; 2) the carbon shell protection derived from MOFs can help to avoid polymerization and degradation of metal nanoparticles in harsh electrolytes. Therefore, POMOFs are the ideal precursors with a variety of optional metal sources to precisely controlled synthesis of TMPs particles with unique structures. However, most reported derivative materials are powders, which are required to deposit onto the conductive substrates (e.g., glassy carbon electrode and nickel foam) for further applications. Meanwhile, the powders on substrates always have weak interaction and are easy to peel off during the electrocatalytic measurement. Therefore, in situ processing of POMOF precursors on conductive substrates uniformly and firmly are a key factor to prepare TMPs particles coated by porous carbon on substrates and directly use as excellent HER electrodes.

Herein, we introduce a powerful solid-phase hot-pressing method to fabricate POMOFs on carbon cloth (POMOFs/CC) rapidly using an electric iron (Figure 1). POMOFs are desired crystal materials that combine the advantages of both POMs and MOFs and can be nucleated rapidly under the mild reaction condition. We hot-press POMOFs on CC using copper acetate (Cu(OAc)$_2$·H$_2$O), benzenetricarboxylate (BTC) and POMs as precursors for the following reasons: 1) in case of copper and BTC, the famous MOFs of HKUST-1 can be synthesized using the simple solvent method traditionally, which is made up of the dimeric cupric tetracarboxylate units to form the porous and stable structure; 2) Keggin-type POMs (e.g., PMO$_{12}$ and PW$_{12}$) have small size (< 1 nm), high stability and water solubility, which could be the best choice for the structure building of POMOFs. Therefore, one guest POMs molecule can be encapsulated in per cavity of HKUST-1 to construct POMs@HKUST-1 easily. Then POMOFs/CC can serve as the self-sacrificing platform to synthesize bimetallic phosphides on CC (Cu-M-P/CC, M = Mo or W) through a phosphidation process. During phosphidation, POMs are easily.

Preparation of POMs@HKUST-1/CC

A mixture of Cu(OAc)$_2$·H$_2$O (0.20 g, 1 mmol), PMO$_{12}$ (0.17 g, 0.093 mmol), H$_3$BTC (0.14 g, 0.67 mmol), 0.10 g PEG and 0.4 mL EG were added into a mortar and ground to form the homogeneous green paste. Then the paste was coated onto the both sides of CC (size, 1 × 2 cm$^2$) with the thickness of about 0.5 mm. The CC was wrapped with the aluminum foil and hot-pressed using an electric iron at 200 °C for 20 min. After peeling off the aluminum foil, PMO$_{12}$@HKUST-1/CC can be obtained. PMO$_{12}$@HKUST-1/CC with different PMO$_{12}$ loadings were also prepared using less PMO$_{12}$ amounts (0.1 g, 0.055 mmol) and excess PMO$_{12}$ amounts (0.3 g, 0.16 mmol), respectively. For comparison, PW$_{12}$@HKUST-1/CC was synthesized similar to PMO$_{12}$@HKUST-1/CC except that PW$_{12}$ was used instead of PMO$_{12}$. Different PW$_{12}$ loadings were studied including 0.14 g (0.055 mmol), 0.26 g (0.093 mmol) and 0.46 g (0.16 mmol). Besides, HKUST-1/CC was prepared without PMO$_{12}$ loadings. PMO$_{12}$/CC was prepared using PMO$_{12}$ (0.17 g, 0.093 mmol) and 0.1 g PEG as the precursors. PW$_{12}$/CC was prepared using PW$_{12}$ (0.26 g, 0.093 mmol) and 0.1 g PEG as the precursors.

Preparation of Cu-M-P/CC

Two slices of PMO$_{12}$@HKUST-1/CC in quartz crucible were placed in the horizontal tube furnace with 0.2 g red phosphorus at the upstream side. The samples were heated to 400 °C for 2 h and then 800 °C for 2 h at a heating speed of 5 °C min$^{-1}$ under N$_2$ atmosphere. After cooling down to the room temperature, Cu-Mo-P/CC was obtained. For comparison, Cu-W-P/CC composite was prepared by phosphidation of PW$_{12}$@HKUST-1/CC directly. Cu$_2$P$_2$CuP$_4$/CC, MoP/CC and WP/CC were prepared by phosphidation of HKUST-1/CC, PMO$_{12}$/CC and PW$_{12}$/CC, respectively.

Material characterizations

Powder X-Ray diffraction (PXRD) patterns were recorded on a D/max 2500VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation (λ = 1.54060 Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out on JEOL-JEM-2100F apparatus at an accelerating voltage of 200 kV. Morphology and microstructure analysis was conducted using a scanning electron microscope (SEM,
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Electrochemical impedance spectroscopy (EIS) were carried out in an interval of 20 min and injected into GC. FE was calculated according to the following equation: \[ \text{FE} = \frac{2nF}{Q} \] where \( n \) (mol) is the total amount of as-produced \( \text{H}_2 \), \( F \) (96485 C mol\(^{-1}\)) is Faraday constant, \( Q \) (C) is the total voltammetric charge, 2 means the two-electron process to per mole of \( \text{H}_2 \) for HER.

**Results and discussion**

Compared with the traditional liquid phase synthesis, the solid-phase hot-pressing method for the preparation of POMOFs has the advantages of solvent-free, fast reaction rate and high yield. The fabrication process of POMOFs/CC and subsequent Cu-M-P/CC are described as follows (Figure 1). Firstly, a paste containing the mixture of \( \text{Cu}(	ext{OAc})_2 \cdot \text{H}_2\text{O}, \text{BTC}, \text{POMs}, \text{polyethylene glycol (PEG)} \) and a few drops of ethylene glycol (EG) were ground and uniformly painted onto a CC (size, \( 1 \times 2 \) cm\(^2\)) with a paste thickness of 0.5 mm on both sides. A piece of aluminum foil was covered on the surface of the CC and then hot-pressing was conducted on both sides (ca. 200 °C, 20 min) to achieve POMOFs/CC. POMs can be encapsulated within the cavities of HKUST-1 to form POMOFs with the formula of \( [\text{Cu}_2(\text{BTC})_6(\text{H}_2\text{O})_4][\text{POMs}] \cdot \text{H}_2\text{O} \) which are denoted as POMs@HKUST-1. Secondly, a phosphidation procedure using red phosphorus as P sources was applied to transfer POMOFs/CC into Cu-M-P/CC (i.e., Cu-Mo-P/CC and Cu-W-P/CC). The average mass loading of Cu-Mo-P on CC is 1.37 mg cm\(^{-2}\) (Table S1). Notably, PEG was used as the adhesives to ensure POMOFs precursors grow on CC substrates tightly and also could provide carbon source for phosphidation. In contrast, CuP/CuP/CC and MoP/CC were synthesized by phosphidation of HKUST-1/CC and PMo\(_{12}\)/CC, respectively.

Two POMs@HKUST-1/CC (i.e., PMo\(_{12}\)@HKUST-1/CC and PW\(_{12}\)@HKUST-1/CC) were investigated in this work. Powder X-ray diffraction (PXRD) patterns show the peaks of PMo\(_{12}\)@HKUST-1/CC and PW\(_{12}\)@HKUST-1/CC match well with the simulated pattern of POMOFs (Figure 2a). As comparison, HKUST-1/CC was fabricated following the same hot-pressing procedures without POMs and the PXRD pattern of HKUST-1/CC is consistent with the simulated one (Figure 2a). In order to see their crystal structures clearly, POMs, HKUST-1 and POMs@HKUST-1 were listed in Figure S1. The single crystal of POMs@HKUST-1 was formed by the co-crystallization of
POMs and HKUST-1 rather than the simple mixture. Additionally, the most obvious difference of PXRD patterns between POMs@HKUST-1 and HKUST-1 is that the first strong peak is at different 2 theta degrees. After introducing POMs into the cavities of HKUST-1, the first strong peak at 6.7° has a left shift to 5.8° to form POMOFs. The CCDC reference number of PMo$_{12}$@HKUST-1, PW$_{12}$@HKUST-1 and HKUST-1 is 686797, 686795 and 112954, respectively, which can be found in the Cambridge Structural Database with detailed crystallographic data in CIF. After phosphidation, taking Cu-Mo-P/CC for example, the PXRD pattern of Cu-Mo-P/CC derived from PMo$_{12}$@HKUST-1/CC exhibits a mixed-phase pattern (Figure 2b). Three phases including molybdenum phosphide of MoP (JCPDS No. 24-771), copper phosphides of Cu$_3$P (JCPDS No. 71-2261) and CuP$_2$ (JCPDS No. 65-6208) are detected. Similar results are also obtained in the PXRD pattern of Cu-W-P/CC derived from PW$_{12}$@HKUST-1/CC. Three phases including Cu$_3$P, CuP$_2$ and tungsten phosphide of WP (JCPDS No. 29-1364) are identified. As comparison, Cu$_3$P/CuP$_2$/CC derived from HKUST-1/CC shows two phases of Cu$_3$P and CuP$_2$.

Prepared from the solid-phase hot-pressing method, the obtained device exhibits high particle dispersity. For instance, PMo$_{12}$@HKUST-1 nanoparticles are uniformly dispersed on CC verified by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure S2). After phosphidation, flexible Cu-Mo-P/CC in black color was produced (size, 2 × 2 cm$^2$) (Figure 3a). SEM images of Cu-Mo-P/CC at different scales demonstrate that Cu-Mo-P nanoparticles (average size, ca. 100 nm) are uniformly decorated on every single string of carbon fiber in Cu-Mo-P/CC (Figure 3b). The uniformly dispersed morphology of Cu-Mo-P nanoparticles was also certified by the TEM image (Figure 3c). To further investigate the structural and composition of Cu-Mo-P nanoparticles, high-resolution TEM (HRTEM) test is performed (Figure 3d). Specially, three kinds of TMPs phases (i.e., MoP, Cu$_3$P and CuP$_2$) are detected and embedded in amorphous porous carbon in the Cu-Mo-P nanoparticles, indicating the strong electron interactions among these phosphides particles. This result is also verified by the high-angle annular dark-filed (HADDF) image and energy dispersive spectroscopy (EDS) element mappings (Figure 3e). Therefore, derived from PMo$_{12}$@HKUST-1/CC, Cu-Mo-P nanoparticles are uniformly dispersed on CC and present amorphous carbon coated morphology. The porosity of Cu-Mo-P/CC, Cu$_3$P/CuP$_2$/CC and MoP/CC are also investigated. Notably, Cu-Mo-P/CC has a
Brunauer-Emmett-Teller (BET) specific surface area of 40.2 m$^2$ g$^{-1}$ supported by the $N_2$ adsorption-desorption test (Figure S3a), which is much higher than the contrast samples of Cu$_3$P/CuP$_2$/CC (39.8 m$^2$ g$^{-1}$) and MoP/CC (36.4 m$^2$ g$^{-1}$). Besides, the total pore volumes of Cu-Mo-P/CC, Cu$_3$P/CuP$_2$/CC and MoP/CC are 5.4 × 10$^{-2}$ cm$^3$ g$^{-1}$, 3.6 × 10$^{-2}$ cm$^3$ g$^{-1}$ and 3.9 × 10$^{-2}$ cm$^3$ g$^{-1}$, respectively. The above three samples all show the hierarchical porosity with pore size distributions ranging from 2.5 nm to 35 nm (Figure S3b). As control experiments, morphologies of HKUST-1/CC and PMo$_{12}$/CC and their derivatives including SEM, TEM and HRTEM images are also tested and showed in Figure S4 to S6. Moreover, large area SEM images of Cu-Mo-P/CC, Cu$_3$P/CuP$_2$/CC and MoP/CC are shown in Figure S7, further proving the advantages of Cu-Mo-P particles on CC without stacking.

With high particle dispersity, amorphous carbon coated morphology and hierarchical porosity, Cu-Mo-P/CC also possesses large amount of active species. Surface chemical states of Cu-Mo-P/CC were studied by X-ray photoelectron spectroscopy (XPS) to illustrate the potential active species in the film. The spectra of Cu, Mo, P, C and O are displayed in Figure S8a. Based on the XPS data, the molar ratio of Cu/Mo for Cu-Mo-P/CC is about 0.78:1, which is consistent with the molar ratio in precursors and the formula of POMOFs (Table S2). The inductively coupled plasma optical emission spectrometry (ICP-OES) is also used to analyze the Cu/Mo molar ratio of Cu-Mo-P particles (0.96:1), which is very close to the Cu/Mo molar ratio in the raw materials. The Cu 2p spectrum (Figure S8b) shows two main peaks of Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ along with their corresponding satellite peaks. Cu 2p$_{1/2}$ region exhibits two deconvoluted peaks at 954.9 and 952.4 eV, assigning to Cu$^{2+}$ and Cu$^{1+}$, respectively. Similarly, Cu 2p$_{3/2}$ region gives Cu$^{2+}$ at 934.8 eV and Cu$^{1+}$ at 932.5 eV. The majority (63.2%) of Cu$^{1+}$ in Cu 2p belongs to the metal-rich Cu$_3$P, which can improve the conductivity and facilitate the electron transfer of Cu-Mo-P/CC. Besides, the Mo 3d spectrum can be deconvoluted into six peaks with different valence states (Figure S8c). Two main peaks at 231.3 eV and 228.1 eV can be ascribed to MoP. The other four peaks are assigned to the partial oxidation form of MoO$_{x}$ on Cu-Mo-P/CC surface. Notably, the electron binding energies of Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ of Cu-Mo-P/CC both have the negative shift of ~0.7 eV compared with the Cu 2p spectrum of Cu$_3$P/CuP$_2$/CC. Both of the Mo$^{δ+}$ 3d$_{3/2}$ and Mo$^{δ+}$ 3d$_{5/2}$ also exhibit the negative shift of ~0.2 eV in contrast to Mo 3d spectrum of MoP/CC. These results prove the strong electronic interactions among the MoP, Cu$_3$P and CuP$_2$ species, implying the successful hybridization of Cu-Mo-P nanoparticles on CC. Furthermore, the P 2p spectrum shows the binding energies of P 2p$_{1/2}$ and P 2p$_{3/2}$ at 130.3 and 129.5 eV, respectively, suggesting the successful preparation of phosphides (Figure S8d). The C 1s spectrum mainly contains C-C/C= and O-OH bonds. As comparison, the XPS spectra of Cu$_3$P/CuP$_2$/CC and MoP/CC are also demonstrated in Figure S9 and S10 in detail. The surface chemical state results imply Cu-Mo-P/CC to be a kind of efficient catalyst with large amount of active sites.
Above all, Cu-Mo-P/CC with the advantages of amorphous carbon coated morphology, high dispersion, hierarchical porosity and large amount of three phases phosphides active species might serve as the efficient electrocatalyst for HER. To estimate the electrocatalytic activity for HER, Cu-Mo-P/CC and other contrasted samples (i.e., 20% Pt/C, CuP/CuP/C and MoP/CC) were directly used as the working electrodes. Three kinds of electrolytes including 0.5 M HSO₄ (pH = 0), 1 M KOH (pH = 14) and 0.5 M PBS (pH = 6.8), which cover all pH ranges, were applied for measurements. All the polarization curves were shown with iR compensation. As the control experiment, the HER performance of bare CC was also investigated at all-pH values electrolytes to verify the results. LSV curves in Figure 4a show that Cu-Mo-P/CC has an overpotential of 145.9 mV vs. RHE at the current density of 10 mA cm⁻², which much lower than CuP/CuP/CC (266.1 mV) and MoP/CC (223.6 mV) and closing to 20% Pt/C (58 mV) in acid medium. In alkaline medium (1 M KOH), the onsetpotential and η₁₀ of Cu-Mo-P/CC are ~15 mV and 90.5 mV, respectively. Remarkably, this result is close to that of commercial Pt/C catalyst (29.2 mV and η₁₀, 29 mV) (Figure 4b, 5a). In contrast, both CuP/CuP/CC and MoP/CC give higher onsetpotential (225.1 and 132.6 mV) as well as η₁₀ (358.7 and 220.2 mV) than Cu-Mo-P/CC in 1 M KOH, respectively (Figure 4b). In 0.5 M PBS, Cu-Mo-P/CC also presents superior HER performance with η₁₀ of 132.6 mV over CuP/CuP/CC (294.8 mV) and MoP/CC (202.2 mV) (Figure 4c).

Tafel slope is an important parameter to reflect the rate-controlling step for HER (Figure 4d-f). The Tafel slopes of Cu-Mo-P/CC are 54.1, 76.9 and 111 mV dec⁻¹ in acid, alkaline and neutral medium, respectively. The Tafel slopes of Cu-Mo-P/CC in different electrolytes were also investigated. LSV curves in Figure 4a show that Cu-Mo-P/CC has an overpotential of 145.9 mV vs. RHE at the current density of 10 mA cm⁻², which imply it is the best phosphonation temperature (Figure S24). Moreover, the performances of Cu-Mo-P/CC in different electrolytes were also investigated. LSV curves in Figure 4a show that Cu-Mo-P/CC has an overpotential of 145.9 mV vs. RHE at the current density of 10 mA cm⁻², which imply it is the best phosphonation temperature (Figure S24). Further the Tafel slopes of Cu-Mo-P/CC in different electrolytes were also investigated. LSV curves in Figure 4a show that Cu-Mo-P/CC has an overpotential of 145.9 mV vs. RHE at the current density of 10 mA cm⁻², which imply it is the best phosphonation temperature (Figure S24). Noteworthy, the Tafel slope of Cu-Mo-P/CC in acid medium is the lowest among all contrast samples and is close to the commercial Pt/C catalyst (30 mV dec⁻¹). In general, the performance of Cu-Mo-P/CC at all pH range is among the best performances for MOF-derived materials and other phosphides on substrates, such as CoP/CC, Co₅Se₄ and CuP NW/CC (Table S4). To highlight the advantages of the solid-phase hot-pressing method, traditional liquid-phase stirring method was used to prepare PMo₁₂@HKUST-1 and further treated with similar phosphidation process to obtain Cu-Mo-P powder. Then the Cu-Mo-P powder was mixed with Nafion and further attached onto the surface of CC to investigate the HER performance. Specially, it shows poorer HER performance than Cu-Mo-P/CC (Figure S13). This might be attributed to the better particle dispersity and tighter connections between Cu-Mo-P nanoparticles and CC in Cu-Mo-P/CC than electrode fabricated through secondary fabrication process.

Furthermore, fabricated through the hot-pressing method, Cu-Mo-P/CC with diverse compositions can be achieved on CC. Adjusting the amounts of PPMo₁₂ (i.e., 0.055 mmol, 0.093 mmol and 0.16 mmol added in the precursor), different Cu-Mo-P/CC with various Mo loadings were achieved. LSV curves and Tafel slopes of Cu-Mo-P/CC were measured to compared their HER performance in different electrolytes (Figure S14). Cu-Mo-P/CC with the medium mass loading of 0.093 mmol PPMo₁₂ in the precursor (Cu/Mo molar ratio is ca. 1:1) shows better HER performance than the less loading or excess loading samples in all pH values electrolytes. Except for Cu-Mo-P/CC, other catalysis systems were also investigated. For example, Cu-W-P/CC can be produced from the phosphidation of PW₁₂@HKUST-1/CC. The structure is similar to PMo₁₂@HKUST-I except that POMs in the center cavity is PW₁₂. This provides a good platform to compare the HER performance of the similar phosphides with different chemical compositions. LSV curves and Tafel slopes of Cu-W-P/CC with different PW₁₂ loadings were also tested in different electrolytes (Figure S15). Cu-W-P/CC presents better HER performance with higher PW₁₂ loadings in the precursors. For instance, Cu-W-P/CC with highest PW₁₂ loadings (0.16 mmol in the precursor) possesses the best activity in 1 M KOH (η₁₀, 167.6 mV and Tafel slope, 110.5 mV dec⁻¹). However, the HER...
Long-term stability is one of the critical prerequisites for practical applications, since it determines the durability of the electrocatalysts under harsh conditions. Remarkably, Cu-Mo-P/CC presents excellent long-term stability. LSV curves of Cu-Mo-P/CC conducted before and after 5000 cyclic voltammetry (CV) cycles (ranging from 0 to -0.3 V vs. RHE) almost overlap in the three kinds of electrolytes (Figure 4g-i). Moreover, Cu-Mo-P/CC exhibits almost no degradation after continuous chronoamperometric (CA) electrolysis for 20 h, which shows 93% retention in 0.5 M H₂SO₄ and 92% retention in 1 M KOH and even a little increase of current density in 0.5 M PBS (inset images in Figure 4g-i).

To further realize the excellent HER electroactivity of Cu-Mo-P/CC, electrochemically active surface area (ECSA) and electrochemical impedance spectroscopy (EIS) were examined. The double-layer capacitance \( (C_d) \) at the solid-liquid interface is proportional to ECSA, which can be calculated to analyze the assessable HER electroactivity. In 1 M KOH, the \( C_d \) value of Cu-Mo-P/CC calculated from CV plot is 169 mF cm\(^{-2}\), which is 6.3-fold and 1.8-fold higher than those of CuP\(_2\)/CuP\(_2\)/CC (27 mF cm\(^{-2}\)) and MoP/CC (92 mF cm\(^{-2}\)) (Figure Sb and Figure S17). This result fits well with the HER activities and similar trends of the \( C_d \) values are calculated in acid and PBS conditions (Figure S18 and S19). As shown in EIS spectra, all samples reveal the semicircles in three kinds of electrolytes and show low charge-transfer resistance (\( R_{ct} \)) at high frequency range (Figure 5c,d, Figure S20 and Table S5). For instance, \( R_{ct} \) values of Cu-Mo-P/CC, CuP\(_2\)/CuP\(_2\)/CC, MoP/CC recorded at the overpotential of 150 mV vs. RHE in 1 M KOH are 0.96, 48.8 and 1.3 Ω, respectively, which are fitted according to the equivalent circuit in the inset of Figure 5c. The ultra-low \( R_{ct} \) value of Cu-Mo-P/CC indicates fast charge-transfer kinetic and high ionic conductivity, which is beneficial for HER performance.

The excellent performance and high long-term stability set fundamental basis for further applications. We set out to investigate the hydrogen production amount of Cu-Mo-P/CC. The hydrogen production test was conducted in the cathode compartment of a gas tight H-type electrolytic cell. In the test, CA was carried out in 1 M KOH for 160 min at the fixed overpotential to reach the current density of 10 mA cm\(^{-2}\) and faradic efficiency (FE) was calculated by comparing the amounts of measured and theoretical H\(_2\) amounts. As showed in Figure S21, Cu-Mo-P/CC has nearly 100% FE, and its H\(_2\) production is close to the theoretical value, suggesting the high selectivity for HER.

A series of physical characterizations of Cu-Mo-P/CC after HER test were carried out to prove the high stability. The morphology of Cu-Mo-P/CC after CA test for 20 h at all pH values is almost unaltered compared with the as-synthesized one proved by SEM images (Figure 3b and Figure S22). Leaching test was also conducted by ICP-OES to reflect the catalysis stability of Cu-Mo-P/CC. Taking acid electrolyte (i.e., 0.5 M H\(_2\)SO\(_4\)) for example, only 9.38 × 10\(^{-10}\) mol mL\(^{-1}\) and 9.30 × 10\(^{-10}\) mol mL\(^{-1}\) of dissolved Mo and Cu amounts were detected after 20 h CA test. The dissolved mass percents of Mo and Cu were 1.3 wt% and 1.9 wt% with the electrolyte volume of 30 mL and the measured mass of 1.37 mg for Cu-Mo-P catalysts. These data indicate the high stability of Cu-Mo-P/CC during the stability tests. In spite of the remained catalysis performance and high stability after 20 h CA test, a special phase-transformation (CuP\(_2\) was transferred to CuP) was observed by PXRD and XPS tests and the real active species are CuP and MoP for Cu-Mo-P/CC in the HER catalysis (Figure S23 and S24). The high stability of Cu-Mo-P/CC might be attributed to the porous carbon coated morphology of Cu-Mo-P nanoparticles and tight adhesion of Cu-Mo-P nanoparticles on CC, which prevent Cu-Mo-P particles from corrosion in harsh electrolytes and ensure the long-term stability. To further clarify the hypothesis, photographs of the electrolyte before and after 5000 CV cycles was taken. After 5000 CV cycles, no color change was observed (Figure S25).

Conclusions

In summary, we report a powerful solid-phase hot-pressing method to fabricate POMOFs (PMo\(_{12}\)@HKUST-1/CC and PW\(_{12}\)@HKUST-1/CC) on CC rapidly for the first time. This facile and non-polluting method perfectly solves the problem that MOFs materials are easy to peel off from the substrates. The unique structure of POMOFs with POMs particles encapsulated in the cavities of HKUST-1 ensures the subsequent phosphidation to synthesize Cu-M-P/CC (\( M = Mo \) or W), which possess porous carbon coated morphology, uniform dispersion and strong electron interactions of nanoparticles on CC, hierarchical porosity and large amount of three phases active phosphides species. All these advantages make Cu-M-P/CC to be the promising HER electrocatalyst. Taking Cu-Mo-P/CC for example, it shows high catalysis stability and excellent HER performance with low overpotential over a wide pH range (e.g., 90.5 mV at 10 mA cm\(^{-2}\) in 1 M KOH), demonstrating one of the best HER performances among recently reported MOFs-derived materials and other phosphides on substrates. Notably, Cu-Mo-P/CC presents high selectivity for H\(_2\) production (nearly 100% FE) and ultra-low charge-transfer resistance (0.96 Ω). It is indicated that the preparation of the fast nucleating MOFs onto the conductive substrates in quantity is a powerful solid-phase hot-pressing method holds the promising applications for electrochemical reactions and future energy devices.

Conflicts of interest

There are no conflicts to declare.

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