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Fabrication of self-supporting hierarchical porous metallic glass for pH-universal hydrogen evolution reaction

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ABSTRACT

The development of efficient pH-universal electrocatalysts is crucial for large-scale hydrogen production via the electrochemical hydrogen evolution reaction (HER). A simple and environmentally benign dissolution manufacturing (DM) strategy is adopted to synthesize a self-supported hierarchical porous Pt-based metallic glass (HPMG) catalyst. In a pH-universal electrolyte, the HPMG demonstrates remarkable HER performance. At 10 mA cm⁻², the optimal HPMG-4 catalyst shows low overpotentials of 35 mV in 1.0 M KOH, 16 mV in 0.5 M H₂SO₄, and 54 mV in a 1.0 M phosphate buffer solution. The catalyst also exhibits a large electrochemically active surface area and outstanding stability. The hierarchical porous structure of HPMG-4 is attributed to its hydrophilic and gas-repellent properties, which are critical factors contributing to the excellent HER activity. Additionally, the continuously renewed active sites are believed to enhance the performance. Computational analyses indicate that the amorphous structure reduces the energy barrier for water adsorption and dissociation, with a hydrogen ad/desorption free energy value close to zero (-0.067 eV). In conclusion, this study provides a universal strategy for developing HER catalysts with exceptional activity and stability across diverse media.

1. Introduction

The growing emphasis on sustainable energy has sparked substantial interest in renewable alternatives to fossil fuels [1–3]. Hydrogen (H₂) is widely recognized as a promising green energy carrier due to its high energy density, carbon-free emissions, and renewable nature [4–7]. Electrocatalytic HER has emerged as a low-cost and highly efficient approach for hydrogen production [8–10]. Developing highly active and durable HER catalysts that exhibit excellent performance in pH-universal electrolytes is crucial for large-scale water electrolysis [11,12].

While platinum-based materials are considered the most efficient HER catalysts, their high cost and limited availability restrict widespread commercial applications [13–15]. Consequently, researchers have extensively explored non-noble metal alternatives, such as transition metal catalysts (Ni [16–18], Fe [19,20], Mo [21–23], Co [24,25]). However, these catalysts often suffer from large overpotentials and poor long-term stability under strongly acidic or alkaline conditions, rendering them unsuitable for large-scale industrial hydrogen production compared to platinum-based materials [26–28].

Amorphous alloys, also known as metallic glasses (MGs), exhibit unique structural and physicochemical properties that could be leveraged for high-performance HER catalysis [29–32]. Notably, MGs exhibit an extreme decrease in viscosity when heated to their supercooled liquid phase region (SLR), allowing them to be processed by stretching and deformation like plastics, i.e., they possess a unique thermoplastic molding characteristic [33–35]. This unique property enables the design of MG-based catalysts with controlled porous structures to maximize the catalytic surface area.

Enhancing the catalytic surface area of HER electrocatalysts is a wellestablished strategy to improve catalytic efficiency by exposing more active sites [36–39]. This work employs an environmentally friendly, rapid, and cost-effective "DM" approach to synthesize a self-supporting HPMG electrocatalyst. By utilizing a soluble template material during the thermoplastic molding process, the resultant porous structure

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features both micrometer- and nanometer-sized pores, which can be readily tuned by controlling the size of the soluble template particles. This allows for optimizing the catalytic surface area to enhance the efficiency of the HER performance. Furthermore, Pt-based metallic glass compositions significantly reduce the amount of platinum required while maintaining excellent catalytic activity.

Notably, the HPMG catalyst exhibits remarkable long-term stability across various pH environments, demonstrating low overpotentials and Tafel slopes in acidic, neutral, and alkaline solutions. These attributes, combined with the facile and scalable fabrication approach, underscore the potential of the HPMG catalyst for large-scale hydrogen production, marking it as a leading candidate in the field of electrocatalysis.

2. Experiment section

2.1. Chemicals and materials

Pt-based amorphous alloys are known for their broad supercooled liquid phase region, excellent glass-forming ability, and good fluidity, which have been demonstrated to exhibit superior catalytic properties. In this study, the Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5} system was selected for investigation. The constituent elements, including platinum, nickel, copper, and phosphorus, were procured from Beijing Zhongnuo New Material Technology Co. Amorphous alloy Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5} strips with a width of 5 mm were prepared using the traditional water-cooled copper mold casting method. The amorphous alloy strips were powdered using a grinding machine to obtain the Pt-based amorphous powder. Sodium chloride (NaCl) powder was obtained from Shanghai McLean Biochemical Technology Co. and was recrystallized to produce particles with a size of approximately 5 μ m.

Preparation of HPMG-4 and HPMG-6: The prepared Pt-based amorphous alloy powder and NaCl powder were combined in grinding bowls at mass ratios of 4:1 and 6:1 to yield HPMG-4 and HPMG-6, respectively. The uniformly mixed powders were placed into a mold cavity. Under a vacuum of 3×10^{-3} Pa, the temperature was increased at 60 K/min. When the temperature reached 235 K, the Pt-based amorphous alloy powder exhibited excellent fluidity within the supercooled liquid phase region. A servo-electric cylinder was then activated, applying a displacement speed of 0.05 mm/s and a load of 10 kN for 15 s to maximize the filling of the voids between the Pt-based amorphous alloy powder and NaCl particles. Subsequently, a pressure of 130 MPa was applied at approximately 443 K. Once the temperature reached 543 K, the heating and pressure were discontinued. The finished thermoplastic mold was then allowed to cool to room temperature, and the catalysts were subsequently removed and washed repeatedly with distilled water to acquire the HPMG-4 and HPMG-6 catalysts.

2.2. Characterizations

X-ray diffractometer (XRD) was used to characterize the amorphous state of the porous Pt-based amorphous alloy electrodes before and after the thermoplastic processing. Nitrogen adsorption/desorption analysis at 77 K was performed using a Micromeritics ASAP 2020, and the specific surface area of the catalysts was calculated using the BET method. A droplet shape analyzer (DSA100S, kr, Germany) was used to measure the contact angle (CA) of the micro-structured surfaces with a 1 μ L volume of water droplets. Surface chemical-state analysis was determined by using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The morphologies and elemental distributions of the catalysts were characterized using an FEI Quanta 450 FEG scanning electron microscope (SEM) instrument, a JEOL 2100F scanning transmission electron microscope (TEM) equipped with double spherical aberration (Cs) correctors and energy dispersive spectroscopy (EDS). The TEM samples were prepared on an FEI Scios scanning electron microscope/focused ion beam (SEM/FIB) system.

2.3. Electrochemical measurements

The electrochemical activity of the HER in pH-universal electrolytes was evaluated using an electrochemical workstation (SP-300, Bio-Logic) in the standard three-electrode mode. HPMG was used as the working electrode, platinum sheet as the counter electrode, and a Hg/HgO (in alkaline medium) or Ag/AgCl (in neutral medium) or SCE (in acid medium) was used as the reference electrode. For electrochemical measurements, the alkaline environment was all potassium hydroxide solution (1 mol/L), the neutral environment was all phosphate buffer solution (PBS, 1 mol/L) and the acidic environment was all dilute sulfuric acid (0.5 mol/L). The solution resistance was determined using electrochemical impedance spectroscopy (EIS) in the range of 0.01 Hz ~ 106 Hz with an amplitude of 5 mV. The measured potentials of the reversible hydrogen electrode (RHE) were reported according to the Nernst equation $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059$ pH or $E_{RHE} = E_{(Ag/$ A_{gCl} + 0.197 + 0.059 pH or $E_{RHE} = E_{SCE}$ + 0.242 + 0.059 pH. A doublelayer capacitance (Cdl) at the electrode-electrolyte interface was measured using cyclic voltammetry (CV) over a small range of potentials, which led to the determination of the electrochemically active surface area (ECSA). The Tafel plots were fitted to the Tafel equation: η $=\beta \log i + \alpha$, where η is the half-wave potential, β is the Tafel slope, i is the current density, and α is the exchange rate current density, *j*, with respect to the Tafel intercept.

2.4. Density functional theory (DFT) calculations

The structural optimizations and electronic structure calculations are carried out by employing density functional theory, which is implemented in the Vienna Ab Initio Simulation Package (VASP) code [40]. The projector augmented wave (PAW) method is utilized with a cutoff energy of 500 eV. All structures are comprehensively optimized [40]. The generalized gradient approximation (GGA) of the exchange-correlation functional (PBE) was adopted [41,42]. Valence-core interactions are characterized by projector-augmented-wave (PAW) pseudopotentials [43]. The Brillouin zone sampling is conducted using $(3 \times 3 \times 1)$ Monkhorst-Pack grids for slab and Gamma for cluster structures [44]. The convergence tolerance for energy is set at 1×10^{-6} eV, the maximum force is 0.002 eV \AA^{-1} , and the maximum displacement is 0.002 Å [44]. The free energy change (ΔG) is computed from the zeropoint energy (ZPE)-corrected total energies as $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$, where $\Delta EZPE$ and ΔS denote the zero-point energy difference and the entropy difference, respectively, and T represents the system temperature (298.15 K) [45]. The value of $\Delta E_{\text{ZPE}} - T\Delta S$ is acquired from previous reports by Nørskov et al., which is approximately 0.24 eV [46].

3. Results and discussion

3.1. Synthesis and characterization of HPMG

The synthesis of the HPMG is schematically illustrated in Fig. 1a. Initially, a powder mixture consisting of Pt-based amorphous alloy and sodium chloride was situated within the working chamber of a high-vacuum thermoplastic molding apparatus and heated to the SLR. A loading period of 15 s was sustained to ensure the complete filling of the NaCl pores by the amorphous alloy. After the thermoplastic molding operation, the sample was immersed in distilled water at room temperature for 10 min, resulting in the dissolution and removal of the internal sodium chloride. This simple dissolution technique enables the efficient generation of the self-supporting hierarchical porous HPMG structure, demonstrating the convenient synthesis, environmental friendliness, and high efficacy of this method.

The micromorphology of the synthesized HPMG-4 is presented in Fig. 1b and c, which reveals a porous structure with irregular sizes formed after the dissolution of NaCl particles. The surface is covered with micropores, and nanopores are distributed on the micropores, thus



Fig. 1. (a) The schematic diagram for synthesis HPMG. (b-c) The SEM images of the micropore and nanopores on the HPMG-4. (d) The TEM images of the nanopores on the HPMG-4. (e) The HPMG-4 nm pore size normal distribution statistics. (f) The N_2 adsorption and desorption curves of HPMG-4. (g) HRTEM image of HPMG-4 and (inset) corresponding SAED image. (h) The HAADF-STEM image of and EDS elemental distribution of HPMG-4.

forming a hierarchical porous structure. The larger pore sizes are attributed to the agglomerated clusters of NaCl particles, while the finer pores at higher magnification reflect the individual NaCl particle contributions. Additional statistical analysis of the micrometer pores (Fig. S1) showed an average pore size of 6.9 μ m, similar to the average size of the 5 μ m recrystallized salt particles. This structural configuration is crucial for enhancing the intimate contact between the electrocatalyst and the electrolyte.

Observations from the TEM in Fig. 1d show the nanoscale holes in the HPMG-4. Further quantifying the nanopore size distribution (Fig. 1e) revealed an average pore size of approximately 26.01 nm. The adsorption and desorption curves of N₂ (Fig. 1f) further demonstrated the hierarchical mesoporous architecture, with a specific surface area of HPMG-4 measured to be $36.4934 \text{ m}^2 \text{ g}^{-1}$ by the Brunauer-Emmet-Teller

(BET) method.

As HPMG-4 is a metallic glass, no clear lattice fringes are observed in the high-resolution transmission electron microscopy (HRTEM) (Fig. 1g), and the corresponding selected area electron diffraction (SAED) pattern exhibits a characteristic diffuse halo ring, indicating the absence of long-range crystalline order. This observation, together with the broad hump in the XRD pattern around 42° (Fig. S2), confirms the amorphous nature of the HPMG-4 after thermoplastic molding. Elemental analysis of the HPMG-4 (Fig. 1h) showed uniform elemental distribution without any segregation, indicating the ability of the DM strategy to maintain the stability of the amorphous structure.

3.2. Electrocatalytic performance of the catalyst

The concentrations of H^+ and OH^- ions are known to significantly influence HER behaviors. Electrocatalysts with a universal response across a range of pH values are highly desirable for practical applications [47,48]. Consequently, a comprehensive evaluation of the HER activity of HPMG was carried out in alkaline, neutral, and acidic electrolytes.

The electrochemical performance of the as-synthesized catalysts was first measured in an N₂-saturated 1.0 M KOH solution using a threeelectrode configuration. Bare Plate-MG and commercial Pt/C were also tested as control electrocatalysts under the same conditions. The results showed that at a current density of 10 mA cm⁻², the overpotential of HPMG-4 (35 mV vs. RHE) was significantly lower than that of HPMG-6 (56 mV vs. RHE) (Fig. S3).

Fig. 2a presents the linear sweep voltammetry (LSV) curves of HPMG-4, Plate-MG, and Pt/C. While all three catalysts display favorable activity for the HER, their performances vary significantly. At a current density of 10 mA cm⁻², the overpotential of HPMG-4 (35 mV vs. RHE) is substantially lower than that of the commercial Pt/C electrode (52 mV vs. RHE) and Plate-MG (110 mV vs. RHE). The differences become more pronounced at a high current density of 100 mA cm⁻², where the overpotential of HPMG-4 (72 mV vs. RHE) remains distinctly lower,

being merely one-third of that of the commercial Pt/C (217 mV vs. RHE) (Fig. S4).

For an in-depth analysis of the catalytic behavior, Tafel plots were generated, and Tafel slopes were determined using the Tafel equation. In these plots, overpotential η was plotted against $\log(-j)$, as shown in Fig. 2b. A lower Tafel slope indicates more favorable HER kinetics [49]. The HPMG-4 catalyst exhibited a Tafel slope of 21 mV dec⁻¹, surpassing the commercial Pt/C catalyst, which showed a Tafel slope of 57 mV dec⁻¹. The Tafel slope of HPMG-4 is close to 30 mV dec⁻¹, suggesting that the Volmer-Tafel mechanism, with the Tafel step as the rate-determining step (RDS), is applicable. Compared to the Plate-MG with a slope of 92 mV dec⁻¹, the result for HPMG-4 emphasizes the impact of the hierarchical porous structure on improving catalytic activity, consistent with the trend observed in the LSV curves.

The ECSA of HPMG-4 was computed from the CV curves, as presented in Fig. S6. It was observed that there is a linear relationship between the current density ($\Delta_{J/2}$) and the scanning rate, and the slope represents the geometric C_{dl}, which is linearly proportional to the ECSA. Consequently, the ratio of the geometric double-layer capacitances of different catalysts can be utilized to assess their ECSAs. For HPMG-4, the C_{dl} was determined to be 43.32 mF cm⁻², a value notably higher than that of the MG plate (0.33 mF cm⁻²) and the commercial Pt/C (7.13 mF cm⁻²). These findings indicate that the ECSA of HPMG-4 is



Fig. 2. (a, d, g) LSV curves of the HPMG-4, Plate-MG and Pt/C in 1.0 M KOH (a), 1.0 M PBS (d), and 0.5 M H₂SO₄ (g) solutions. (b, c, e, f, h, i) Corresponding Tafel slope of these catalysts in 1.0 M KOH (b, c), 1.0 M PBS (e, f), and 0.5 M H₂SO₄ (h, i) solutions.

approximately 131 times that of the MG Plate and 6 times that of Pt/C. This substantial increase in ECSA points to the effectiveness of the dissolution manufacturing strategy, which yields a hierarchical porous electrocatalyst structure capable of revealing an increased number of active sites, thereby enhancing the catalytic activity. The EIS spectrum of the HMPG-4 and Plate-MG was observed to show a notably smaller series resistance (R_S) than that of Pt/C (Fig. S5). At the same time, the charge transfer resistance (R_{ct}) of HMPG-4 was also found to be smaller than that of Pt/C, which suggests an expedited reaction rate and enhanced charge transportation efficiency. The presence of microscale or nanoscale pores within the catalyst scaffolds is presumed to expose more active sites, thereby lowering the R_{ct}, consistent with the electrochemically determined ECSA testing result.

Neutral media microbial electrolysis cells and seawater electrolysis have received considerable attention due to their environmental benignity and instrument adaptability, which require a neutral-effective electrocatalyst to improve energy efficiency [50]. Therefore, the electrocatalytic activity of HPMG-4 was evaluated in 1 M PBS ($pH \sim 6.5$) to examine its suitability as a candidate. As shown by the LSV curves in Fig. 2d, HPMG-4 requires an overpotential of only 54 mV to achieve a current density of 10 mA cm⁻² in neutral electrolytes, which is comparable to the commercial Pt/C electrode (45 mV) and outperforms Plate-MG (136 mV). Moreover, at a high current density of 100 mA cm⁻², HPMG-4 exhibits a significantly lower overpotential of 299 mV (vs. RHE) compared to the commercial Pt/C, which requires an overpotential of 564 mV (vs. RHE), indicating excellent performance and stability under high current density. Meanwhile, HPMG-4 exhibits a Tafel slope of 109 mV/dec in neutral environments, outperforming Plate-MG (140 mV dec⁻¹) and comparable to Pt/C (92 mV dec⁻¹) (Fig. 2e), suggesting superior reaction kinetics. Furthermore, the electrochemical double-layer capacitance of HPMG-4 reaches 34.31 mF cm⁻², significantly higher than Pt/C (21.99 mF cm⁻²) and Plate-MG (1.20 mF cm⁻²) (Fig. 2f), further confirming its substantially larger

active surface area in neutral electrolytes compared to other catalysts.

Finally, the catalytic HER activity of the HPMG-4 catalyst was also evaluated in acidic solutions. LSV curves, Tafel slopes, and ECSA were examined. From the LSV curve in Fig. 2g, an overpotential of just 16 mV was achieved by HPMG-4 at a current density of 10 mA cm^{-2} versus the RHE, which is significantly lower than that of Plate-MG (142 mV) and slightly better than commercial Pt/C (17 mV). At a higher current density of 100 mA cm⁻², the overpotential of HPMG-4 (71 mV vs. RHE) was also found to be comparable to that of the Pt/C catalyst (68 mV vs. RHE). Furthermore, the Tafel slope of HPMG-4 was determined to be 41 mV dec $^{-1}$, as shown in Fig. 2h, which is substantially lower than that of Plate-MG (96.0 mV dec⁻¹) and close to the Pt/C catalyst (44.0 mV dec⁻¹), indicating excellent reaction kinetics. Additionally, the electrochemical double-layer capacitance of HPMG-4 in acidic media was found to reach an impressive 71.56 mF cm⁻², far exceeding that of Plate-MG (1.47 mF cm⁻²) and Pt/C (20.99 mF cm⁻²), as indicated in Fig. 2i, highlighting the significantly larger active surface area of HPMG-4.

In addition to catalytic activity, long-term stability is also a key element in producing hydrogen from electrolyzed water for commercial applications. In this study, the long-term stability of HPMG-4 was tested using chronopotentiometry in an N2-saturated 0.5 M H2SO4 solution at a current density of 10 mA cm $^{-2}$. As shown in Fig. 3a, during the 265-hour voltage test period, no significant fluctuations were observed and the HPMG-4 exhibited excellent stability, in contrast to the Pt/C under the same conditions, which showed an apparent voltage increase in less than 20 h. Although the Pt loading in HPMG-4 reached 250.8 mg cm $^{-2}$, such a value is reasonable for a self-supporting electrode, and its outstanding long-term durability indicates strong potential for practical application. For comparison, the overpotentials and Tafel slopes of HPMG-4 were summarized at a current density of 10 mA cm⁻² in acidic, neutral, and alkaline environments, and compared with the studied materials reported in the literature, which mainly include transition metal phosphides, noble metals, transition metal oxides, transition metal sulfides,



Fig. 3. (a) The HPMG-4, Pt/C stability test. (b, c) The HER catalyst Tafel slope, overpotential investigation plots.

transition metal nitrides, transition metal carbides, and metal-free catalysts (Fig. 3b and c). The results show that the HPMG-4 exhibit excellent catalytic performance in pH-universal electrolytes, outperforming most previously reported catalysts.

To further assess the structural and electrochemical stability of HPMG-4 after extended HER operation, a series of post-characterization analyses were performed. As shown in Fig. S9a-f, high-magnification SEM images confirm that the hierarchical porous structure is largely preserved after long-term testing, with only slight pore refinement observed. This microstructural retention is consistent with ECSA measurements (Fig. S9g), which reveal negligible changes in the electrochemically active surface area, indicating that the density of accessible active sites remains essentially unaffected. XRD analysis (Fig. S9h) further confirms that the amorphous structure of HPMG-4 is maintained, with only minor crystallization detected. This subtle phase transition is attributed to mild surface dealloying that occurs during prolonged electrochemical operation. Despite these limited structural changes, the LSV curves recorded before and after the HER test (Fig. S9i) exhibit minimal variation in overpotential, confirming that the catalytic performance remains stable over time. Together, these results demonstrate that HPMG-4 exhibits excellent structural integrity and electrochemical durability under long-term operating conditions, further supporting its potential for practical hydrogen production across a wide pH range.

3.3. Micro-Nano structures enhance HER

The structural changes are closely related to the increase of catalytic activity [37,51,52]. In order to explore the relationship between the excellent catalytic activity of HPMG-4 and its structure, the contact angle of HPMG-4 was tested and compared with Plate-MG. Fig. 4a shows the dynamic change of the water contact angle and bubble contact angle of HPMG-4 and Plate-MG. The results indicate that the water contact angle of HPMG-4 changed from 25° to 0° in less than 1 s, demonstrating excellent hydrophilicity, while the bubble contact angle of HPMG-4 remained unchanged at 139°. In contrast, the water contact angle of Plate-MG changed from 48° to 39° in 5 s, and the bubble contact angle was 123°. A summary of the dynamic water contact angle and bubble contact angle of HPMG-4 and Plate-MG within 15 s is presented in Fig. 4b. The excellent hydrophilicity and hydrophobicity of HPMG-4 play an important role in the HER process [53,54]. To observe the bubble dynamic process of HPMG-4 more intuitively, a high-speed camera was used to photograph the bubble movement process (Movie S1, Fig. 4c), which shows that the bubbles leave the surface of HPMG-4 immediately after contacting it, exhibiting excellent air evacuation performance. As illustrated in Fig. 4d, due to the hydrophilic nature of the HPMG-4 surface, the contact surface area between HPMG-4 and the electrolyte is larger compared to the surface of Plate-MG of the same size. This enables the water molecules in the electrolyte to more readily access the active sites, thereby significantly enhancing the reaction rate. When water molecules in the solution react on the surface to generate hydrogen bubbles, the excellent gas-phobic property of the HPMG-4 surface allows the tiny bubbles to escape quickly, ensuring that the generated bubbles do not occupy the active sites. Therefore, the hydrophilic and gas-phobic HPMG-4 provides a more straightforward pathway for water molecules to react at the active sites and for bubbles to escape, making it an efficient HER catalyst compared to Plate-MG.

3.4. Element variation after HER

Despite the excellent morphological stability of HPMG-4 after longterm HER operation, XPS analysis reveals significant evolution in surface composition and electronic structure. As shown in Fig. 5a, the Pt 4f spectra exhibit no significant changes in peak intensity or valence states of Pt^o and Pt²⁺ after HER, confirming the chemical stability of Pt and the preservation of its catalytic functionality. However, both Pt^o and Pt²⁺ peaks display a positive binding energy shift of approximately + 0.2 eV,

which suggests an increased localization of outer electrons around the Pt nucleus. This shift likely arises from the weakened coordination with neighboring elements such as Ni, Cu, and P during operation [36]. The Ni 2p spectra (Fig. 5b) show a slight attenuation in peak intensity, indicating partial surface dissolution of Ni, although a majority remains intact. In contrast, the Cu 2p signals (Fig. 5c) for Cuº (~933.5 eV) and Cu²⁺ (~953.2 eV) diminish substantially, suggesting preferential leaching of Cu species from the catalyst surface during electrolysis. A similar trend is observed for P 2p (Fig. 5d), where reduced peak intensity implies that P is more susceptible to removal, possibly due to its lower binding stability in the nanoporous framework under electrochemical conditions [55]. These observations point toward a surface selfreconstruction mechanism driven by selective dealloying of Cu and P, which continuously exposes fresh Pt-rich active sites. This dynamic surface renewal not only enhances the intrinsic activity by increasing accessible active sites, but also contributes to the long-term durability of the catalyst through self-stabilizing structural adjustments. The synergistic interplay between electronic reconfiguration and element redistribution plays a critical role in maintaining high HER performance across diverse pH conditions.

3.5. DFT calculations of HPMG-4 catalysts

To further investigate the intrinsic HER activities of HPMG-4, Pt/C and Plate-MG in different electrolytes, DFT calculations and analyses were conducted. Given that the HPMG-4 catalyst is an amorphous metallic glass, it lacks long-range atomic order and does not exhibit any well-defined crystalline planes. To construct a representative model for theoretical investigation, we initiated the simulation with a Pt (111) surface, the most thermodynamically stable low-index facet and a widely adopted reference in HER catalysis studies. Ni, Cu, and P atoms were randomly substituted into the Pt (111) lattice, and the system was subsequently subjected to ab initio molecular dynamics (AIMD) simulations at 400 K to induce structural disorder [56]. The resulting configuration, which captures the amorphous characteristics of HPMG, was employed for subsequent electronic structure analyses and HER activity evaluations. Under neutral or alkaline conditions, due to the scarcity of protons, the HER processes were found to initiate with the dissociation of H₂O molecules to generate H* (adsorbed hydrogen) (Volmer step or discharge reaction step). Subsequently, hydrogen desorption was observed to occur via Heyrovsky or Tafel steps [57]. As shown in Fig. 6a, the Volmer step of water molecule adsorption (H_2O^*) and water dissociation (H*-OH*) of HPMG-4 was evidently simpler than that of Pt/C, and the free energy values of hydrogen adsorption and desorption were closer. The optimized structures of the intermediate's H₂O* and H*+OH* on HPMG-4 and Pt/C are presented in Fig. S10. The DFT calculation results suggest that the reduced adsorption and dissociation energy barriers of water on HPMG-4 endow it with suitable HER performance in neutral or alkaline environments, which is consistent with the experimental results presented in Fig. 2a.

Under acidic conditions, the HER processes were found to begin with the adsorption of H⁺ to form H^{*} due to the abundance of protons, followed by a Heyrovsky or Tafel desorption step to produce H2. The Gibbs free energy of H^* (ΔG_{H^*}) is usually considered a valuable criterion for evaluating the HER activity of electrocatalysts. The lower the ΔG_{H^*} , the stronger the hydrogen adsorption; the higher the ΔG_{H^*} , the weaker the adsorption [11]. As shown in Fig. 6b, the Gibbs free energy change for the H* adsorption of HPMG-4 (-0.067 eV) was slightly lower than the thermoneutral value compared to that of Pt/C (-0.089 eV). These results suggested that the reaction barriers for dissociation of water and adsorption of H* processes were smaller in HPMG-4, ultimately leading to its higher performance for the HER process, which is consistent with the experimental results presented in Fig. 2g. Meanwhile, the optimized adsorption structures of H* on the surfaces of HPMG-4 and Pt/C and are shown in Fig. S11. To further illustrate the origin of the superior HER activity, the charge density difference was calculated and shown in



0 \$ HPMG-4 2 mm



Fig. 4. (a) Evolution of water droplets in the initial stage of HPMG-4 and Plate-MG (b) Variation of contact angle with time under different experimental conditions (c) Bubble movement process (d) The schematic diagram of HER on HPMG-4 and Plate-MG surfaces.



Fig. 5. XPS spectra of (a) Pt 4f; (b) Ni 2p; (c) Cu 2p; (d) P 2p for the HPMG-4 before and after HER.

Fig. 6c and d. It confirms that H atoms have a more significant charge transfer to Pt atoms. The charges at the interface are redistributed compared to the region away from the interface. Such changes in electronic states account for the reasonable adsorption strength of hydrogen atoms, accelerating the charge-transfer kinetics and thus improving the HER activity.

In conclusion, the HPMG-4 catalyst possessing a hierarchical porous structure was found to considerably accelerate the dissociation of H_2O and/or boost the absorption/desorption of H. The electrocatalytic HER process was demonstrated to be conducted across the entire pH spectrum, a unique trait considered conducive to HER electrocatalysis, as shown by the electrochemical tests above. Given the relatively high catalytic activity of the HPMG-4 catalyst, it is believed to hold extensive application potential.

3.6. Mechanisms of enhanced pH-Universal HER activity in HPMG-4

The superior pH-universal HER activity of HPMG-4 arises from the synergistic effects of atomic-level disorder, hierarchical porosity, enhanced interfacial wettability, and the dynamic renewal of active sites.

The metallic glass framework provides abundant unsaturated coordination sites and flexible atomic environments, effectively lowering the kinetic barriers for hydrogen adsorption, water dissociation, and electron transfer [29]. DFT calculations offer deeper mechanistic insights into the pH-dependent HER pathways. Under acidic conditions, HPMG-4 exhibits a near-optimal Gibbs free energy for hydrogen adsorption (ΔG_{H^*} = -0.067 eV), facilitating efficient proton reduction [45]. In neutral and alkaline media, the disordered atomic structure significantly reduces the energy barrier for water dissociation, thereby promoting the Volmer step even under limited proton availability. Moreover, charge density difference analyses reveal enhanced interfacial charge redistribution, accelerating electron transfer and improving overall HER kinetics.

The hierarchical porous network formed via the DM strategy markedly increases the specific surface area, exposing a dense array of accessible active sites and facilitating rapid electrolyte penetration and mass transport. Surface wettability measurements further demonstrate that HPMG-4 exhibits strong hydrophilicity, as evidenced by the rapid decrease in water contact angle from 25° to 0° within 1s, and excellent gas-repellent properties, as indicated by a stable bubble contact angle of 139°, which together ensure efficient contact with the electrolyte and promote swift hydrogen bubble detachment. These structural and interfacial advantages collectively enhance catalytic turnover and reaction kinetics under a wide range of reaction conditions.

The dynamic evolution of the catalyst surface during HER operation further contributes to its performance. Post-HER XPS analysis reveals the selective dissolution of Cu and P, leading to Pt surface enrichment and the continuous regeneration of fresh active sites. This selfreconstruction process maintains high catalytic activity throughout prolonged operation [55].

Additionally, the observed positive shift in Pt binding energies suggests stronger electron localization around Pt atoms, which stabilizes the surface against degradation. Such dynamic surface restructuring not only preserves the initial catalytic functionality but also progressively enhances catalytic efficiency over time.

4. Conclusion

In summary, a self-supporting, efficient and electrocatalyst (HPMG-4) with hierarchical porosity for pH-universal HER was synthesized by a simple, green and efficient process of dissolution fabrication. The HPMG-4 was found to possess more active sites and excellent hydrophilic and hydrophobic properties due to the hierarchical porous



Fig. 6. (a) Free energies of H adsorption on HPMG-4 and Pt/C. (b) The calculated water dissociation barriers on HPMG-4 and Pt/C. Distribution of charge density difference of H adsorbed on the (c) HPMG-4 and (d) Pt/C. The accumulation and reduction of the charge were denoted by yellow and cyan colors, respectively.

structure. Moreover, due to the unique atomic arrangement of amorphous alloys, the overall electrical conductivity and corrosion resistance are enhanced. The results show that the as-prepared HPMG-4 exhibits relatively low η_{10} values of 35 mV, 54 mV, and 16 mV in 1.0 M KOH, 1.0 M PBS, and 0.5 M H₂SO₄ solutions respectively, and demonstrates strong stability, maintaining the overall catalytic activity. In addition to the experimental characterizations, a DFT-based theoretical study was conducted to investigate the intrinsic HER activity of HPMG-4 with different electrolytes due to the high exposure of surface-active sites on the HPMG-4, which accelerated the electron transport and enhanced electrochemical stability. Layered porous electrocatalysts were synthesized and exhibit excellent HER activity in pH-universal electrolytes, demonstrating the universality of our synthetic strategy and the great potential of these Pt-based alloy electrocatalysts for practical applications.

CRediT authorship contribution statement

Xingran Zhao: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. Junsheng Liu: Visualization, Methodology, Investigation, Data curation. Heting Zhang: Methodology, Data curation. Jihan Jiang: Investigation, Conceptualization. Jiaqing Lin: Supervision, Methodology. Jianan Fu: Writing – review & editing, Methodology, Data curation. Yu Zhang: Investigation, Formal analysis. Xin Li: Investigation. Wenqing Ruan: Writing – review & editing, Supervision, Data curation, Conceptualization. Jiang Ma: Writing – review & editing, Visualization, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2025.163667.

Data availability

Data will be made available on request.

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