Abstract

Modulating lattice strain in intermetallic compounds could effectively alter their electronic structure and binding energy, thus impacting catalytic activity. Strain is usually induced through lattice mismatch, achieved by constructing core-shell nanostructures or metal-substrate interfaces with complex reciprocity and distractors. However, in situ induced strain without interface-construction or lattice mismatch presents challenges. In this study, we precisely manipulate consecutive compressive strain from -0.5% to -0.8% in CoPt$_3$Pd intermetallic compound by inducing interior atomic radius mismatch. Precise strain control results in a negative shift of d-band center, dynamic charge distribution, and facilitates water dissociation, leading to the enhanced electrocatalytic activity. The CoPt$_3$Pd catalyst with -0.5% compressive strain exhibits exceptional hydrogen evolution activity, with an overpotential of 169 mV at 1 A cm$^{-2}$. Our approach offers a straightforward method to manipulate compressive strain on intermetallic compound by atomic size mismatch, with broad implications for catalytic processes.

Atomic size mismatch induced consecutive compressive strain on intermetallic compound towards boosted hydrogen evolution

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**Keywords:** Intermetallic compounds, Atomic size mismatch, Compressive strain, Water dissociation, Hydrogen evolution

**INTRODUCTION**

Intermetallic compound with precise atom stoichiometry and ordered arrangement have garnered considerable interest across various disciplines.\(^1\)\(^-\)\(^6\) These compounds serve as valuable model systems for investigating the effects of ligands, geometry, and ensembles on electrocatalytic performance and mechanisms.\(^7\)\(^-\)\(^10\) The introduction of strain in surface can modulate the electronic properties of catalyst, which is closely associated with the adsorption energy and activation energy barriers of reaction intermediates during catalytic processes.\(^11\)\(^-\)\(^13\) However, strain is usually generated through lattice mismatch via constructing core-shell nanostructures, metal-substrate interfaces, or amorphous-crystalline phase boundaries.\(^14\)\(^-\)\(^19\) For instance, researchers successfully controlled strain in Pt(100) shells deposited on Pd cores by employing phosphorization and dephosphorization processes in the Pd@Pt-P system.\(^20\) Another example involved the use of intermetallic PtPb cores, which induced a conformal four-layer Pt shell with a tensile strain of 7.5% in PtPb/Pt core-shell nanoplates.\(^21\) It is important to acknowledge that strain resulting from lattice mismatch exhibits spatial dependence, typically diminishing as one moves away from the interface towards the outermost surface, and eventually dissipating beyond a few atomic layers.\(^22\) The presence of interface and multi-phase means complex reciprocity and distractors, e.g., ligand effect is always convoluted by strain effect in core-shell nanostructure.\(^23\) Nonetheless, these strategies primarily control strain through the interface-construction, rather than achieving a uniform distribution of strain on the catalyst’s surface without lattice mismatch. Meanwhile, the strain-fine-tune is usually restricted to simple substance shell (Pt-skin), not intermetallic compounds. Consequently, the development of a straightforward and homogeneous approach for modulating lattice strain in intermetallic compounds, without the need for constructing interfaces, remains an unresolved challenge in the field.

Constructing atomic size mismatch by the atomic radius difference between elements to induce strain is a potential strategy to amplify strain effect without lattice mismatch. Herein, we report a strategy to continuously manipulate compressive strain (from -0.5% to -0.8%) on intermetallic compound Pt\(_3\)Pd by atomic size mismatch via substitution with cobalt atom of smaller atomic radius, and comprehensively investigate how compressive strain continuously modifies electronic structure, efficiently facilitates water dissociation, and further manipulates HER performance (Figure 1). The optimized Pt\(_3\)Pd with moderate strain showed excellent pH-universal HER performance with extraordinarily low overpotential and robust stability. Ultimately, Pt\(_3\)Pd with compressive strain of -0.5% enabled stable hydrogen production at a high current of 4 A in both proton exchange membrane (PEM) and anion exchange membrane (AEM) electrolyzers for 50 hours under industrial conditions. This strategy with precise tuning of compressive strain in intermetallic compounds holds great promise in opening new avenues for catalytic applications and beyond.
EXPERIMENTAL SECTION

Synthesis of preparation of CoPt₃, CoPt₃Pd, CoPt₃-Pd, and Pt₃Pd

A galvanostat (Metrohm, Multi Autolan m204) was used to perform simultaneous electrodeposition under a three-electrode system. We used a porous transport layer (PTL) of 304 steel mesh (400 mesh) as the working electrode, a mercurous sulfate electrode as the reference electrode, and a graphite rod as the counter electrode. Before electrodeposition, the steel mesh substrate was treated with 0.5 M H₂SO₄ at ambient temperature for 30 min to remove surface oxide, washed with deionized water, vacuum dried, and then mounted on a Teflon electrode holder exposing an area of 1.0 cm². The electrolyte was prepared by dissolving 10 mg H₂PtCl₆·6H₂O, 2.5 mg K₂PdCl₄, and CoCl₂·6H₂O (0.05 g, 0.2 g, 0.4 g, and 0.6 g) in 100 ml 0.5 M H₂SO₄, and stirring for 30 min. The sample with 0.05 g CoCl₂·6H₂O was named as CoPt₃Pd in the manuscript. Then the electrolyte was purged by bubbling N₂ gas for 30 min to remove the dissolved O₂ before electrodeposition. The electrodeposition was carried out under ambient conditions at a constant current of -400 mA for 15 min.

RESULTS AND DISCUSSION

Strain manipulate and structure analysis

The intermetallic compounds with compressive strain were synthesized utilizing a one-step simultaneous electrodeposition method (Scheme S1). The crystal structures of the synthesized catalysts were investigated using X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). XRD patterns of CoPt₃Pd (with -0.5 % strain) and Pt₃Pd displayed peaks between the standard peaks of L1₂-CoPt₃(PDF #29-0499) and Pd (PDF #72-0710), with a face-centered cubic metallic phase, assignable to the standard peaks of B11-Pt₃Pd (PDF #17-6714). Peaks at 43.6°, 50.8°, and 74.7° corresponded to the austenite matrix (PDF #33-0397) feature in the steel substrate (SS) (Figure 2A). HRTEM images revealed lattice spacings of 0.23 nm and 0.19 nm (Figure S1), which, in combination with XRD results, could be indexed to the (112) and (200) planes. Characteristic peak shifts in CoPt₃Pd relative to the Pt₃Pd pattern occurred due to Co substitution during simultaneous electrodeposition, resulting in an increased...
compressive strain on lattice. We further controlled the additive amount of Co resource from 0.05 g to 0.6 g to investigate atomic size mismatch effect on the lattice distance. As shown in XRD patterns (Figure S2), the obvious positive shifts could be found in the pattern, confirming that the stronger compressive strain (from -0.5% to -0.8%) presented on Pt$_3$Pd because of the smaller Co atomic radius than Pt and Pd. The steel mesh substrate (aperture of 0.03 mm, fiber diameter of 0.03 mm) provided an ordered structure as a gas diffusion electrode for catalyst assembly and formed a particle packing structure during the electrodeposition process (Figures S3 and S4, different additive amount of Co had no obvious effect on the morphology of catalysts). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed to analyze the ordered structure of the intermetallic compound and compressive strain. The HAADF signal intensity was proportional to the square of the atomic number, making Pt atoms appear brighter than neighboring Pd atoms, while lighter Co atoms remained unobservable. EDS mapping of CoPt$_3$Pd and Pt$_3$Pd confirmed the ordered arrangement of Pt and Pd atoms (Figure 2B and Figure S5). With the substitution of Co in the Pt$_3$Pd lattice, the intensity profiles of Pt and Pd lattices exhibited a noticeable negative shift, corresponding well to the compressive strain from atomic size mismatch (Figure 2C,D). The geometric phase analysis indicated that an apparent in-plane compressive strain (ε$_{\text{xx}}$ $\neq$ $\phi$ $\delta$) field presented in CoPt$_3$Pd compared with Pt$_3$Pd. The (112) and (200) lattice spacings of CoPt$_3$Pd were further measured at 0.2229 nm and 0.1948 nm (Figure 2E,F, and Figure S6), which displayed a reduced lattice constant compared to Pt$_3$Pd (0.2241 nm and 0.1995 nm), providing additional evidence that the construction of compressive strain in Pt$_3$Pd by Co substitution.

To further elucidate the reciprocity between compressive strain, chemical states, and local coordination, X-ray photoelectron spectroscopy (XPS) was employed to study the underlying mechanisms of compressive strain. The peaks of Pt 4f shifted to lower binding energy as the strain increased, reaching a maximum when the strain was -0.5%. The characteristic peaks of Pd 3d orbitals exhibited the same trend (Figure S7 and S8, and Table S1). Additionally, the high-resolution XPS valence band demonstrated a similar tendency, with CoPt$_3$Pd (-0.5% compressive strain) exhibiting the highest value of valence band (Figure S9). The results indicated that a moderate compressive strain in the lattice of Pt$_3$Pd can modulate chemical states within a dynamic region. The chemical states of Pt were highly sensitive to strain, shifting negatively as the lattice contracts. In accordance with the $d$-band center theory for late transition metals, the widely tunable electronic structure is expected to correspond to tunable absorption strength of chemical species. Similar behaviors have been observed in modulating tensile or compressive strain in Pt. X-ray absorption fine structure spectroscopy (XAFS) was conducted to obtain deeper and more accurate insights into the local bonding environment and electronic structure. Regarding the Pt L$_3$-edge XANES spectra (Figure 2G,H), the white-line intensity of CoPt$_3$Pd was close to Pt in CoPt$_3$ and slightly higher than Pt foil, confirming that the moderate compressive strain could alter the electron distribution between Pt and Pd. In contrast, the white line intensity of Pt in Pt$_3$Pd was lower than Pt foil. These observations were in good agreement with the XPS results. The local coordination environment was further elucidated by the extended X-ray absorption fine structure (EXAFS) spectra of Pt L$_3$-edge (Figure 2I, Figure S10, and Table S2). CoPt$_3$Pd exhibited two prominent peaks between 2 and 3 Å; the one located at approximately 2.5 Å was assigned to the Pt-Co scattering path, while another one at around 2.7 Å was attributed to the Pt-Pd scattering path. Furthermore, a slight leftward shift to a shorter scattering path was observed in CoPt$_3$Pd relative to Pt$_3$Pd (Figure S11). According to the wavelet-transform patterns (Figure 2J and Figure S12), for CoPt$_3$, only two intensity maximums were detected, one located at about 8.3 Å$^{-1}$ (lighter atom, assigned to Co), and another located at about 12.3 Å$^{-1}$ (heavier atom, assigned to Pt). For Pt$_3$Pd, two obvious intensity maximums located at 12.1 Å$^{-1}$ and 14.3 Å$^{-1}$, assigned to Pd-Pd and Pt-Pt scattering paths, respectively. As for CoPt$_3$Pd, three intensity maximums presented in its pattern, which could be assigned to Co-Pt, Pt-Pd, and Pt-Pt scattering path respectively. Above results further confirmed the substitution of Co induced compressive strain on Pt$_3$Pd lattice through atomic size mismatch.
FIGURE 2 Structure analysis of compressive strain from atomic size mismatch. (A) XRD patterns of different samples. (B) Aberration-corrected HAADF-STEM images of CoPd$_3$Pd and high-resolution EDX mapping images for Co, Pt, and Pd elements. (C, D) Intensity profiles and strain mapping of CoPt$_3$Pd and Pt$_3$Pd samples. (E, F) HAADF-STEM images of CoPt$_3$Pd and Pt$_3$Pd samples. (G, H) Normalized Pt L$_3$-edge XANES. (I) EXAFS of different samples. (J) WT of Pt-foil, CoPt$_3$, CoPt$_3$Pd, Pt$_3$Pd, and PtO$_2$.

Electrochemical hydrogen evolution reaction

These intermetallic compounds were subsequently utilized as HER catalysts to investigate the influence of compressive strain and intermetallic interactions on catalyst performance. The acidic HER performance of electrocatalysts was initially tested in 0.5 M H$_2$SO$_4$. Linear sweep voltammetry (LSV) curves indicated that CoPt$_3$Pd exhibits significant activity superiority compared to CoPt$_3$, CoPt$_3$-Pd, and Pt$_3$Pd (Figure 3A). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed to determine the mass ratio of each element in CoPt$_3$Pd, revealing approximately 0.25 mg$_{Pt}$ cm$^{-2}$, 0.25 mg$_{Pd}$ cm$^{-2}$, and 0.05 mg$_{Co}$ cm$^{-2}$ (Table S3). Consequently, the HER performance of commercial Pt/C catalysts on steel with the same mass loading of 0.5 mg cm$^{-2}$ was assessed. CoPt$_3$Pd demonstrates enhanced activity compared to commercial Pt/C under similar potential (Figure S13a). CoPt$_3$-Pd exhibited nearly identical performance as CoPt$_3$, indicating no interaction between Co-Pt-Pd in the absence of the alloying process. The impact of compressive strain on activity was further investigated. The performance decreases with the increase of compressive strain (CoPt$_3$Pd-0.5% > CoPt$_3$Pd-0.6% > CoPt$_3$Pd-0.7% > CoPt$_3$Pd-0.8% > Pt$_3$Pd), further confirming that compressive strain could continuously regulate HER performance (Figure 3C and Figure S13b). The sample Pt$_3$Pd-Co (Pt$_3$Pd with Co covered, not doped into lattice) was synthesized and tested, the performance is a little lower than Pt$_3$Pd, and a lot lower than CoPt$_3$Pd (with Co substitution into lattice to initiate compressive strain, Figure S13c), further confirming that no compressive strain or just Co
atoms doped into system has no improvement on performance. Additionally, CoPt₃Pd possessed the lowest overpotential to achieve current densities of 200 mA cm⁻² at 92.5 mV, 500 mA cm⁻² at 121 mV, and 1000 mA cm⁻² at 169 mV (Figure 3B).

To further demonstrate the outstanding performance of CoPt₃Pd, we systematically compared the HER performance metrics of CoPt₃Pd with other samples, including Co₃Pd, turnover frequency, and mass activity at an overpotential of 200 mV (Figure 3D). The Tafel slope of CoPt₃Pd (38.9 mV dec⁻¹) was significantly lower than the others. CoPt₃-Pd exhibited a lower slope than CoPt₃, despite their similar performance, suggesting that Pd-doping in the system could alter the HER kinetics. Moreover, CoPt₃Pd-0.6 had a lower slope value than Pt₃Pd but a higher value than CoPt₃Pd, confirming that optimization effect on HER kinetics from compressive strain (Figure S14), and all samples outperformed commercial Pt/C. Evidently, the CoPt₃Pd catalyst surpassed all compared samples in terms of overpotential, Tafel slope, and ECSA, demonstrating exceptional HER activity among the latest top-ranked noble metal-based electrocatalysts under acidic conditions (Figure 3E, Table S4). The performance of CoPt₃Pd was further assessed in alkaline (1.0 M KOH) and neutral electrolytes (1.0 M PBS) to evaluate the catalyst’s universality. Remarkably, CoPt₃Pd required only 420 mV and 680 mV to achieve current densities of 1000 mA cm⁻² and 400 mA cm⁻² in alkaline and neutral electrolytes, respectively, demonstrating superiority over the latest noble metal-based electrocatalysts (Figure S15 and Table S5). The long-term durability of CoPt₃Pd was evaluated using chronopotentiometry at a current density of 1000 mA cm⁻² for potential industrial applications. CoPt₃Pd was able to maintain its performance for more than 80 hours without significant degradation in both alkaline and acidic electrolytes, indicating a promising future for its application in water splitting (Figure 3F).

**FIGURE 3** HER performance. (a) HER polarization curves conducted in 0.5 M H₂SO₄. (b) Overpotential at 200, 500, and 1000 mA cm⁻² of different samples. (c) The relationship between Co additive amount,
performance, and compressive strain. (d) Comparison of the HER performance metrics between different samples. (e) Comparison of the overpotential at 1000 mA cm\(^{-2}\) and the Tafel slope for reported catalysts in the literatures. (f) Chronopotentiometry measurements of CoPt\(_3\)Pd at 1000 mA cm\(^{-2}\) in 0.5 M H\(_2\)SO\(_4\) and 1.0 M KOH

**Strain effects on interfacial charge transfer and water dissociation**

To further investigate the underlying mechanism of the promoting effect from compressive strain, the interfacial charge transfer was assessed for CoPt\(_3\), Pt\(_3\)Pd, and CoPt\(_3\)Pd using operando electrochemical impedance spectroscopy (EIS) in both acidic and alkaline electrolytes. Nyquist plots confirmed that CoPt\(_3\)Pd exhibited the lowest values of charge transfer resistance (R\(_{ct}\)) (Figure S16a,c), smaller low-frequency-dominant specific resistance (Z\(_s\)) with phase angle, and a distinct decreasing tendency (Figure 4A, Table S6) in the HER region compared to CoPt\(_3\) and Pt\(_3\)Pd, according to the fitting results. These findings convincingly demonstrated that compressive strain could enhance the charge transfer at the interface, thereby accelerating the HER kinetics in acidic environments. Regarding the EIS plots in alkaline environments, two sequential electrochemical processes were simulated for Pt\(_3\)Pd and CoPt\(_3\)Pd (Figure S17 and Table S7): intermediate adsorption, modeled by CPE\(_\phi\)R\(_\phi\), and Faradaic electron transfer modeled by CPE\(_{ct}\)R\(_{ct}\). CoPt\(_3\) displayed the largest R\(_{ct}\), Z\(_s\), and phase angle relative to Pt\(_3\)Pd and CoPt\(_3\)Pd, suggesting a sluggish kinetic process during the HER in alkaline conditions (Figure S16d,f). Concurrently, the phase angle of CoPt\(_3\) exhibits a positive shift with the decrease in potential, while no significant shifts are observed in the phase angles of Pt\(_3\)Pd and CoPt\(_3\)Pd. This confirms that the rate-determining step (RDS) of CoPt\(_3\) differs from that of Pt\(_3\)Pd and CoPt\(_3\)Pd in alkaline electrolytes. The presence of compressive strain in the system may accelerate water dissociation and further alter RDS in reaction process. According to the simulation results of Pt\(_3\)Pd and CoPt\(_3\)Pd (Figure 4B,C), the R\(_{ct}\) and R\(_\phi\) of CoPt\(_3\)Pd exhibited smaller values compared to Pt\(_3\)Pd in the HER region, suggesting that a greater number of electrons involved at the catalyst/electrolyte interface could contribute to surface interaction and Faradaic electron transfer. This further confirmed that compressive strain enhances water dissociation kinetics.\(^{57}\)

In order to elucidate the underlying principles governing the enhancement of HER performance due to compressive strain, a comprehensive analysis of surface properties and hydrogen binding energy (HBE) values for CoPt\(_3\), Pt\(_3\)Pd, and CoPt\(_3\)Pd catalysts were conducted. The electrochemical properties were evaluated under identical conditions using cyclic voltammetry (Figure 4D and Figure S18). CoPt\(_3\)Pd exhibited the optimized HBE when compared with CoPt\(_3\) and Pt\(_3\)Pd in an acidic environment. In an alkaline environment, the peak corresponding to strongly bonded hydrogen of CoPt\(_3\)Pd shifted to a lower potential, while an inconspicuous peak assigned to OH anion adsorption/desorption emerged. Conversely, the peak corresponding to weakly bonded hydrogen of CoPt\(_3\)Pd shifted to a higher potential, suggesting that the adsorption of hydrogen becomes more robust. These results further supported the outstanding performance of CoPt\(_3\)Pd in alkaline solution, which leads to faster water dissociation kinetics. *In situ* Raman spectroscopy measurements were performed to elucidate the reaction mechanism involved. The band observed within the 3000-3600 cm\(^{-1}\) range could be attributed to the O-H stretching of H\(_2\)O molecules.\(^{48}\) Notably, a significant decrease in peak intensity was evident in CoPt\(_3\)Pd compared to CoPt\(_3\) and Pt\(_3\)Pd, as illustrated in Figure 4E-G. The peak situated at approximately 1636 cm\(^{-1}\) was ascribed to the H-O-H bonding mode of interfacial water molecules.\(^{49}\) When comparing the peak intensities of CoPt\(_3\) and Pt\(_3\)Pd, it was apparent that the intensities for CoPt\(_3\)Pd enhanced as the applied potentials decrease, indicating favorable proton transfer kinetics. Furthermore, the intensity of the band at ~550 cm\(^{-1}\) may be associated with the degree of orderliness in the interfacial water structure.\(^{50}\) Consequently, the increased intensity of the band corresponding to CoPt\(_3\)Pd, in comparison to the other samples, suggested that compressive strain had the potential to modulate interfacial water, resulting in a more ordered water structure.\(^{51}\)
FIGURE 4 Electrochemical characterization and Raman spectra. (a) In situ EIS fitting results in 0.5 M H$_2$SO$_4$ of CoPt$_3$, Pt$_3$Pd and CoPt$_3$Pd. (b) In situ EIS fitting results in 1.0 M KOH of CoPt$_3$. (c) In situ EIS fitting results in 1.0 M KOH of Pt$_3$Pd and CoPt$_3$Pd. d, CVs of CoPt$_3$, Pt$_3$Pd, and CoPt$_3$Pd in 0.5 M H$_2$SO$_4$. The dotted line indicates the shifting trend of the H$_{upd}$ peak. (e-g) In-situ Raman spectra of CoPt$_3$, Pt$_3$Pd and CoPt$_3$Pd in 0.1 M KOH.

DFT calculation on compressive strain and atomic size mismatch

For investigating the effect of compressive strain on electrocatalysis trends, we firstly performed density functional theory (DFT) calculations to evaluate how strain influences the main descriptors involved in HER. Four stable types for H$_2$O adsorption and six stable types for H* adsorption was examined: top, hollow, and bridge sites (Figure S19). The Pd-sites were the most active for water dissociation and OH* adsorption, whereas adsorption of H* switched to the hollow sites of Pt (Figure S20). The moderate compressive strain could facilitate water dissociation, enhance the H$_2$O* adsorption in alkaline solutions, and optimize the adsorption of H* in acid solutions, whereas the increase compressive strain has the opposite effect (Figure 5A,B, Table S8). The sample with 0.5% compressive strain showed an obvious charge transfer from Pd to Pt, and the compressive strain continuously manipulate electron transfer in a dynamic region followed a volcano trend (Figure 5C and Figure S21). Charge redistribution could optimize the reciprocity between intermediates and active sites. These strain-induced changes of binding strengths and charge transfer agreed well with the prediction from the d-band center theory, Pd-top site and Pt-hollow site (Figure S19). The metal d states increases with further lattice contraction, which suggests that CoPt3Pd with -0.5% strain owns the lowest d-band center, while a concurrent up-shift of the metal d states increases with further lattice contraction, which suggests that CoPt3Pd with -0.5% strain possess highly intrinsic HER activity (Figure 5D-F and Figure S22). As displayed in the surficial deformation electron density analysis (Figure 5G), the electron density distribution of Pt$_3$Pd was affected by different compressive strain. The electron density of Pd-site on Pt$_3$Pd with -0.5% strain lost the most charge transferred to Pt, corresponding well with Bader charge analysis, and meaning an optimized charge distribution and moderate binding between adsorbates and slab were achieved, which suggests a better water dissociation ability for HER in alkaline.

The effects of atomic size mismatch on electrocatalysis trends were also investigated using DFT (The models of Pt, CoPt$_3$, Pt$_3$Pd, and CoPt$_3$Pd slabs were depicted in Figure S23). The adsorption of intermediate H* on
Pt in an acidic environment was too strong (-0.259 eV), inhibiting the formation of H₂ (H* - * + H₂), whereas the H* adsorption energy of CoPt₃ and Pt₃Pd decreased to -0.248 eV and -0.181 eV. When Co is doped into the Pt₃Pd lattice, the energy further improves to -0.113 eV (Figure S24). The total density of states confirmed that Pt₃Pd and CoPt₃Pd possessed better conductivity than pure Pt and CoPt₃, promoting charge transfer during the reaction process (Figure S25), in accordance with the EIS fitting results. The binding energy of different intermediates during alkaline HER was further calculated (Figure S26). The energy required for water dissociation on CoPt₃Pd was even lower than the binding energy of water. Consequently, the atomic size mismatch also facilitated water dissociation and altered the rate-limiting step (Figure S27, Table S9). Bader charge calculations revealed that trace amounts of Co substitution supplied charges to Pt and Pd (Table S10, Figure S28). The more locally negative the charge on active sites, the stronger the *H bonded and the weaker the *H₂O bonded with active sites. Consequently, the energy of H₂O bonding with Pt₃Pd (0.284 eV) was lower than in pure Pt (0.338 eV), while the energy for CoPt₃Pd (0.319 eV) was marginally higher than in Pt₃Pd, and the energy for CoPt₃ was only 0.253 eV. As for the Pd atoms in Pt₃Pd and CoPt₃Pd, they provided fewer charges compared to Co. Hence, when Co was doped in Pt₃Pd, Pd atoms contributed a lesser charge to Pt, resulting in the binding energy of *H on Pd in CoPt₃Pd (-0.113 eV) being lower than its counterpart in Pt₃Pd (-0.181 eV). The trend of ΔG_H was evidently consistent with the d-band center (Figure S29 and S30). Moreover, the trend of energy required for water dissociation corresponded well with the rule (Figure S31). The above analysis suggested that the compressive strain on intermetallic compounds induced by atomic size mismatch effectively modulates the electronic structure of active sites and the binding energy of key intermediates on them. As a result, CoPt₃Pd achieved remarkable HER performance in both acidic and alkaline solutions by simultaneously enhancing water dissociation and H₂ formation.

![Deformation charge density analysis](image)

**Figure 5** DFT calculations. (a) Free energy diagrams for HER on Pt₃Pd with different compressive strain. (b) Tendency of adsorption energy of H*, H₂O* and the water dissociation energy related to compressive strain. (c) Tendency of Bader charge related to compressive strain. (d) Tendency of d-band center related to compressive strain. (e, f) d-DOS of Pt-hollow site and Pd site with different compressive strain. (g) Deformation charge density analysis of Pt₃Pd with different compressive strain (grey atom is Pt and orange atom is Pd). Isosurface is 0.001 bohr⁻³, cyan represent charge depletion and yellow represent charge
accumulation.

Electrolyzer performance and universality

To further assess the potential for industrial applications, CoPt$_3$Pd was employed as a cathode catalyst in both proton exchange membrane (PEM) electrolyzers and anion exchange membrane (AEM) electrolyzers (Figure S34), with commercial IrO$_2$ and NiFe foam serving as the anode catalyst (Figure S35). Polarization curves, tested at 80°C in 0.5 M H$_2$SO$_4$ and 1.0 M KOH respectively, revealed that CoPt$_3$Pd could achieve a current density of 1 A cm$^{-2}$ below 2.2 V in both acidic and alkaline feeds (Figure S36a,c). The Nyquist plots for PEMWE and AEMWE were further investigated (Figure S36b,d). The ohmic resistance was determined by the intersection of the high-frequency region's first semi-circle with the x-axis. The resistances induced by HER, charge transfer resistance coupled with double layer effects, or the first charge transfer of the two-electron process of the OER, were represented by the high-frequency arc. The medium- and low-frequency arcs described the charge transfer of the OER rate-determining step and mass transport losses, respectively. It was evident that mass transport effects were more pronounced in alkaline solutions (Figure S37). When applying a constant current of 4 A (10000 A m$^{-2}$) at 60°C, no significant increase in cell voltage and obvious effects on catalysts were observed over 50 hours of overall water electrolysis (Figure S38-S41). These findings strongly suggested that CoPt$_3$Pd held considerable promise for practical green hydrogen production.

For further investigating the little atomic radius doping effect on the intermetallic compounds, four different transition metals elements (Fe, Ni, Cu, and Zn) were used as doping elements for comparison with CoPt$_3$Pd. From Fe to Zn, all elements could improve the performance of Pt$_3$Pd in acidic HER, but CoPt$_3$Pd still presents the best performance among all samples (Figure S42). XRD confirmed that all elements could induce compressive strain in the lattice of Pt$_3$Pd, and Co could own the lowest peak location among all samples, further proving the versatility of our strategy on designing intermetallic compounds catalysts (Figure S43). The relationship between performance, atomic radius, and peak position of (112) lattice facet was analogous to a volcano-plot (Figure S44). This work further demonstrated the universality of the regulatory strategy for intermetallic compounds.

CONCLUSIONS

In conclusion, this study presents a consecutive compressive strain manipulate strategy resulting from atomic size mismatch through substitution of Co with smaller atomic radius into intermetallic Pt$_3$Pd compounds, optimizes performance and modulates the electronic structure of active sites. This approach further improves the binding energy of key intermediates, ultimately promoting water dissociation and H$_2$ formation concurrently. Notably, CoPt$_3$Pd exhibits exceptional HER activity across all pH environments. More significantly, CoPt$_3$Pd demonstrates efficient and stable hydrogen production in both PEM and AEM electrolyzer at a large current of 4 A for over 50 hours, highlighting its potential for practical applications. The strain construction strategy by atomic size mismatch not only provides fundamental insights into how strain influences the Pt-based HER performance and electronic structure modulation, but also proposes a promising pathway for developing other high-performance intermetallic compounds as electrocatalysts for renewable energy conversion reactions.

AUTHOR CONTRIBUTIONS

Jiankun Li: Conceptualization, investigation; writing-original draft; methodology; formal analysis; data curation; visualization; software. Zeyu Guan: Formal analysis; data curation; and visualization. Haoran Wu: Formal analysis; data curation. Yixing Wang: Formal analysis; data curation. Linfeng Lei: Formal analysis; data curation. Minghui Zhu: Formal analysis; data curation. Linzhou Zhuang: Supervision; funding acquisition; project administration. Zhi Xu: Supervision; funding acquisition; project administration.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The numerical data for XRD patterns, XANES, EXAFS, and wavelet transform in Figure 2; LSV of HER, overpotential, tendency and performance comparison, and stability test in Figure 3; tendency of in situ EIS, \( H_{\text{upd}} \), and in situ Raman in Figure 4; DFT results in Figure 5 are available as a .zip file in Supplementary Material.

REFERENCES


