

Decoupling activity and stability in PtNiMoRu nanowires for durable acid oxygen electroreduction

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Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94908870>

<https://www.sciopen.com/journal/1998-0124> on May. 23, 2026

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Research Article

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Received: 27 March 2026; **Revised:** 8 May 2026; **Accepted:** 23 May 2026

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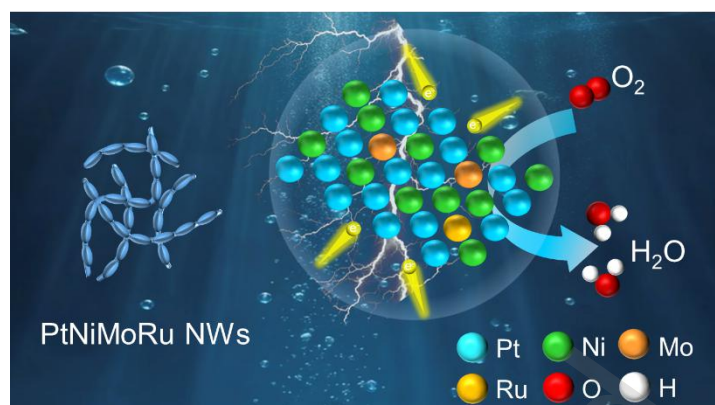
 **Cite this article:** *Nano Research*, 2026, 19, 94908870 <https://doi.org/10.26599/NR.2026.94908870>

ABSTRACT

Unlocking the full potential of PtNi alloy electrocatalysts for the acidic oxygen reduction reaction (ORR) is significantly restricted by the inevitable dissolution of Ni species. Herein, we present a rational design of tetrametallic PtNiMoRu nanowires (NWs) that decouples the origins of stability and activity via a dual-doping strategy. By coordinating the distinct roles of constituent elements, we demonstrate that Mo doping primarily acts as a lattice stabilizer by increasing the Ni vacancy formation energy to immobilize Ni atoms, while Ru doping optimizes the d-band center of Pt active sites to facilitate intermediate kinetics. Consequently, the optimized PtNiMoRu NWs/C exhibits an exceptional mass activity of $1.04 \text{ A mg}_{\text{Pt}}^{-1}$ and specific activity of 2.81 mA cm^{-2} at 0.9 V vs. RHE, representing 5.2-fold and 8.3-fold enhancements over commercial Pt/C, respectively. Most notably, the catalyst demonstrates superior durability with a negligible half-wave potential decay of only 9 mV after 30,000 accelerated durability test cycles. In a proton exchange membrane fuel cell (PEMFC), this nanowire catalyst delivers a peak power density of 1.18 W cm^{-2} . This work provides a paradigm for designing durable multi-metallic catalysts by precisely engineering element-specific functionalities within the alloy architecture.

KEYWORDS: oxygen reduction reaction; PtNi nanowires; multicomponent alloy; stability mechanism; proton exchange membrane fuel cell

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The PtNiMoRu nanowire catalyst is synthesized via the sol-gel method. This catalyst exhibits a high half-wave potential of 0.885 V vs RHE, with a potential decline of only 9 mV after 30k ADT cycles. Experimental and theoretical calculations indicate that Mo doping reduces Ni solubility, while Ru doping modulates the electronic structure of Pt, optimizing adsorption of ORR intermediates.

Introduction

Proton exchange membrane fuel cells (PEMFCs) are regarded as a critical technology for clean energy conversion, yet their widespread application is constrained by the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode^[1-3]. Platinum (Pt)-based nanomaterials remain the most effective electrocatalysts for the ORR; however, commercial Pt/C catalysts suffer from high cost and insufficient durability under operating conditions^[4, 5]. To address these limitations, alloying Pt with 3d transition metals (e.g., Ni, Co, Fe) has been extensively explored to enhance activity through ligand and strain effects^[6-9]. Among these, PtNi alloys exhibit superior intrinsic activity, but the thermodynamic instability of Ni in acidic environments leads to rapid dissolution of the transition metal component^[10]. This leaching process results in the formation of a thick Pt-skin or skeleton structure, eventually causing a loss of geometric strain and a significant decline in catalytic performance over long-term operation^[11-13].

Strategies involving morphological control, particularly the design of one-dimensional (1D) nanostructures such as nanowires (NWs), have proven effective in mitigating physical degradation modes like Oswald ripening and particle aggregation^[14-17]. The high aspect ratio and anisotropic nature of 1D nanowires provide inherent structural stability and improved electron transport compared to zero-dimensional nanoparticles^[18-20]. Despite these geometric advantages, 1D morphology alone does not fundamentally alter the chemical stability of surface alloy atoms. In acidic electrolytes, the Ni component within PtNi nanowires remains vulnerable to electrochemical dissolution, which compromises the integrity of the alloy phase^[21]. Consequently, developing a strategy that simultaneously stabilizes the transition metal component within the lattice and further optimizes the activity of Pt sites remains a key challenge for practical PEMFC catalysts.

Multi-component alloying offers a promising pathway to independently tailor both the stability and activity of Pt-based catalysts by introducing specific elements with distinct functionalities^[22-24]. Theoretical studies suggest that doping with refractory metals, such as molybdenum (Mo), can enhance the corrosion resistance of Pt-based alloys by strengthening the metal-metal bond and increasing the vacancy formation energy of the unstable transition metal component^[25, 26]. Meanwhile, the incorporation of a second noble metal, such as ruthenium (Ru), can effectively modulate the electronic structure (d-band center) of Pt, thereby optimizing the binding energy of oxygen-containing intermediates (*OOH, *OH) and enhancing reaction kinetics^[27, 28]. Therefore, integrating Mo and Ru into a PtNi nanowire

system could theoretically decouple the origins of stability and activity, providing a robust solution to the durability issues of PtNi alloys^[29-31].

In this work, we report the synthesis of tetrametallic PtNiMoRu nanowires (PtNiMoRu NWs/C) via a facile solvothermal method, designed to achieve highly active and durable acidic ORR performance. By precisely controlling the composition, we construct a quaternary alloy system where the synergistic effects of Mo and Ru are fully utilized. Experimental characterization and density functional theory (DFT) calculations demonstrate that Mo doping primarily functions to stabilize the Ni species by increasing the Ni vacancy formation energy, thereby suppressing Ni dissolution. Concurrently, Ru doping modulates the electronic structure of the Pt active sites, optimizing the adsorption strength of reaction intermediates. Benefiting from this dual-regulation strategy, the PtNiMoRu NWs/C catalyst exhibits a mass activity of 1.04 A mg_{Pt}⁻¹ at 0.9 V vs. RHE, which represents a 5.2-fold enhancement compared to commercial Pt/C. Moreover, the catalyst demonstrates exceptional durability with a negligible half-wave potential shift of only 9 mV after 30,000 accelerated durability test cycles, significantly outperforming the rapid degradation observed in commercial Pt/C. Finally, the catalyst delivers a peak power density of 1.18 W cm⁻² in a single-cell PEMFC test, validating its potential for practical applications. Unlike conventional Pt-based alloy catalysts that typically require a trade-off between activity and stability, this work proposes a universal dual-doping strategy to decouple these two properties by rationally incorporating different functional elements into the PtNi alloy lattice. Through this design concept, we achieved simultaneously enhanced ORR activity and durability, providing a versatile approach for developing high-performance multimetal electrocatalysts.

2. Results and discussion

2.1 Synthesis and structural characterization

PtNiMoRu NWs/C catalyst was synthesized via a facile solvent-thermal method. As shown in **Figure 1a**, metal acetylacetonate salts served as metal precursors, with oleylamine acting as both solvent and surfactant, CTAC as the morphology directing agent, and glucose/Mo(CO)₆ as reducing agents. All reactions were conducted at 220 °C for 2 hours to ensure complete nanowire growth. For comparison, Pt NWs/C, PtNi NWs/C, and PtNiMo NWs/C were also prepared under identical conditions. Inductively coupled plasma optical emission spectroscopy (ICP-OES) confirmed the final elemental compositions (**Table S1**), revealing a relatively low Pt loading of 8.67 wt.% in the PtNiMoRu NWs/C, which is significantly beneficial for cost reduction compared to commercial 20 wt.% Pt/C.

The crystal structures of the as-prepared catalysts were investigated by X-ray diffraction (XRD). As shown in **Figure 1b**, all samples exhibit a broad peak at $\sim 25.1^\circ$ assigned to the C (002) plane of the XC-72 support. Notably, the diffraction peak corresponding to the Pt (111) plane shifts positively from 39.76° for pure Pt NWs/C to 40.26° for PtNi NWs/C, 40.35° for PtNiMo NWs/C and PtNiMoRu NWs/C^[32, 33]. This continuous positive shift indicates that the incorporation of Ni (atomic radius: 1.24 Å) into the Pt lattice (1.39 Å) induces significant compressive strain, which is known to be favorable for weakening the adsorption of oxygenated intermediates^[34]. The doping of trace Mo and Ru maintains this strained lattice structure without inducing phase segregation.

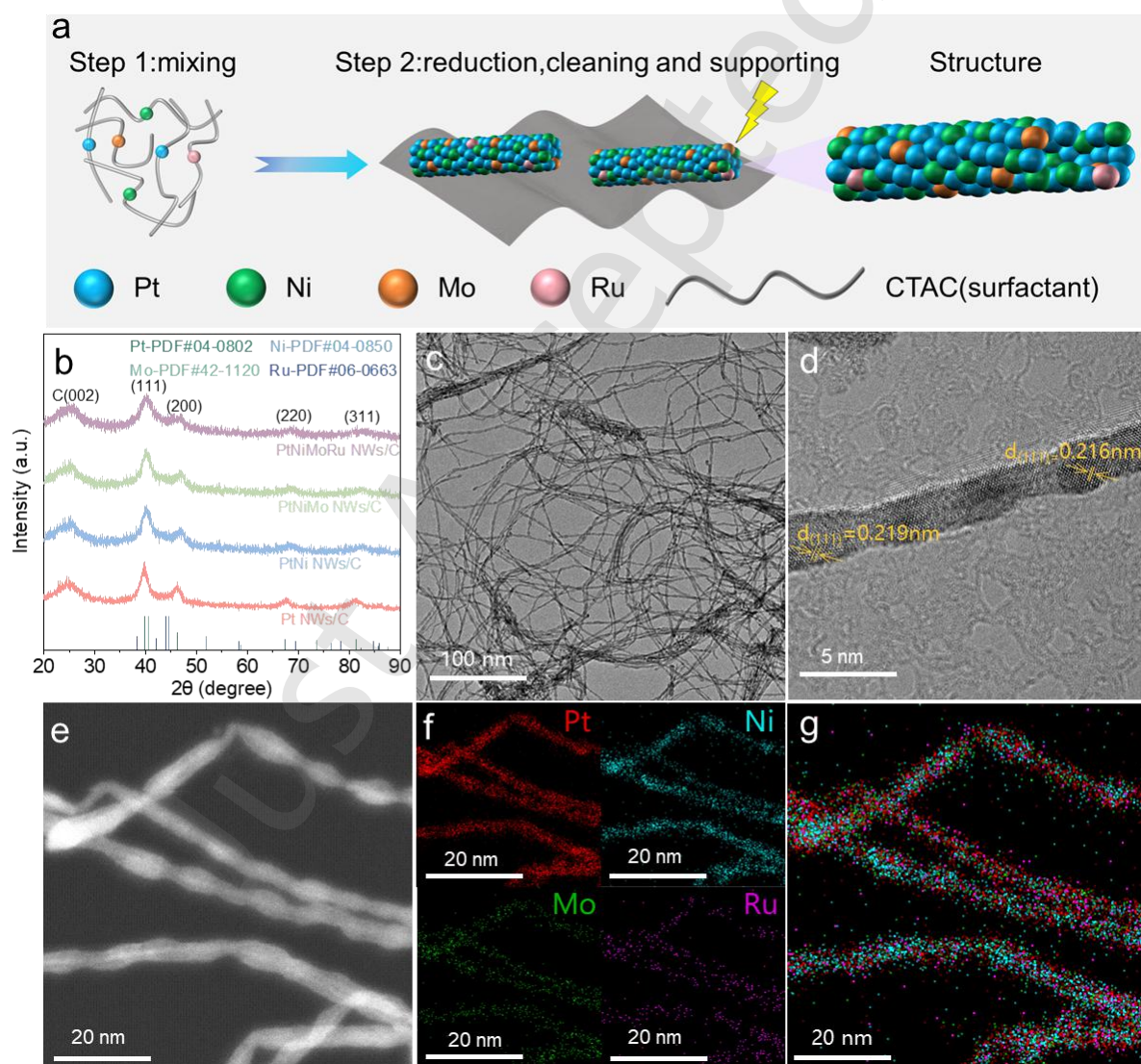


Figure 1. a) Schematic illustration of the PtNiMoRu NWs/C synthesis process. b) XRD patterns of Pt NWs/C, PtNi NWs/C, PtNiMo NWs/C and PtNiMoRu NWs/C. c) TEM images of PtNiMoRu NWs/C. d) HRTEM image of PtNiMoRu NWs/C. e) HAADF-STEM images of PtNiMoRu NWs/C. f) EDS elemental maps of PtNiMoRu NWs/C. g) EDS elemental map of PtNiMoRu NWs/C.

of PtNiMoRu NWs/C. f) EDX elemental mappings of PtNiMoRu NWs/C. g) Overlay of EDX mappings for four elements (Pt, Ni, Mo, Ru).

The morphology and microstructure were further elucidated by electron microscopy. Scanning electron microscopy (SEM) images (**Figure S1-S2**) confirm that the carbon support structure remains intact after catalyst loading. Transmission electron microscopy (TEM) images (**Figure 1c**) clearly reveal that the PtNiMoRu catalyst possesses a uniform 1D nanowire morphology with high aspect ratios, forming an interwoven network that facilitates electron transport^[35, 36]. Interestingly, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (**Figure 1e**) and high-resolution TEM (HRTEM) (**Figure 1d**) images uncover a rough surface with periodic protrusions along the nanowires. This rough surface is expected to provide abundant low-coordinated active sites. HRTEM analysis measured lattice fringes with interplanar spacings of 0.216 nm and 0.219 nm at different locations, both of which are smaller than the standard Pt (111) spacing (0.227 nm). This lattice contraction aligns perfectly with the XRD results, confirming the formation of a strained alloy phase. Furthermore, energy-dispersive X-ray spectroscopy (EDX) elemental mapping (**Figure 1f, g**) demonstrates the homogeneous distribution of Pt, Ni, Mo, and Ru throughout the nanowires, verifying the successful formation of a tetrametallic alloy rather than separate phases.

2.2 Electronic structure analysis

To probe the surface chemical states and electronic interactions among the metallic components, X-ray photoelectron spectroscopy (XPS) was performed (**Figure 2**). The high-resolution Pt 4f spectra (**Figure 2a**) show that metallic Pt⁰ is the dominant species in all samples. Firstly, compared with commercial platinum-on-carbon catalysts, the Pt⁰ 4f_{7/2} peak in the Pt NWs/C catalyst shifts 0.33 eV to the left. This shift is attributed to the fact that the active component of commercial Pt/C catalysts consists of platinum nanoparticles measuring 2–5 nm, whereas Pt NWs/C features a one-dimensional nanowire structure with a unique atomic arrangement and exposed crystal planes; This unique structure alters the surface electronic states, ultimately leading to a negative shift in the position of the Pt⁰ 4f_{7/2} peak. Compared to pure Pt NWs/C, the Pt⁰ 4f_{7/2} peak in PtNi NWs/C exhibits a positive binding energy shift of 0.43 eV. Since the peak position of the Pt⁰ binding energy is influenced by both electronic structure regulation and strain effects, the compressive strain induced by Ni doping is more pronounced in PtNi NWs/C, resulting in a shift of the Pt⁰ binding energy peak towards higher energy. This upshift is attributed to the modification of the Pt electronic

structure by Ni via ligand and strain effects^[31, 37]. Upon further doping with Mo and Ru, the Pt⁰ peak shifts negatively by 0.1 eV and 0.07 eV, respectively. These binding energy shifts indicate a redistribution of electron density at the Pt sites, suggesting that the introduction of Ru and Mo modulates the d-band center of Pt, which is critical for optimizing the adsorption strength of oxygenated intermediates during the ORR process.

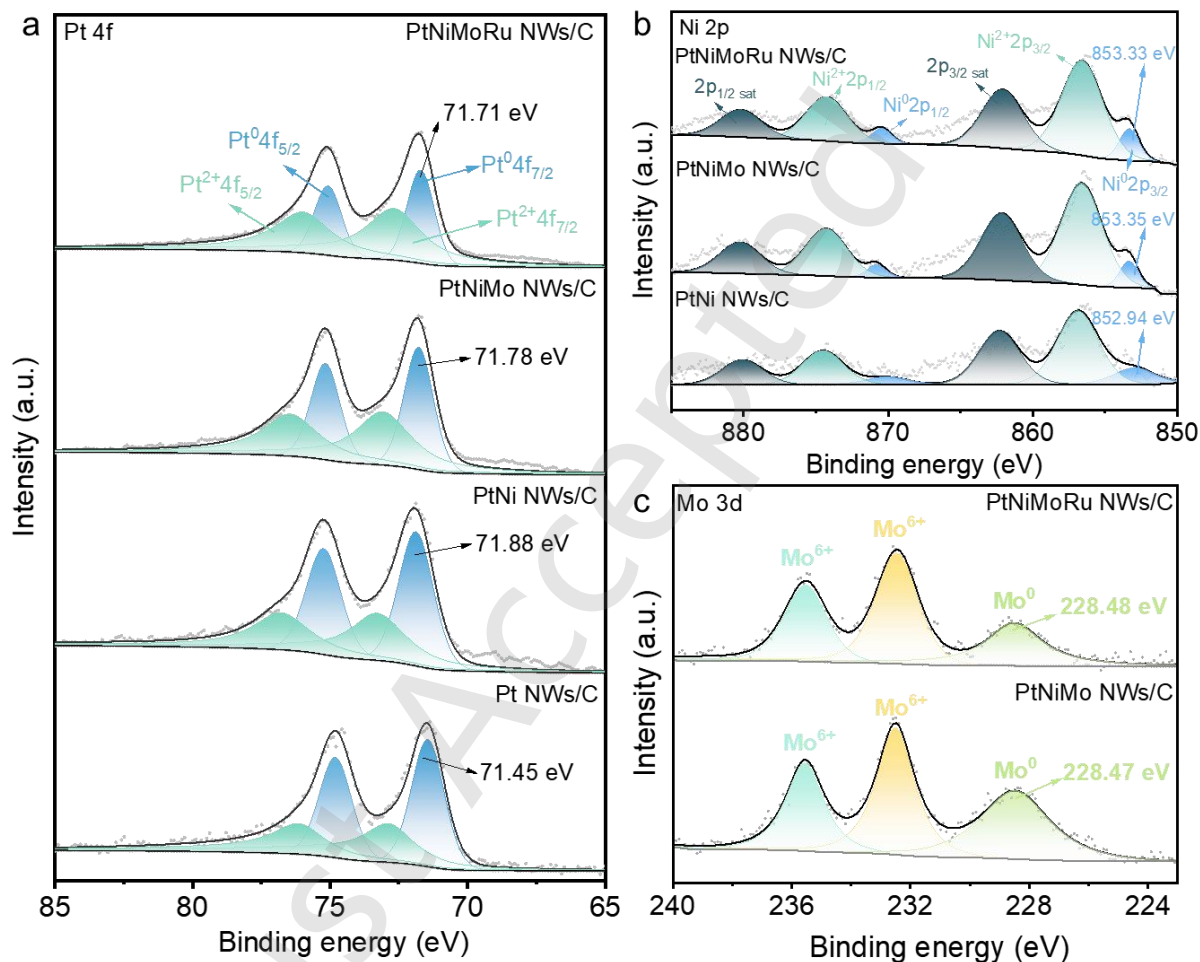


Figure 2. a) High-resolution XPS spectra of Pt 4f for Pt NWs/C, PtNi NWs/C, PtNiMo NWs/C, PtNiMoRu NWs/C. b) High-resolution XPS spectra of Ni 2p for PtNi NWs/C, PtNiMo NWs/C, PtNiMoRu NWs/C. c) High-resolution XPS spectra of Mo 3d for PtNiMo NWs/C, PtNiMoRu NWs/C.

Crucially, the interaction between Mo and Ni is key to the stability mechanism. As shown in the Ni 2p spectra (**Figure 2b**), the introduction of Mo into PtNi NWs/C causes a significant positive shift of 0.41 eV in the Ni⁰ 2p_{3/2} peak. This substantial shift indicates a strong electronic interaction between Mo and Ni atoms. Such interaction implies an electron transfer or hybridization process that alters the chemical state of Ni, potentially increasing the

energy barrier for electrochemical dissolution in acidic media. In contrast, the subsequent addition of Ru causes a negligible shift (-0.02 eV) in the Ni peak, implying that Ru primarily interacts with Pt rather than Ni. Similarly, the Mo 3d spectra (**Figure 2c**) show minimal change after Ru doping. These XPS results collectively suggest a distinct functional separation within the quaternary system where Mo primarily interacts with and stabilizes the Ni species, whereas Ru principally modulates the electronic structure of Pt. This selective electronic regulation supports the hypothesis that the tetrametallic design effectively decouples the origins of stability and activity.

2.3 Enhanced ORR activity and stability

The electrochemical ORR performance of the synthesized nanowire catalysts was evaluated using a rotating disk electrode (RDE) in O₂-saturated 0.1 M HClO₄. The CV plot shows that the reduction peak of the PtNiMoRu NWs/C catalyst is located at 0.82 V vs. RHE, whereas that of the commercial Pt/C catalyst is at 0.8 V vs. RHE, indicating that the PtNiMoRu NWs/C catalyst exhibits superior ORR activity. The linear sweep voltammetry (LSV) curves (**Figure 3a**) reveal a clear trend in catalytic activity. The quaternary PtNiMoRu NWs/C catalyst exhibits the highest half-wave potential ($E_{1/2}$) of 0.885 V vs. RHE, significantly surpassing PtNiMo NWs/C (0.831 V), PtNi NWs/C (0.853 V), Pt NWs/C (0.825 V), and commercial 20% Pt/C (0.820 V). Notably, while the introduction of Mo into PtNi NWs/C (resulting in PtNiMo) leads to a slight negative shift in $E_{1/2}$ due to the strong Ni-Mo interaction potentially altering surface adsorption, the subsequent addition of Ru (forming PtNiMoRu) significantly enhances the activity. This enhancement is attributed to the optimized electronic modulation of Pt sites by Ru, as suggested by the XPS analysis.

The superior kinetics of PtNiMoRu NWs/C are further quantified by Tafel analysis (**Figure 3b**). It exhibits the lowest Tafel slope of 59.2 mV dec⁻¹, compared to 60.4, 61.1, 77.3, and 67.2 mV dec⁻¹ for PtNiMo, PtNi, Pt NWs/C, and commercial Pt/C, respectively. This low slope indicates a more efficient electron transfer process and faster reaction kinetics on the quaternary surface. Furthermore, the mass activity (MA) and specific activity (SA) at 0.9 V vs. RHE were calculated to assess intrinsic catalytic efficiency. As shown in **Figure 3c, e** PtNiMoRu NWs/C achieves a remarkable MA of 1.04 A mg_{Pt}⁻¹ and SA of 2.81 mA cm⁻². These values represent impressive 5.2-fold and 8.3-fold enhancements over commercial Pt/C (0.20 A mg_{Pt}⁻¹ and 0.34 mA cm⁻²), respectively. Such high activity also outperforms many state-of-the-art Pt-based alloy catalysts reported recently (**Table S3**). The optimal synthesis conditions (220 °C for 2 hours) were confirmed to be critical for maximizing this activity, as detailed in **Figures S11-S15**.

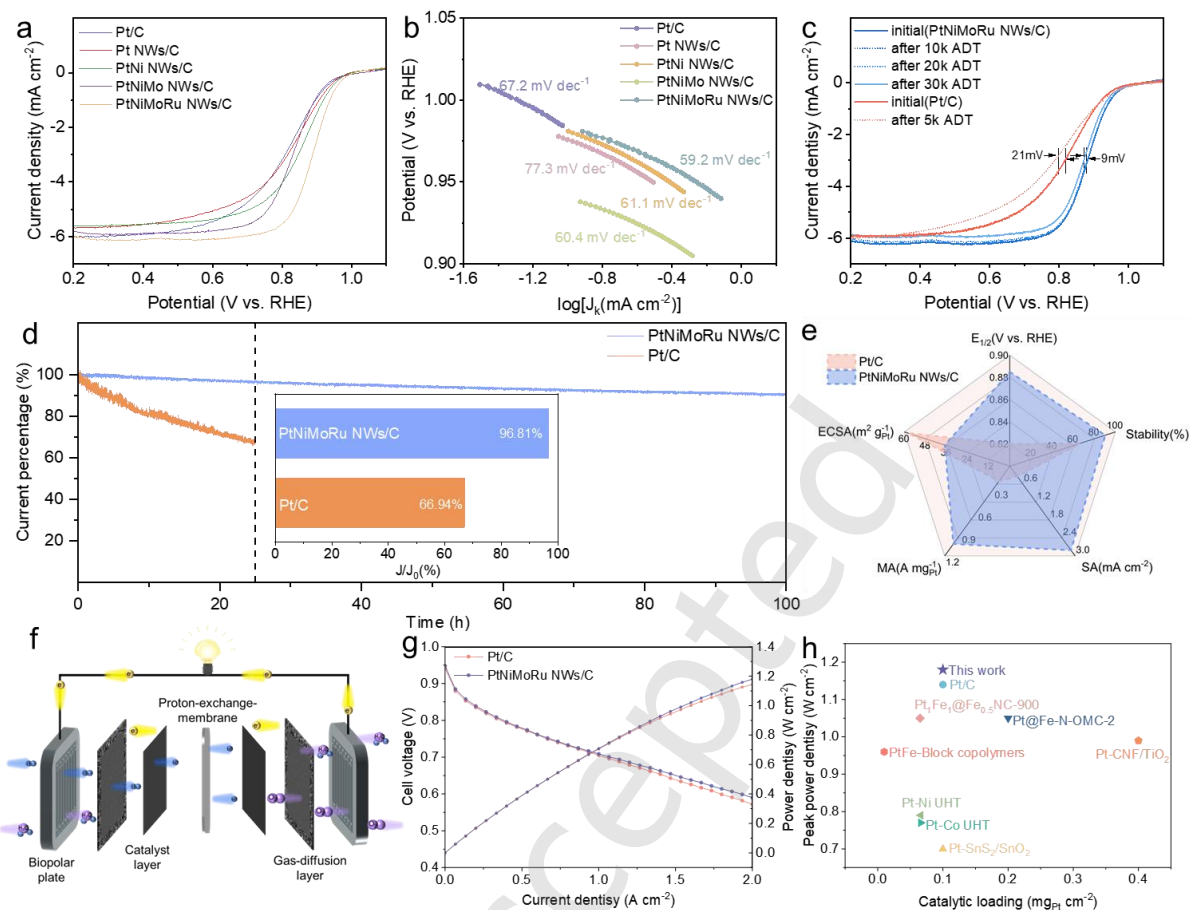


Figure 3. a) LSV polarization curves for ORR tested in O₂-saturated 0.1 M HClO₄ using RDE in a 3-electrode cell, the current densities were normalized to the geometric surface area of the electrode (0.196 cm²). b) Tafel slopes. c) ORR polarization curves of PtNiMoRu NWs/C and commercial 20% Pt/C before and after ADT. d) Chronoamperometry response of Pt/C and PtNiMoRu NWs/C catalyst operated at 0.8 V versus RHE. e) Comprehensive comparison of the performance of PtNiMoRu NWs/C and commercial 20% Pt/C. f) Schematic illustration of PEMFC device. g) Discharging polarization curves and the power density plots of the PEMFC with PtNiMoRu NWs/C and commercial 20% Pt/C (operation condition: 150 kPa_{abs}, H₂/O₂ 0.5/1.0 L min⁻¹, 80 °C, 100% RH). h) Comparison of PEMFC performance with reported catalysts in Table S4 (Supporting Information).

The durability of the PtNiMoRu NWs/C was systematically evaluated using an accelerated durability test (ADT) by cycling the potential between 0.6 and 1.0 V vs. RHE. As shown in **Figure 3d**, after 30,000 continuous cycles, the LSV curve of PtNiMoRu NWs/C shows a negligible negative shift in E_{1/2} of only 9 mV. In sharp contrast, the commercial Pt/C catalyst exhibits a severe degradation of 21 mV after only 5,000 cycles under identical conditions. The MA and SA of the PtNiMoRu NWs/C catalyst were 0.89 A mg_{Pt}⁻¹ and 2.40 mA cm⁻²

respectively, demonstrating its excellent stability. This result highlights the exceptional electrochemical stability of the quaternary nanowire structure. Long-term stability was further verified by chronoamperometry at 0.80 V vs. RHE. The PtNiMoRu NWs/C retained 90.46% of its initial current density after a 100-hour test (**Figure 3e**), whereas commercial Pt/C lost nearly 35% of its activity within just 25 hours.

To understand the structural origin of this stability, post-ADT characterizations were performed. XPS analysis (**Figure S9**) reveals no significant shifts in the binding energies of the metallic components, confirming that the electronic structure remains robust during long-term operation. TEM images after 30k cycles (**Figure S10**) show that the nanowire morphology is largely preserved without the severe particle agglomeration or Ostwald ripening typically observed in commercial Pt/C. Although some degree of nanowire fragmentation was observed, the absence of significant Ni leaching or structural collapse validates the effectiveness of Mo-doping in stabilizing the alloy lattice structure (**Table S2**).

2.4 Performance in PEMFC device

Given the exceptional half-cell performance, we further fabricated membrane electrode assemblies (MEAs) to evaluate the practical applicability of PtNiMoRu NWs/C in proton exchange membrane fuel cells (PEMFCs). **Figure 3f** illustrates the single-cell configuration. The polarization and power density curves measured under H_2/O_2 conditions are shown in **Figure 3g**. The MEA utilizing PtNiMoRu NWs/C as the cathode catalyst delivers a high peak power density of 1.18 W cm^{-2} , which is substantially higher than that of the commercial 20% Pt/C benchmark. This enhanced device performance is attributed to the unique 1D nanowire morphology, which tends to form a porous, three-dimensional (3D) interconnected network within the catalyst layer. Such a structure not only improves the catalyst utilization but also facilitates efficient mass transport of reactants and rapid electron conduction. Furthermore, a comprehensive comparison with recently reported Pt-based catalysts (**Figure 3h and Table S4**) confirms that the PtNiMoRu NWs/C stands out as a leading candidate for high-performance PEMFC cathodes.

2.5 Reaction mechanism

To gain atomistic insights into the enhanced activity and stability of the PtNiMoRu NWs/C catalyst, we combined electrokinetic analysis, in situ spectroscopy, and density functional theory (DFT) calculations. First, Koutecky-Levich (K-L) analysis based on rotation-speed-dependent LSV curves shown in **Figure S17** yielded an electron transfer number (n) of 3.94, confirming a highly efficient four-electron pathway for the ORR on the quaternary nanowire

surface. To directly probe the reaction intermediates and understanding the activity enhancement, in situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was performed as illustrated in **Figure 4a**. The potential-dependent spectra for commercial Pt/C and PtNiMoRu NWs/C are presented in **Figure 4b** and **Figure 4c**, respectively. In both cases, a distinct band attributed to the superoxide intermediate (*OOH) is observed^[38]. We plotted **Figure 4d** by integrating the OOH* adsorption peaks for the two catalysts at different operating voltages during in-situ IR testing. As seen, this *OOH band appears at 1044 cm⁻¹ for PtNiMoRu NWs/C, exhibiting a redshift relative to the 1047 cm⁻¹ band observed for commercial Pt/C^[39, 40]. This redshift indicates a weakening of the O-O bond in the adsorbed intermediate, which implies a stronger interaction between the Pt active sites and the *OOH species. Such optimized interaction facilitates the subsequent O-O bond cleavage, thereby accelerating the reaction kinetics^[41, 42]. The variation of peak intensity with potential further tracks the coverage of intermediates, showing a maximum near the half-wave potential. Based on these spectroscopic findings, we further elucidate the mechanism of enhanced activity in PtNiMoRu tetrametallic NWs/C through DFT calculations. XRD and HRTEM results (Figure 1b, d) indicate that PtNiMoRu NWs/C exhibits a face-centered cubic (fcc) structure with predominantly exposed (111) crystal planes, which is consistent with the fact that Pt (111) surface has the lowest surface energy. Therefore, we employed a seven-layer 2 × 2 Pt (111) slab model as the foundation, which is a commonly used approach in DFT studies of Pt-based alloys. Additionally, ICP-OES measurements revealed that the atomic ratio of Pt:Ni:Mo:Ru was approximately 1:0.84:0.068:0.011. Since the Pt:Ni ratio was close to 1:1, we first constructed a 2 × 2 PtNi (111) slab (Pt:Ni = 1:1), and then doped the subsurface layer with one Mo atom and one Ru atom, respectively. Considering the tendency of surface Ni atoms to dissolve under acidic conditions, we replaced the outermost layer with a pure Pt monolayer to form a Pt-skin structure. Therefore, a series of Pt-skin structured crystal plane models composed of similar elements including PtNi (111), PtNiMo (111), and PtNiMoRu (111), were constructed to represent PtNi, PtNiMo, and PtNiMoRu NWs/C respectively (**Figure 4e** and **Figure S22**).

Based on the principle of energy minimization, the preferred positions for Mo and Ru atoms are the first and fourth subsurface sites of the PtNi (111) crystal plane, respectively (**Figure 4e**). Subsequent DFT simulations calculated the PDOS of Pt (111) and PtNiMoRu (111), revealing that doping with Mo and Ru atoms induces a negative shift in the d-band center (**Figure 4f**), weakening the strong binding capability to oxygen-containing species

(**Figure 4g**) and enhances ORR activity. To elucidate the structural origin of the superior durability, DFT calculations were performed to determine the vacancy formation energy (E_v) of Ni atoms^[31, 43]. As shown in **Figure 4h**, the calculated Ni vacancy formation energy for the PtNiMoRu (111) surface is 1.30 eV. This value is significantly higher than that of the binary PtNi (111) surface (1.09 eV) and is comparable to the ternary PtNiMo (111) surface (1.30 eV). A higher vacancy formation energy signifies that removing a Ni atom from the lattice is energetically more demanding. These results confirm that the incorporation of Mo primarily functions to stabilize the alloy lattice by increasing the energy barrier for Ni vacancy formation. The strong electronic interaction between Mo and Ni limits the segregation and dissolution of Ni atoms, thereby preserving the active alloy phase even under acidic conditions. This theoretical insight corroborates the ADT and XPS results, providing a mechanistic explanation for the enhanced stability of the tetrametallic nanowire catalyst.

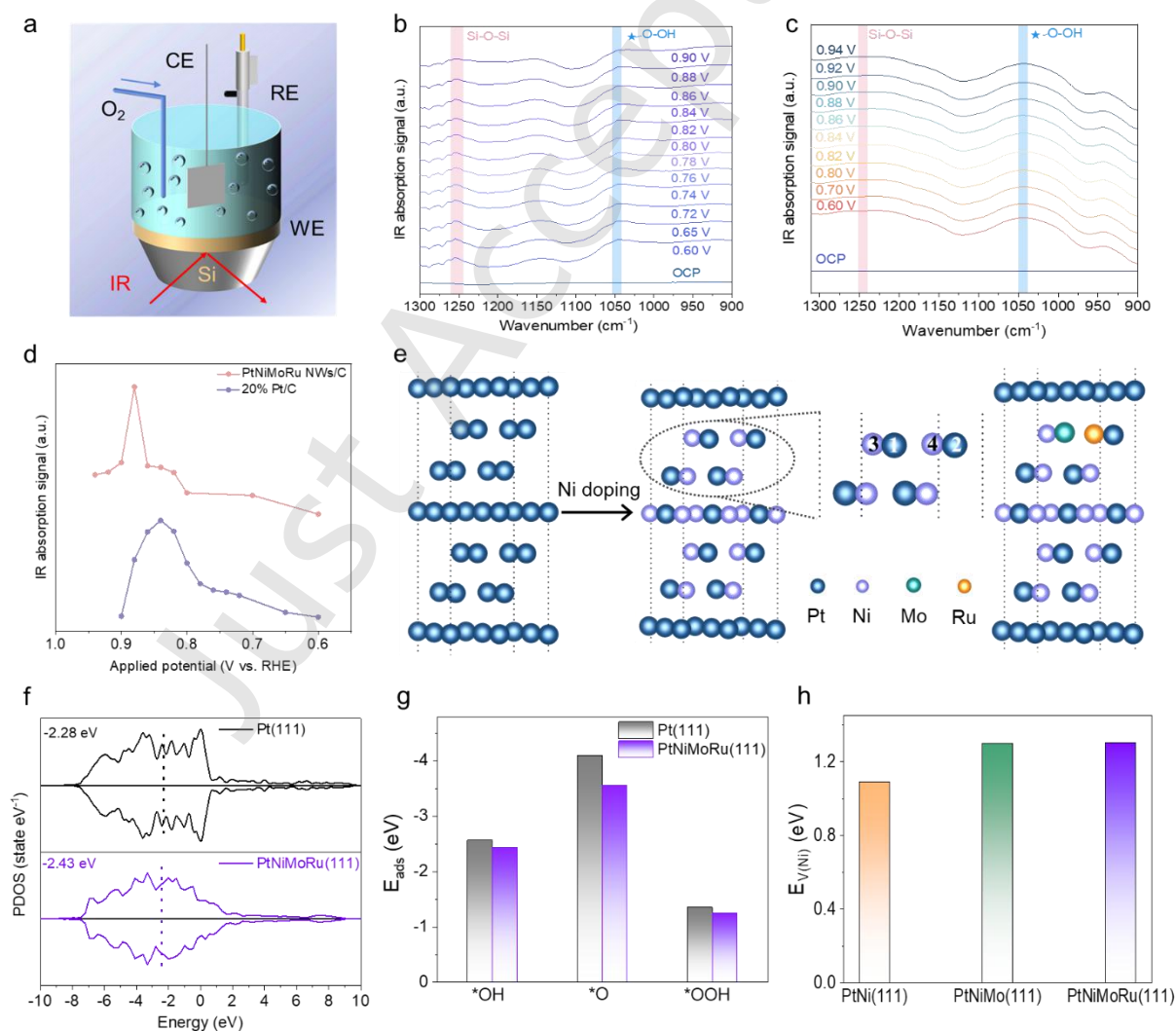


Figure 4. a) Schematic diagram of the in situ FTIR. b) In situ FTIR spectra of 20% Pt/C. c) In situ FTIR spectra of PtNiMoRu NWs/C. d) FTIR absorption stretching at 1044 cm⁻¹ for

PtNiMoRu NWs/C and 1047 cm^{-1} for 20% Pt/C. e) Diagram of the location of the incorporation of Mo atoms and Ru atoms in the PtNi (111). f) The plots of projected d-density of states (PDOS) for surface Pt atoms on Pt (111) and PtNiMoRu (111) slabs. g) Adsorption energies of OH, O, OOH on Pt (111) and PtNiMoRu (111) surfaces. h) Ni vacancy formation energies ($E_{V(\text{Ni})}$) for PtNi (111), PtNiMo (111), and PtNiMoRu (111) slabs.

3. Conclusion

In summary, we successfully synthesized tetrametallic PtNiMoRu nanowire electrocatalysts via a solvothermal method to address the stability and activity trade-off in the acidic oxygen reduction reaction. The design strategy relies on the distinct functions of molybdenum and ruthenium dopants within the platinum-nickel alloy structure. Experimental characterization and theoretical calculations reveal that molybdenum doping increases the vacancy formation energy of nickel, which effectively suppresses the electrochemical dissolution of the transition metal component in acidic environments. Simultaneously, ruthenium doping modulates the d-band center of platinum active sites, thereby optimizing the adsorption strength of oxygenated intermediates and enhancing reaction kinetics. By combining this synergistic regulation with the structural advantages of one-dimensional nanowires, the optimized PtNiMoRu catalyst exhibits exceptional performance. It achieves a mass activity of $1.04\text{ A mg}_{\text{Pt}}^{-1}$ at 0.9 V vs. RHE, representing a 5.2-fold enhancement compared to commercial Pt/C. Furthermore, the catalyst demonstrates superior durability with a negligible half-wave potential decay of only 9 mV after 30,000 accelerated durability test cycles. In proton exchange membrane fuel cell tests, the catalyst delivers a peak power density of 1.18 W cm^{-2} . This study highlights the effectiveness of element-specific engineering in multicomponent alloys and offers a general approach for designing highly active and stable platinum-based electrocatalysts for fuel cell applications.

Experimental Section

Materials. Platinum (II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 98%), Nickel (II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 99%), Molybdenum (II) acetylacetonate ($\text{Mo}(\text{acac})_2$, 99%) were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Ruthenium (III) acetylacetonate ($\text{Ru}(\text{acac})_3$, 98%) was purchased from Shanghai Acme Biochemical Technology Co., Ltd. CTAC ($\text{C}_{19}\text{H}_{42}\text{ClN}$, 99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, 99%), oleylamine ($((\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{NH}_2)$, OAm, 80-90%) were purchased from Heowns Biochem LLC. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, >99.8%), perchloric acid (HClO_4) were purchased from Aladdin. Isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$, 99.9%) was purchased

from Macklin. Cyclohexane (C_6H_{12} , $\geq 99.7\%$), Molybdenum hexacarbonyl ($Mo(CO)_6$, 98%) were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. High purity oxygen (99.999%) and high purity argon (99.999%) were purchased from Linde gas (Tianjin). Nafion solution (5 wt.%) was purchased from Sigma-Aldrich. Commercial Pt/C catalyst (20 wt%, 2-5 nm Pt NPs) was obtained from E-TEK. All the chemicals were used as received without further purification. The water ($18.25\text{ M}\Omega\cdot\text{cm}$) used in all experiments was prepared by passing through a Milli-Q system.

Synthesis of PtNiMoRu NWs. For the synthesis of the PtNiMoRu NWs, $Pt(acac)_2$ (10 mg), $Ni(acac)_2$ (6.4 mg), $Mo(acac)_2$ (3 mg), $Ru(acac)_3$ (1.0 mg), glu (60mg), $Mo(CO)_6$ (20mg), CTAC (10 mg) and OAm (5.0 mL) were added together into a 20 mL glass vial. Then, the mixed solution was stirred and ultrasonicated for around 60 min to form a homogeneous solution, followed by heating in the sand bath at $220\text{ }^\circ\text{C}$ for 2 h. After the solution was cooled down to room temperature, the products were collected by centrifugation and washed five times with ethanol/cyclohexane mixture. After washing, it was stored in a cyclohexane solution.

Synthesis of Pt NWs, PtNi NWs, PtNiMo NWs, PtRu NWs. The method was the same as above, only Pt precursors, Pt and Ni precursors, Pt, Ni and Mo precursors, and Pt,Ru precursors were added respectively.

Physicochemical characterization. Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-8100 microscope with an acceleration voltage of 530 kV. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM), and energy dispersive X-ray spectroscopy (EDX) were carried out on the Tecnai G2 F-200 microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI-1600 X-ray photoelectron spectrometer using Al $K\alpha$ radiation, and C 1s peak (284.8 eV) of contamination carbon was adopted to calibrate binding energy.

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Before the electrochemical tests, the as prepared Pt-based NWs was loaded on carbon supports (Vulcan XC-72). The homogeneous catalyst ink was prepared by mixing 5 mg of catalyst, 725 μL of isopropanol, 245 μL deionized water and 30 μL of Nafion solution (5 wt.%) with 3 h of sonication to obtain a uniform suspension. Then, a thin film catalyst layer (0.255 mg cm^{-2} catalyst) was obtained by depositing 10 μL of catalyst ink onto the rotating disk electrode (RDE, 0.196 cm^2). The electrode potential was calibrated against reversible hydrogen electrode (RHE) by the equation:

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with a custom-fabricated electrochemical cell. The working electrode was an Au-plated silicon wafer loaded with catalyst.

Density functional theory calculations. All of the DFT calculations were performed using the Vienna Ab-initio simulation package program, which uses a plane-wave basis set and a projector augmented wave method (PAW) for the treatment of core electrons. The Perdew-Burke-Ernzerh of exchange-correlation functional within a generalized gradient approximation (GGA-PBE) was used in our calculations, and the van der Waals (vdW) correction proposed by Grimme (DFT-D3) was employed due to its good description of long-range vdW interactions. For the expansion of wavefunctions over the plane-wave basis set, a converged cutoff was set to 450 eV.

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The vacancy formation energy is calculated as:

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where $E_{slab-V(Ni)}$ represents the energy of a slab with one Ni vacancy, μ_{Ni} represents the chemical energy of a Ni atom, E_{slab} represents the energy of a perfect slab.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908870>.

Acknowledgments

The authors appreciate the support from the National Key R&D Program of China (2023YFA1508700) and the National Natural Science Foundation of China (22278307, 22222808, and 21978200).

Declaration of competing interest

The authors declare no competing financial interest.

Author contribution statement

Xingchao Dong: conceptualization, methodology, validation, investigation, writing-original draft. **Xinquan Wu:** conceptualization, methodology, validation, writing-review and editing. **Huayang Wang:** writing-review and editing. **Xiaokang Liu:** methodology, writing-review and editing. **Tianqing Yan:** analysis of the devices, writing-review and editing. **Kenjie Ho:** writing-review and editing. **Ruijie Gao:** investigation. **Kang Xue:** investigation. **Minhua Ai:** validation. **Lun Pan:** validation. **Xiangwen Zhang:** validation, investigation. **Zhen-Feng Huang:** conceptualization, supervision, project administration, writing-review and editing. **Ji-Jun Zou:** conceptualization, supervision, project administration, writing-review and editing.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None

References

- [1] Huang, L.;Niu, H.;Xia, C.;Li, F.;Shahid, Z.; Xia, B. Integration construction of hybrid electrocatalysts for oxygen reduction. *Adv. Mater.* **2024**, *36*, 2404773.
- [2] Wang, J.;Li, B.;Yersak, T.;Yang, D.;Xiao, Q.;Zhang, J.; Zhang, C. Recent advances in Pt-based octahedral nanocrystals as high performance fuel cell catalysts. *J. Mater. Chem. A* **2016**, *4*, 11559-11581.
- [3] Liu, M.;Zhang, J.;Su, H.;Jiang, Y.;Zhou, W.;Yang, C.;Bo, S. W.;Pan, J.; Liu, Q. In situ modulating coordination fields of single-atom cobalt catalyst for enhanced oxygen reduction reaction. *Nat. Commun.* **2024**, *15*, 1675.
- [4] Ahn, C. Y.;Park, J. E.;Kim, S.;Kim, O. H.;Hwang, W.;Her, M.;Kang, S. Y.;Park, S.;Kwon, O. J.;Park, H. S.;Cho, Y. H.; Sung, Y. E. Differences in the electrochemical

- performance of Pt-based catalysts used for polymer electrolyte membrane fuel cells in liquid half- and full-cells. *Chem. Rev.* **2021**, *121*, 15075-15140.
- [5] Wu, Y.; Geng, S.; Liu, J.; Liu, Y.; Wang, K.; Wang, Y.; Song, S. Unveiling the catalytic potential of facet heterojunctions in platinum alloys for oxygen reduction reaction. *Angew. Chem. Int. Edit.* **2025**, *64*, e202505699.
 - [6] Li, F.; Noh, H. J.; Che, W.; Jeon, J. P.; Han, G.; Shin, T. J.; Kim, M. G.; Wang, Y.; Bu, Y.; Fu, Z.; Lu, Y.; Baek, J. B. Tin nanoclusters confined in nitrogenated carbon for the oxygen reduction reaction. *Acs Nano* **2022**, *16*, 18830-18837.
 - [7] Xie, X.; Briega-Martos, V.; Alemany, P.; Sandhya, A. L. M.; Skála, T.; Rodríguez, M. G.; Nováková, J.; Dopita, M.; Vorochta, M.; Bruix, A.; Cherevko, S.; Neyman, K. M.; Matolínová, I.; Khalakhan, I. Balancing activity and stability through compositional engineering of ternary PtNi-Au alloy ORR catalysts. *ACS Catal.* **2024**, *15*, 234-245.
 - [8] Li, H.; Di, S.; Niu, P.; Wang, S.; Wang, J.; Li, L. A durable half-metallic diatomic catalyst for efficient oxygen reduction. *Energy Environ. Sci.* **2022**, *15*, 1601-1610.
 - [9] Alfaifi, S. M.; Balu, R.; Chiang, K.; Choudhury, N. R.; Dutta, N. K. Electrocatalysts for the oxygen reduction reaction in proton exchange membrane fuel cells: significant advances, major challenges, and future directions. *Acs Catal.* **2025**, *15*, 9301-9345.
 - [10] Huang, J.; Sementa, L.; Liu, Z.; Barcaro, G.; Feng, M.; Liu, E.; Jiao, L.; Xu, M.; Leshchev, D.; Lee, S. J.; Li, M.; Wan, C.; Zhu, E.; Liu, Y.; Peng, B.; Duan, X.; Goddard, W. A.; Fortunelli, A.; Jia, Q.; Huang, Y. Experimental sabatier plot for predictive design of active and stable Pt-alloy oxygen reduction reaction catalysts. *Nat. Catal.* **2022**, *5*, 513-523.
 - [11] Jiao, K.; Xuan, J.; Du, Q.; Bao, Z. M.; Xie, B.; Wang, B.; Zhao, Y.; Fan, L. H.; Wang, H.; Hou, Z.; Huo, S.; Brandon, N. P.; Yin, Y.; Guiver, M. D. Designing the next generation of proton-exchange membrane fuel cells. *Nature* **2021**, *595*, 361-369.
 - [12] Wang, X.; Swihart, M. T.; Wu, G. Achievements, challenges and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation. *Nat. Catal.* **2019**, *2*, 578-589.
 - [13] Tian, X.; Zhao, X.; Su, Y.; Wang, L.; Wang, H.; Dang, D.; Chi, B.; Liu, H.; Hensen, E. J. M.; Lou, X.; Xia, B. Engineering bunched Pt-Ni alloy nanocages for efficient oxygen reduction in practical fuel cells. *Science* **2019**, *366*, 850-856.
 - [14] Yu, B.; Niu, W.; Cai, C.; Xu, L.; Wang, F. Advances and directions of ordered Pt-based transition metal alloys supported on carbon with different dimensions for boosting ORR catalytic activity toward PEMFCs. *Adv. Funct. Mater.* **2026**, *36*.
 - [15] Luo, Y.; Zhou, T.; Molochas, C.; Tan, Y.; Huang, X.; Chen, Z.; Zhu, J.; Tsiakaras, P.; Shen, P. Synthesis of polyhedral Pt-Pd-Ni nanobelts regulated by W(CO)₆ and applied as a highly performing oxygen reduction reaction electrocatalyst. *Chem. Eng. J.* **2024**, *497*.
 - [16] Bu, L. Z.; Liang, J.; Ning, F.; Huang, J.; Huang, B.; Sun, M.; Zhan, C.; Ma, Y.; Zhou, X.; Li, Q.; Huang, X. Low-coordination trimetallic PtFeCo nanosaws for practical fuel cells. *Adv. Mater.* **2023**, *35*.
 - [17] Cademartiri, L.; Ozin, G. A. Ultrathin nanowires - a materials chemistry perspective. *Adv. Mater.* **2009**, *21*, 1013-1020.
 - [18] Xiao, F.; Sun, H.; Geng, S.; Hu, X.; Jiang, K.; Zhang, Q.; Zheng, Z.; Liu, W.; Huang, X.; Bu, L. Z. Rare earth-decorated platinum-nickel-cobalt knot-like nanowires achieve efficient bifunctional electrocatalysis for PEMFC. *Nano Energy* **2025**, *144*, 111379.
 - [19] Huang, X.; Zhao, Z.; Cao, L.; Chen, Y.; Zhu, E.; Lin, Z.; Li, M.; Yan, A.; Zettl, A.; Wang, Y.; Duan, X.; Mueller, T.; Huang, Y. High-performance transition metal-doped Pt₃Ni octahedra for oxygen reduction reaction. *Science* **2015**, *348*, 1230-1234.

- [20] Liu, J.;Liu, S.;Yan, F.;Wen, Z.;Chen, W.;Liu, X.;Liu, Q.;Shang, J.;Yu, R.;Su, D.; Shui, J. Ultrathin nanotube structure for mass-efficient and durable oxygen reduction reaction catalysts in PEM fuel cells. *J. Am. Chem. Soc.* **2022**, *144*, 19106-19114.
- [21] Lim, J.;Shin, H.;Kim, M.;Lee, H.;Lee, K. S.;Kwon, Y.;Song, D.;Oh, S.;Kim, H.; Cho, E. Ga-doped Pt-Ni octahedral nanoparticles as a highly active and durable electrocatalyst for oxygen reduction reaction. *Nano Lett.* **2018**, *18*, 2450-2458.
- [22] Wang, P.;Cui, H.; Wang, C. Ultrathin PtMo-CeOx hybrid nanowire assemblies as high-performance multifunctional catalysts for methanol oxidation, oxygen reduction and hydrogen oxidation. *Chem. Eng. J.* **2022**, *429*, 132435.
- [23] Yin, S.;Song, Y.;Liu, H.;Cui, J.;Liu, Z.;Li, Y.;Xue, T.;Tang, W.;Zhang, D.;Li, H.;Li, H.; Li, C. Well-defined PtCo@Pt core-shell nanodendrite electrocatalyst for highly durable oxygen reduction reaction. *Small* **2025**, *21*, 2410080.
- [24] Song, M.;Li, F.;Zhang, Q.;Shen, T.;Luo, G.;Li, D.; Wang, D. Phase engineering of Pt-Mn intermetallics for durable oxygen reduction reaction electrocatalysis. *Chem. Eng. J.* **2023**, *478*, 147287.
- [25] Wang, Z.;Wu, W.;Jiang, H.;Chen, S.;Chen, R.;Zhu, Y.;Xiao, Y.;Lv, H. F.;Zhong, J.; Cheng, N. Ti single atom enhancing Pt-based Intermetallics for efficient and durable oxygen reduction. *Adv. Funct. Mater.* **2024**, *34*, 2406347.
- [26] Li, J.-L.;Li, Y.-F.; Liu, Z.-P. In situ structure of a Mo-doped Pt-Ni catalyst during electrochemical oxygen reduction resolved from machine learning-based grand canonical global optimization. *JACS Au* **2023**, *3*, 1162-1175.
- [27] Lin, L.;Kuo, C.;Hsu, Y.;Hsu, L.;Chen, H.;Chen, J.; Pan, Y. High-performance intermetallic PtCo oxygen reduction catalyst promoted by molybdenum. *Appl. Catal. B Environ.* **2022**, *317*, 121767.
- [28] Cai, G.;Hua, C.;Ren, H.;Yu, R.;Xu, D.;Khan, M. A.;Guo, J.;Sun, Y.;Tang, Y.;Qian, H.;Xia, Z.;Ye, D. X.;Zhang, J.; Zhao, H. Ultrathin ternary PtNiRu nanowires for enhanced oxygen reduction and methanol oxidation catalysis via d-band center regulation. *J. Colloid Interface Sci.* **2025**, *678*, 599-608.
- [29] Gao, L.;Sun, T.;Chen, X.;Yang, Z.;Li, M.;Lai, W.;Zhang, W.;Yuan, Q.; Huang, H. Identifying the distinct roles of dual dopants in stabilizing the platinum-nickel nanowire catalyst for durable fuel cell. *Nat. Commun.* **2024**, *15*, 508.
- [30] Hu, X.;Jiang, K.;Wang, F.;Geng, S.;Liu, Y.;Meng, S.;Su, H.;Zhu, S.;Bu, L.;Chen, C.; Zheng, S. Gas dynamically confined synthesis of platinum-based intermetallic nanowires for active and ultrastable oxygen reduction catalysis. *Acs Nano* **2025**, *19*, 31201-31212.
- [31] Chattot, R.;Asset, T.;Bordet, P.;Drnec, J.;Dubau, L.; Maillard, F. Beyond strain and ligand effects: microstrain-induced enhancement of the oxygen reduction reaction kinetics on various PtNi/C nanostructures. *ACS Catal.* **2017**, *7*, 398-408.
- [32] Mo, Y.;Feng, S.;Yu, T.;Chen, J.;Qian, G.;Luo, L.; Yin, S. Surface unsaturated WOx activating PtNi alloy nanowires for oxygen reduction reaction. *J. Colloid Interface Sci.* **2022**, *607*, 1928-1935.
- [33] Liang, L.;Jin, H.;Zhou, H.;Liu, B.;Hu, C.;Chen, D.;Zhu, J.;Wang, Z.;Li, H.;Liu, S.;He, D.; Mu, S. Ultra-small platinum nanoparticles segregated by nickel sites for efficient ORR and HER processes. *J. Energy Chem.* **2022**, *65*, 48-54.
- [34] Zhuang, Y.;Iguchi, Y.;Li, T. C.;Kato, M.;Hutapea, Y. A.;Hayashi, A.;Watanabe, T.; Yagi, I. Platinum-nickel alloy nanowire electrocatalysts transform into Pt-skin beads-on-nanowires keeping oxygen reduction reaction activity during potential cycling. *ACS Catal.* **2024**, *14*, 1750-1758.

- [35] Wang, Y.;Zhang, X.;He, H.;Chen, J.; Liu, B. Ordered mesoporous high-entropy intermetallics for efficient oxygen reduction electrocatalysis. *Adv. Energy Mater.* **2024**, *14*, 2303923.
- [36] Cao, W.;Thakur, N.;Kumar, M.;Uchiyama, T.;Gao, Y. F.;Tominaka, S.;Machida, A.;Watanabe, T.;Sato, R.;Teranishi, T.;Matsumoto, M.;Imai, H.;Sakurai, Y.;Uchimoto, Y. Structural insights and electronic state analysis of PtNi nanowire catalysts by operando high-energy resolution fluorescence detection X-ray absorption spectroscopy. *J. Mater. Chem. A* **2024**, *12*, 29843-29853.
- [37] Tao, L.;Wang, K.;Lv, F.;Mi, H.;Lin, F.;Luo, H.;Guo, H.;Zhang, Q.;Gu, L.;Luo, M.;Guo, S. Precise synthetic control of exclusive ligand effect boosts oxygen reduction catalysis. *Nat. Commun.* **2023**, *14*, 6893.
- [38] Chen, S.;Luo, T.;Li, X.;Chen, K.;Fu, J.;Liu, K.;Cai, C.;Wang, Q.;Li, H.;Chen, Y.;Ma, C.;Zhu, L.;Lu, Y.;Chan, T.;Zhu, M.;Cortes, E.; Liu, M. Identification of the highly active Co-N₄ coordination motif for selective oxygen reduction to hydrogen peroxide. *J. Am. Chem. Soc.* **2022**, *144*, 14505-14516.
- [39] Hao, Y.;Hung, S.;Zeng, W.;Wang, Y.;Zhang, C.;Kuo, C.;Wang, L.;Zhao, S.;Zhang, Y.;Chen, H.; Peng, S. Switching the oxygen evolution mechanism on atomically dispersed Ru for enhanced acidic reaction kinetics. *J. Am. Chem. Soc.* **2023**, *145*, 23659-23669.
- [40] Lin, C.;Li, J.;Li, X.;Yang, S.;Luo, W.;Zhang, Y.;Kim, S. H.;Kim, D. H.;Shinde, S. S.;Li, Y.;Liu, Z.;Jiang, Z.; Lee, J. H. In-situ reconstructed Ru atom array on α -MnO₂ with enhanced performance for acidic water oxidation. *Nat. Catal.* **2021**, *4*, 1012-1023.
- [41] Lin, Y.;Yu, L.;Tang, L.;Song, F.;Schlögl, R.; Heumann, S. In situ Identification and time-resolved observation of the interfacial state and reactive intermediates on a cobalt oxide nanocatalyst for the oxygen evolution reaction. *ACS Catal.* **2022**, *12*, 5345-5355.
- [42] Vivek, J. P.;Berry, N. G.;Zou, J.;Nichols, R. J.; Hardwick, L. J. In situ surface-enhanced infrared spectroscopy to identify oxygen reduction products in nonaqueous metal-oxygen batteries. *J. Phys. Chem. C* **2017**, *121*, 19657-19667.
- [43] Curulla, D.;Clotet, A.;Ricart, J. M.; Illas, F. Ab initio cluster model study of the chemisorption of CO on low-index platinum surfaces. *J. Phys. Chem. B* **1999**, *103*, 5246-5255.

Electronic Supplementary Material

Decoupling activity and stability in PtNiMoRu nanowires for durable acid oxygen electroreduction

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Supporting information to <https://doi.org/10.26599/NR.2026.94908870>

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Supporting Information Note 1: Different gas-flow methods during the preparation of PtNiMoRu NWs/C catalysts via solvothermal reduction

Since argon gas protection is employed during the synthesis of PtNiMoRu NWs/C catalysts, we have designed three distinct argon protection methods: Method 1: Argon gas is continuously introduced throughout the entire process—from preheating and temperature ramp-up to reaction completion and cooling to room temperature—ensuring the reaction system remains under dynamic flow protection. Method 2: Argon gas flow is maintained until 220°C, after which it is stopped, but the entire reaction system remains sealed. Method 3: Argon gas flow is maintained for half an hour at 70°C, then stopped. The entire reaction system remains sealed, and heating continues until the reaction is complete.

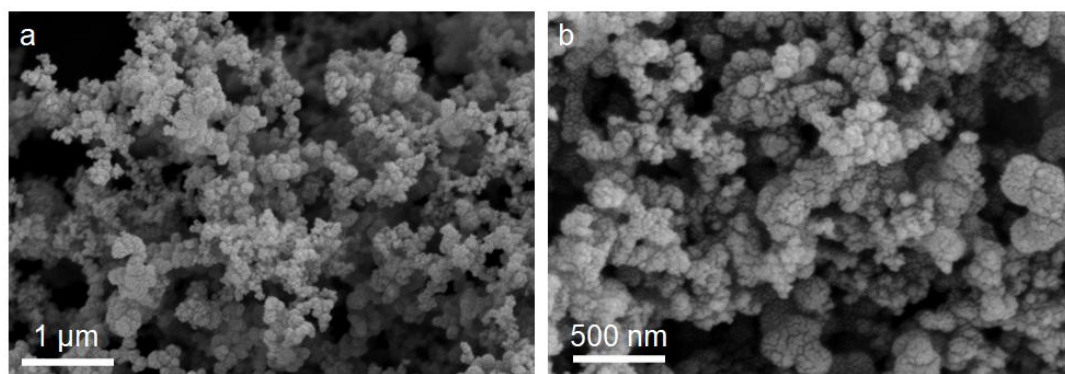


Figure S1 a, b) SEM image of XC-72.

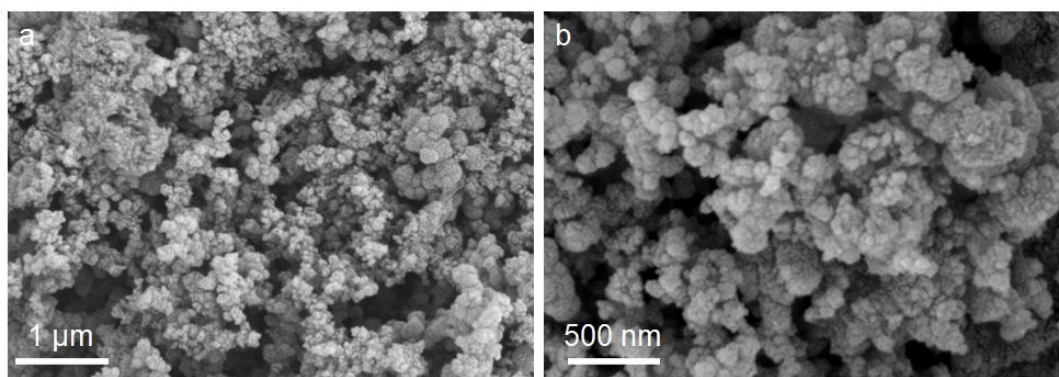


Figure S2 a, b) SEM image of PtNiMoRu NWs/C.

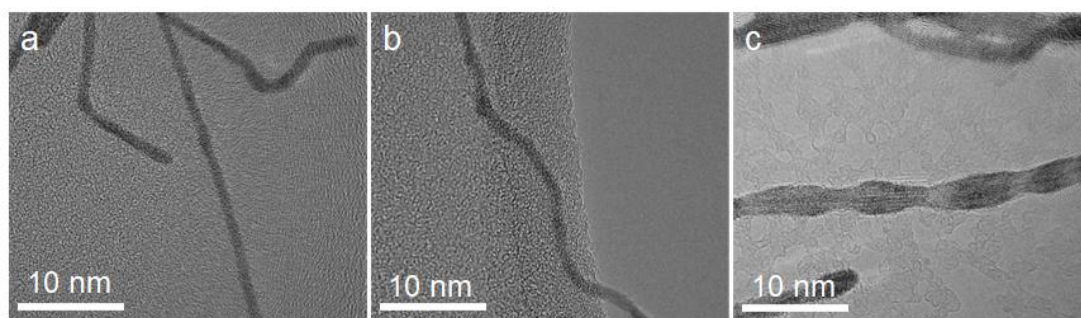


Figure S3 a, b, c) TEM image of Pt NWs/C, PtNi NWs/C, PtNiMo NWs/C.

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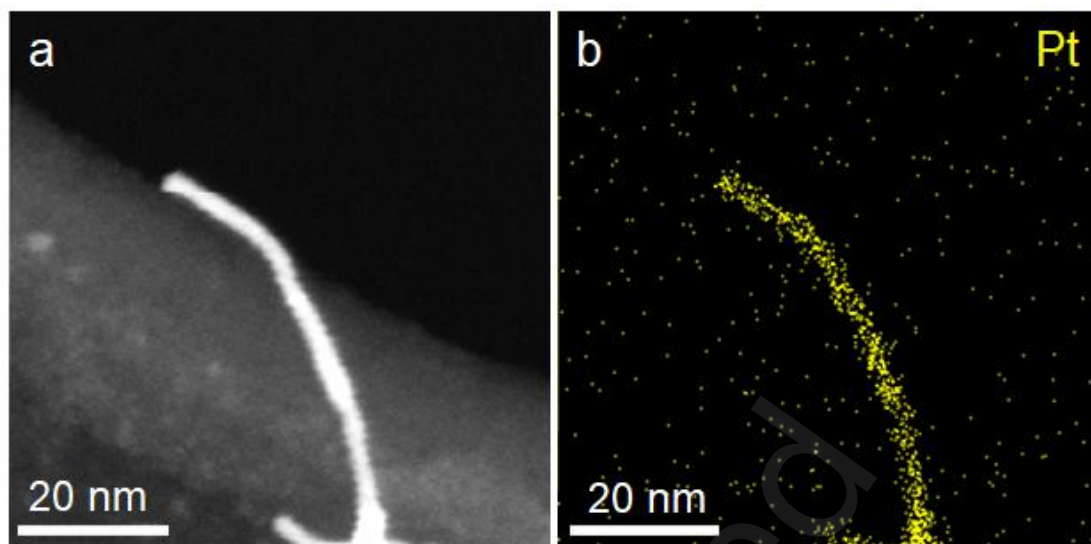


Figure S4 a) HAADF-STEM images of Pt NWs/C. b) EDX elemental mappings of Pt NWs/C.

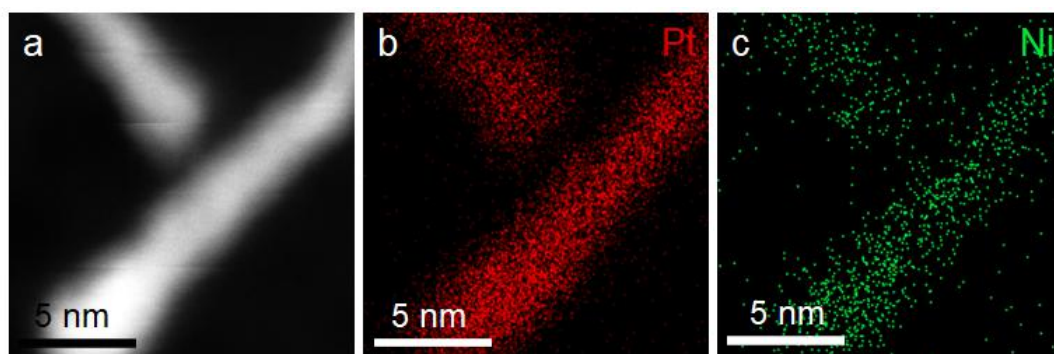


Figure S5 a) HAADF-STEM images of PtNi NWs/C. b, c) EDX elemental mappings of PtNi NWs/C.

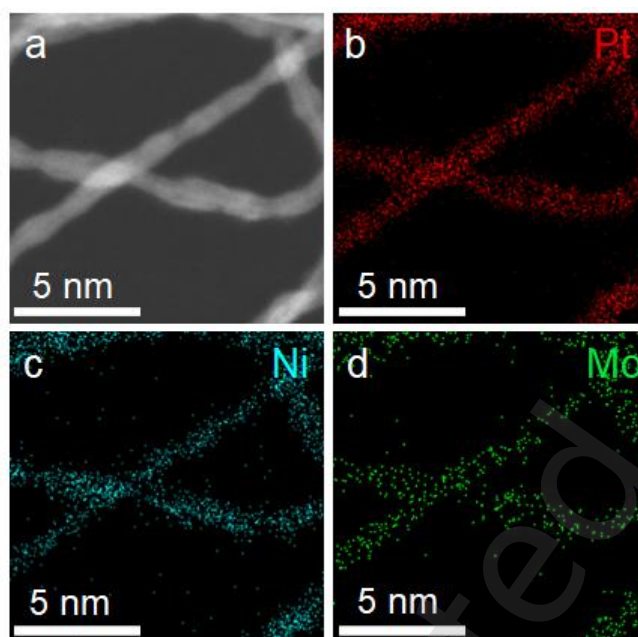


Figure S6 a) HAADF-STEM images of PtNiMo NWs/C. b, c, d) EDX elemental mappings of PtNiMo NWs/C.

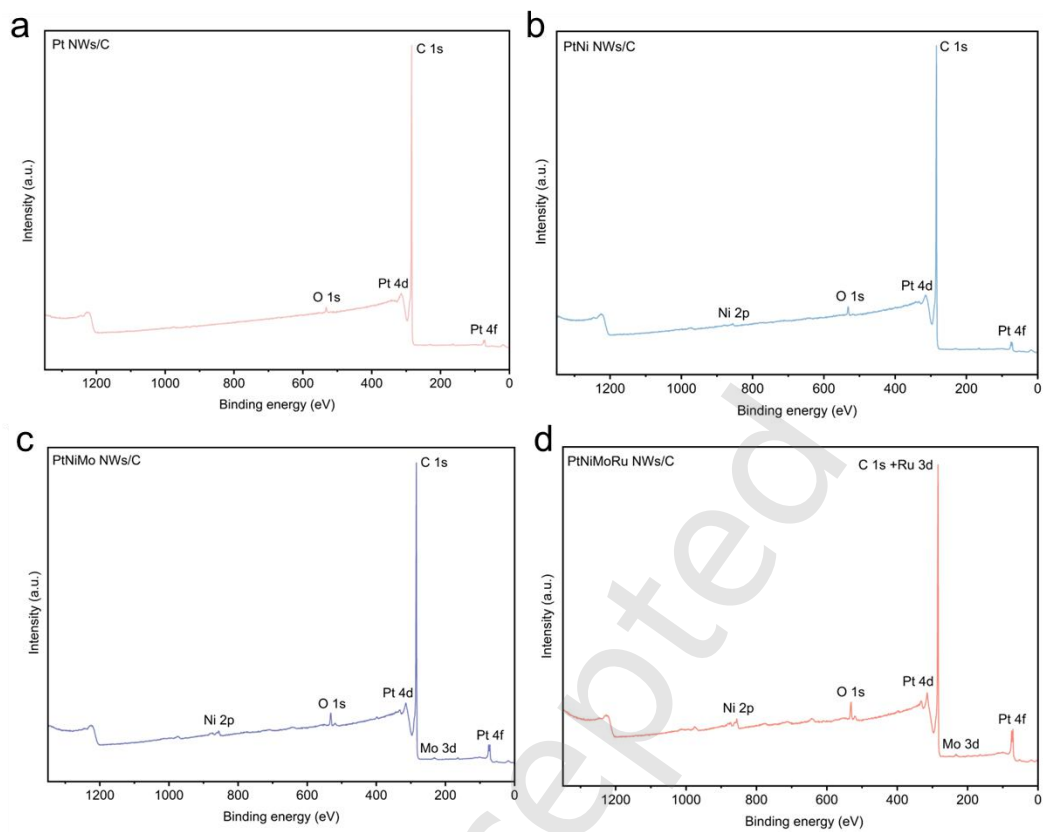


Figure S7 a) XPS full spectrum of Pt NWs/C. b) XPS full spectrum of PtNi NWs/C. c) XPS full spectrum of PtNiMo NWs/C. d) XPS full spectrum of PtNiMoRu NWs/C.

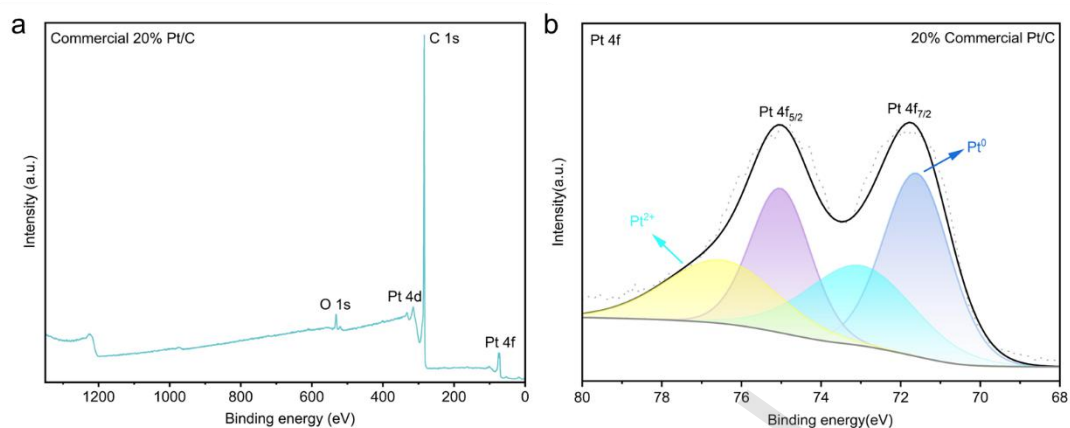


Figure S8 a) XPS full spectrum of commercial 20% Pt/C. b) High-resolution XPS spectra of Pt 4f for commercial 20% Pt/C.

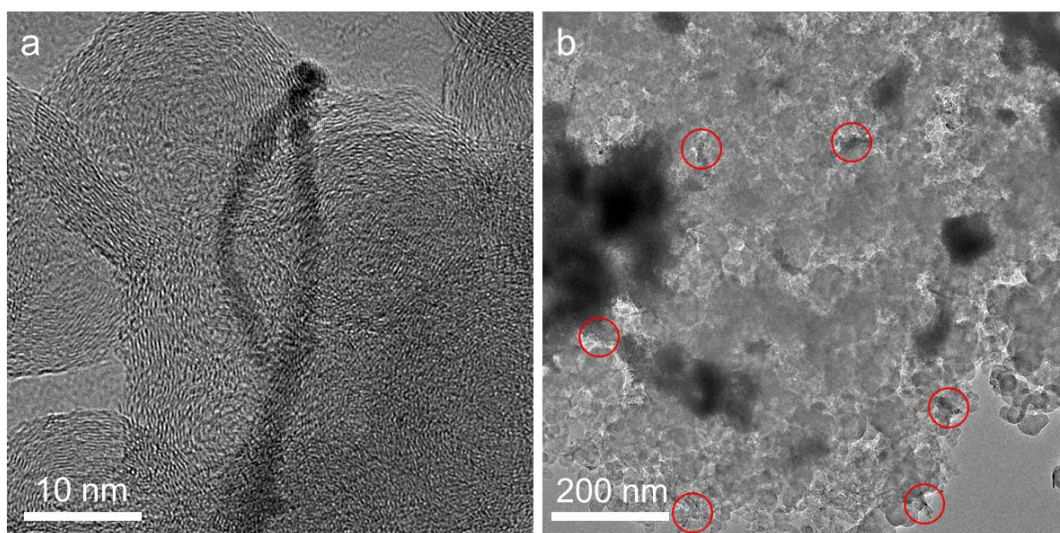


Figure S9 a, b) TEM image of PtNiMoRu NWs/C after 30k ADT.

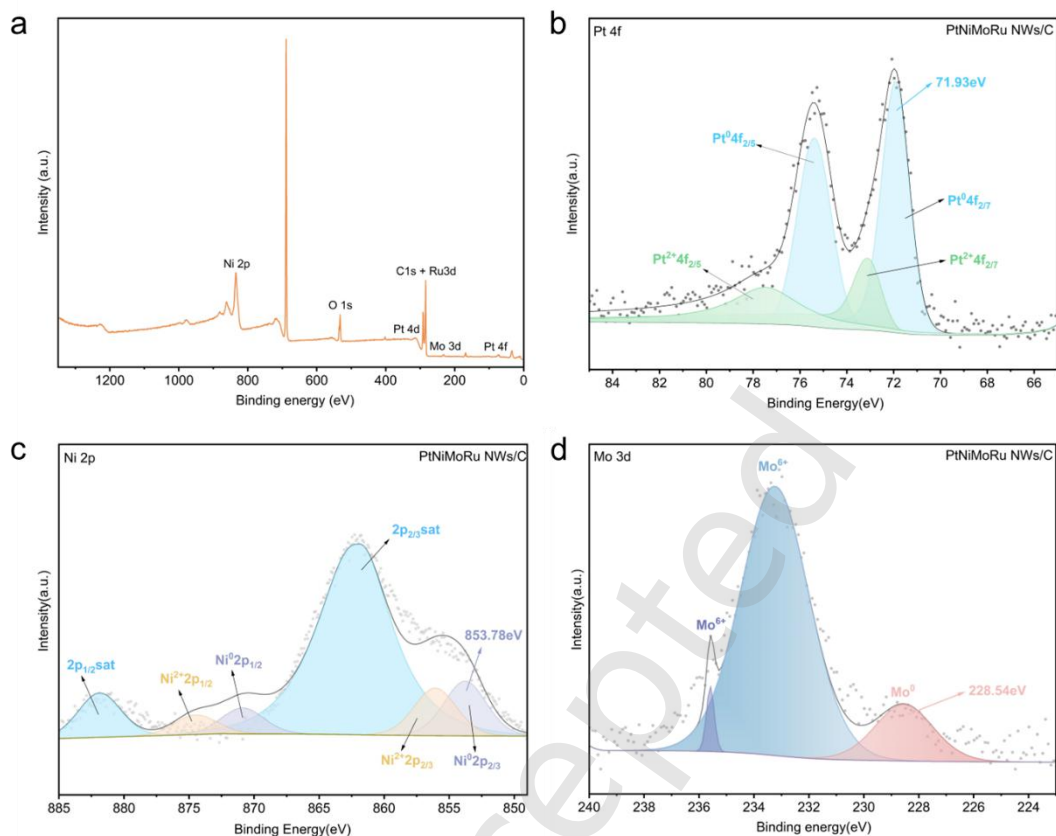


Figure S10 a) XPS full spectrum of PtNiMoRu NWs/C after 30k ADT. b, c, d) High-resolution XPS spectra of Pt 4f, Ni 2p, Mo 3d for PtNiMoRu NWs/C after 30k ADT.

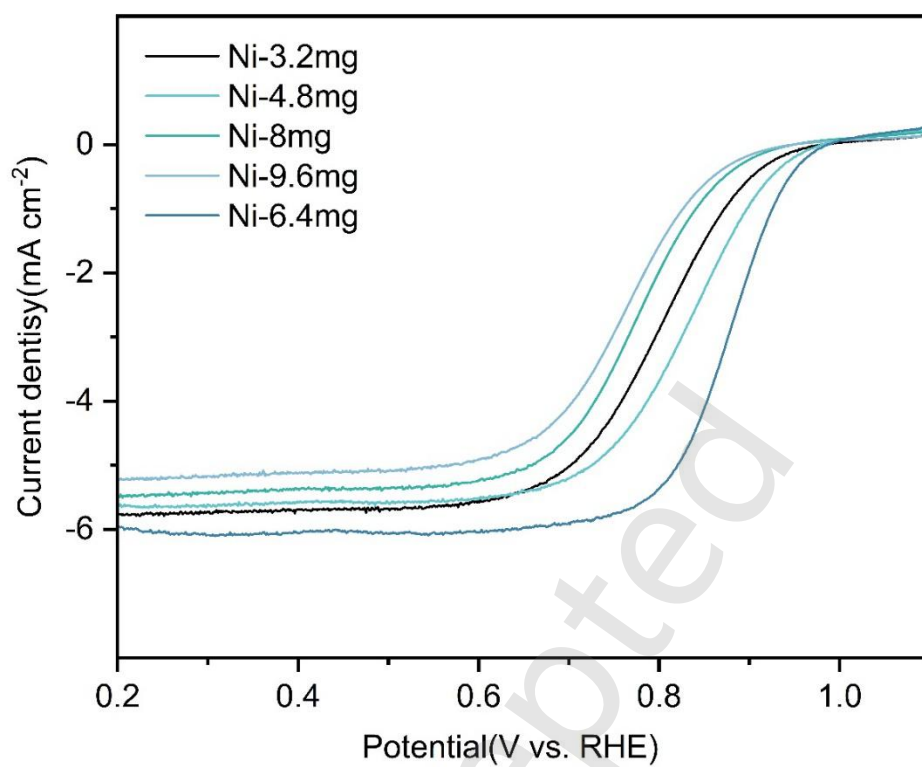


Figure S11 The LSV plots of PtNiMoRu NWs/C catalysts synthesized with different Ni precursor loading amounts.

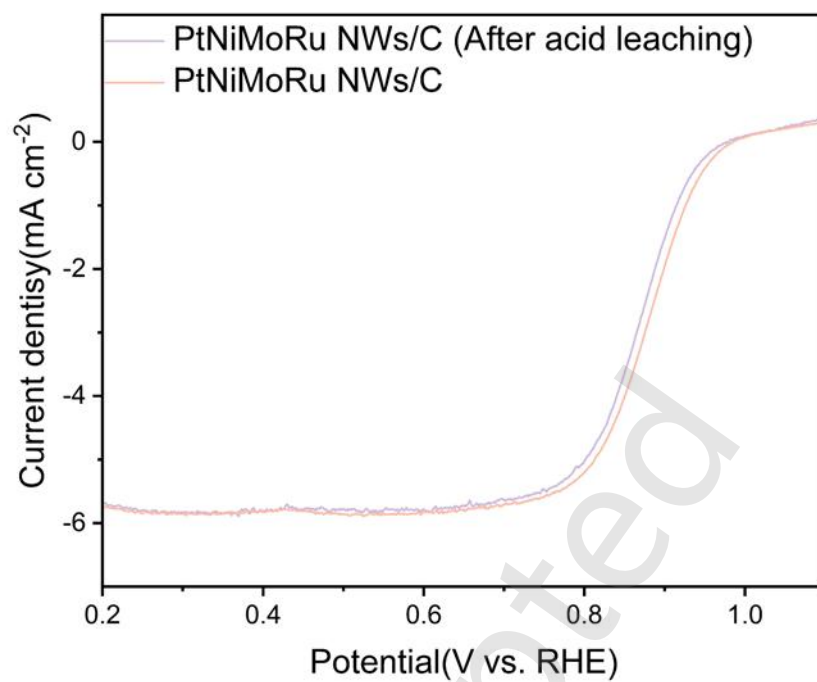


Figure S12 Comparison of LSV curves for PtNiMoRu NWs/C catalyst before and after acid leaching.

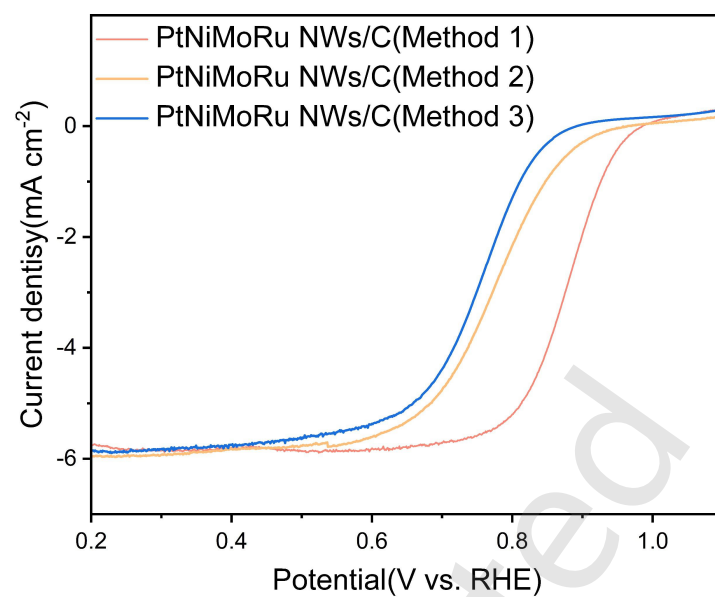


Figure S13 The LSV plots of PtNiMoRu NWs/C catalysts prepared by different gas-permeation methods

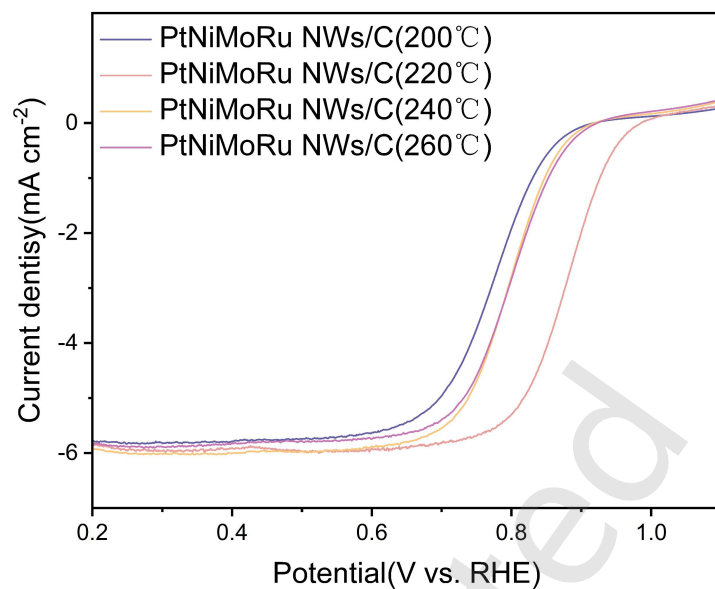


Figure S14 The LSV plots of PtNiMoRu NWs/C catalysts prepared by different temperature

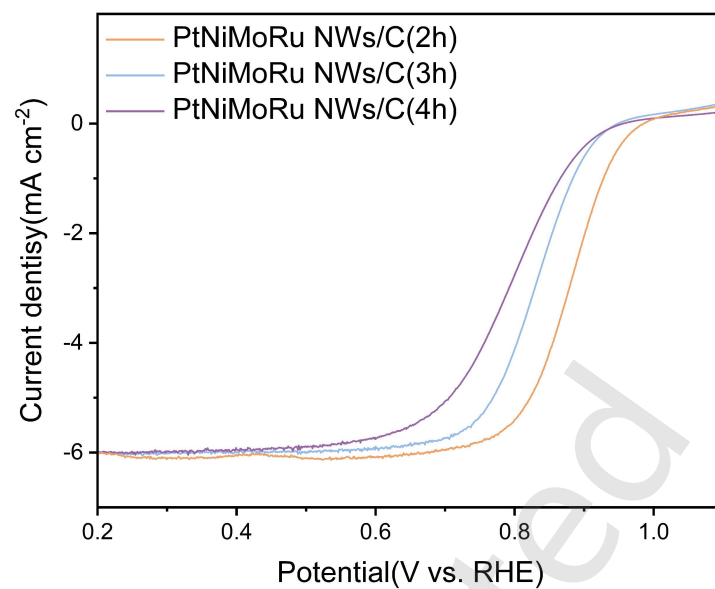


Figure S15 The LSV plots of PtNiMoRu NWs/C catalysts prepared by different reaction time

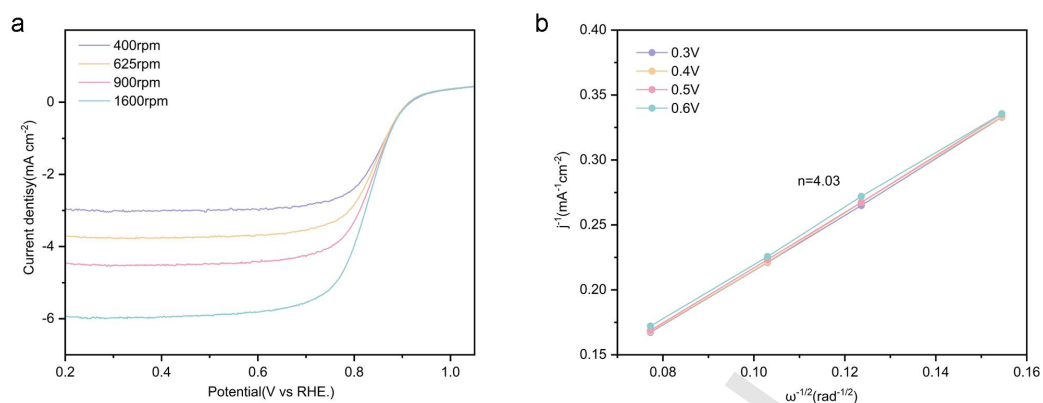


Figure S16 a) Polarization curves of commercial 20% Pt/C at different rotating speeds from 400 to 1600 rpm, b) corresponding Koutecky-Levich plot.

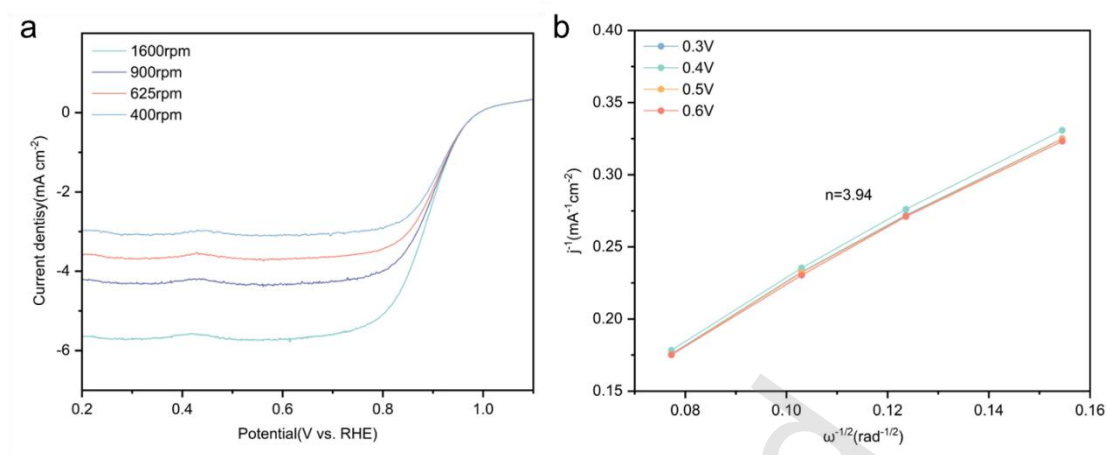


Figure S17 a) Polarization curves of PtNiMoRu NWs/C at different rotating speeds from 400 to 1600 rpm, b) corresponding Koutecky-Levich plot.

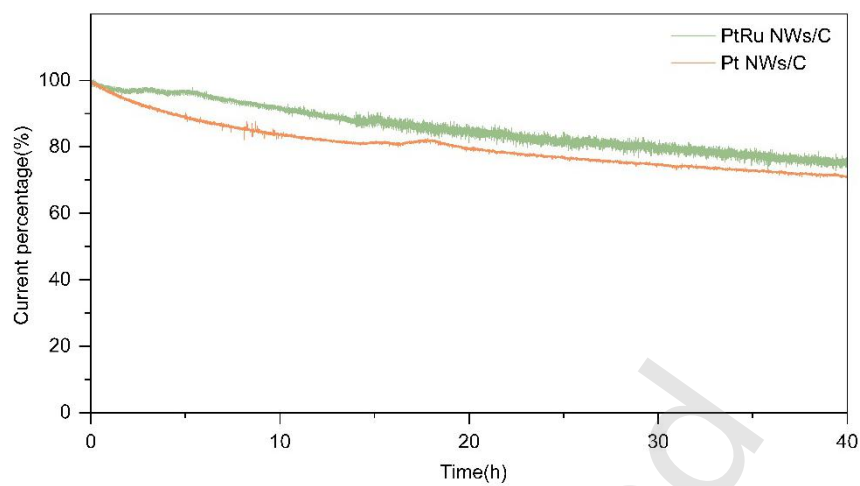


Figure S18 Chronoamperometry response of PtRu NWs/C and Pt NWs/C catalyst operated at 0.8 V versus RHE.

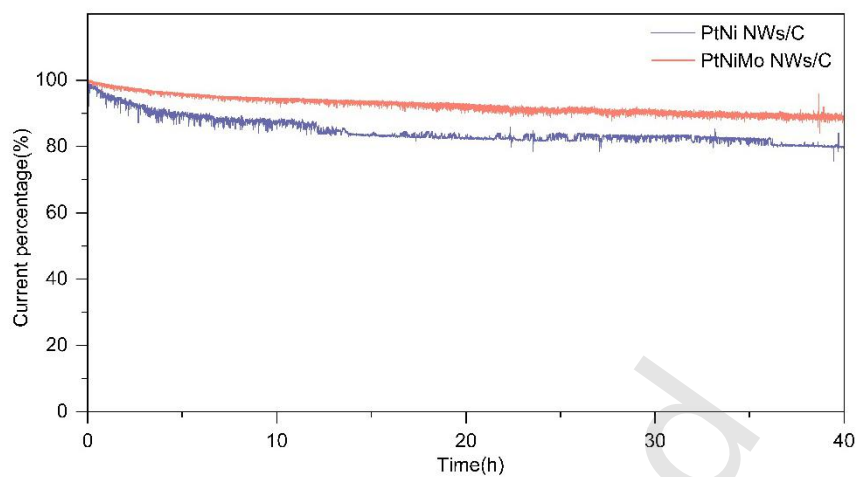


Figure S19 Chronoamperometry response of PtNi NWs/C and PtNiMo NWs/C catalyst operated at 0.8 V versus RHE.

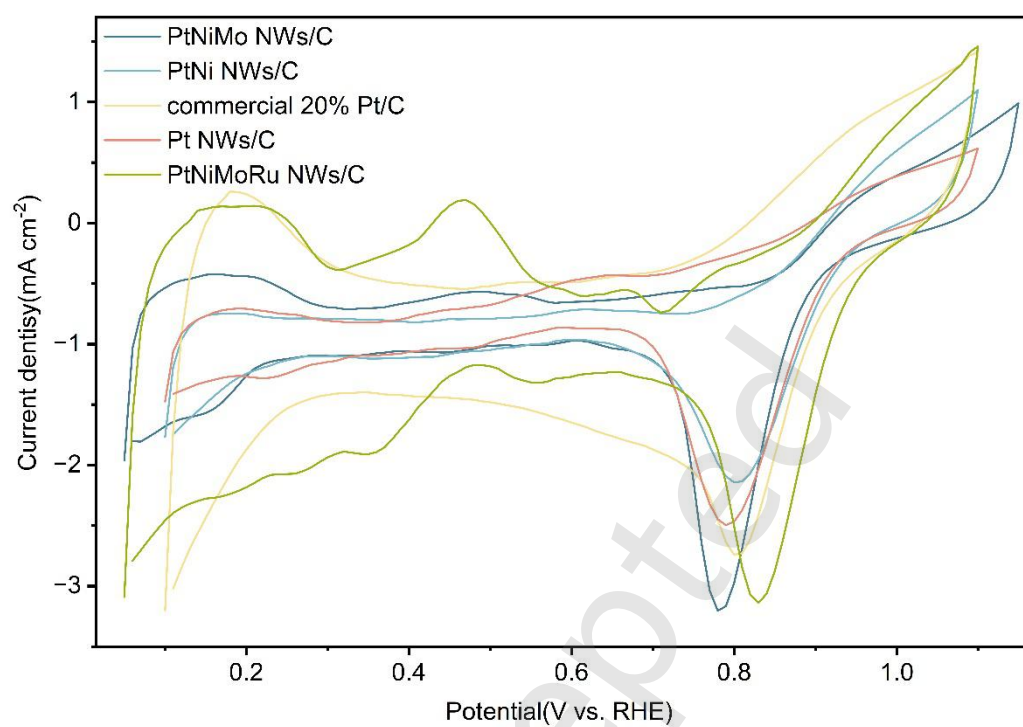


Figure S20 CV curves of Pt NWs/C, PtNi NWs/C, PtNiMo NWs/C, PtNiMoRu NWs/C and commercial 20% Pt/C catalysts.

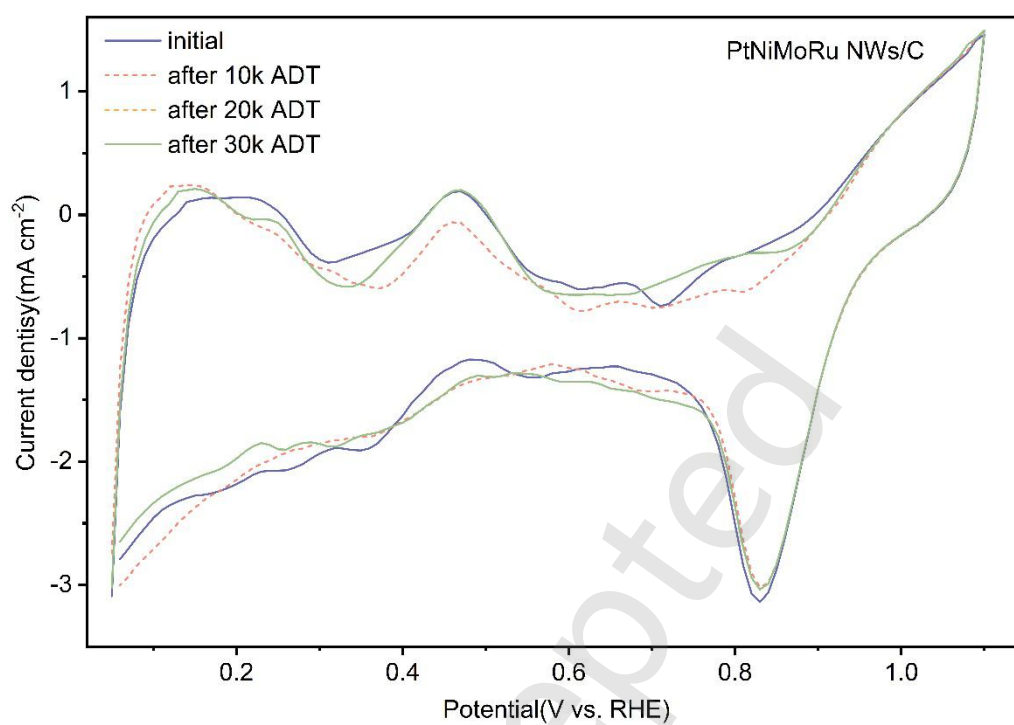


Figure S21 CV curves of PtNiMoRu NWs/C catalyst before and after ADT of different cycles.

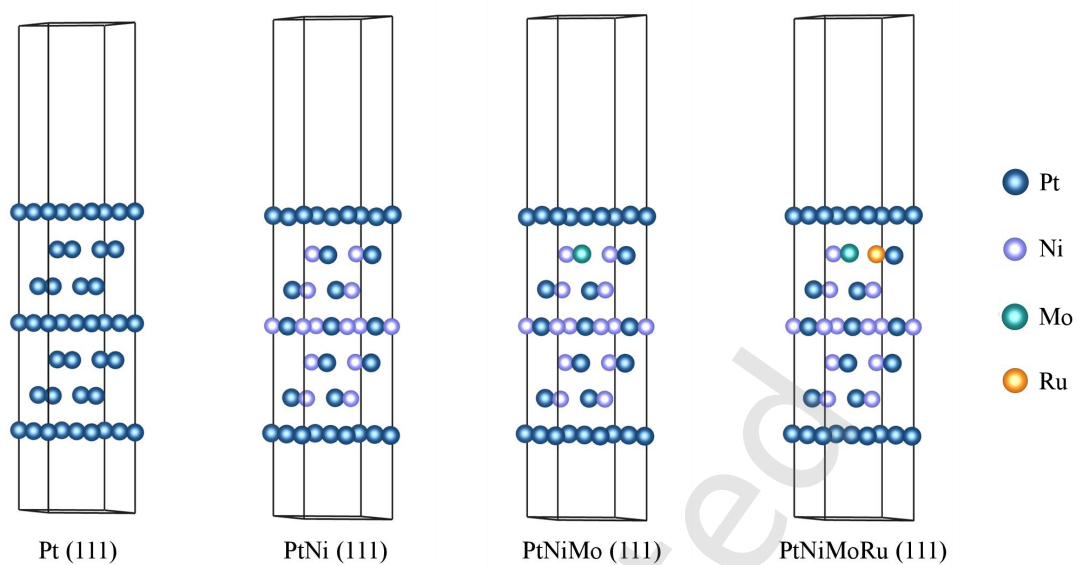


Figure S22 The theoretical model structures of Pt (111), PtNi (111), PtNiMo (111), PtNiMoRu (111) slabs.

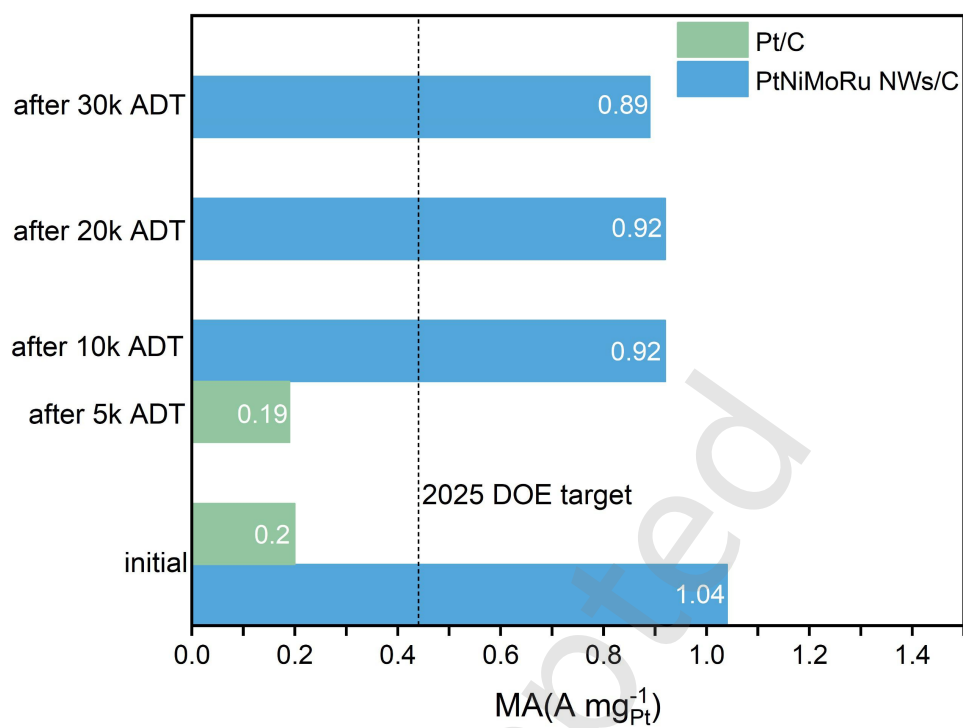


Figure S23 Mass activity of PtNiMoRu NWs/C and commercial 20% Pt/C before and after ADT.

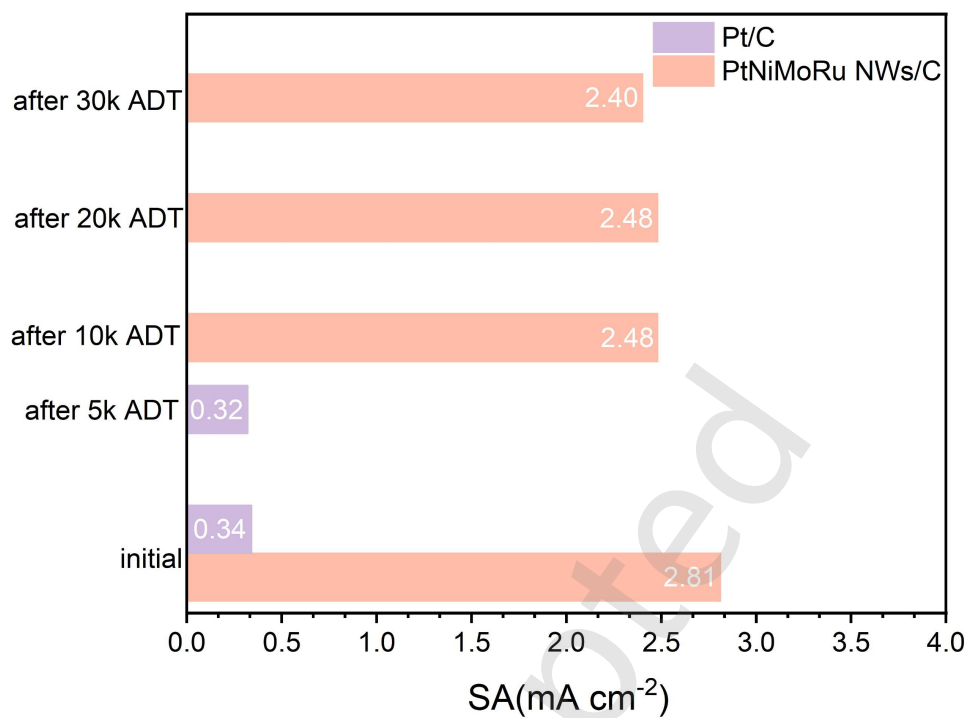


Figure S24 Specific activity of PtNiMoRu NWs/C and commercial 20% Pt/C before and after ADT.

Table S1. The mass fractions and atomic ratios of different elements obtained via ICP-OES testing for the four catalysts

catalysts	Mass fraction percentage(wt%)	Metal atom ratio(Using platinum atoms as a unit of calculation)
PtNiMoRu NWs/C	Pt: 8.67	1
	Ni: 2.22	0.84
	Mo: 0.33	0.068
	Ru: 0.05	0.011
PtNiMo NWs/C	Pt: 8.71	1
	Ni: 2.16	0.82
	Mo: 0.41	0.09
PtNi NWs/C	Pt: 9.33	1
	Ni: 2.18	0.787
Pt NWs/C	Pt: 8.37	1

Table S2. Testing of four catalysts using ICP-OES to measure Pt and Ni leaching in electrolyte after 40h stability testing

catalysts	Metal element leaching(mg/L)
Pt NWs/C (Pt)	0.00
PtRu NWs/C (Pt)	0.00
PtNi NWs/C (Ni)	0.1764
PtNiMo NWs/C (Ni)	0.1036

Table S3. Summary of activity and durability for recently reported Pt-based catalysts in acidic oxygen reduction environment.

Materials	$E_{1/2}$ (V vs RHE.)	MA @ 0.9 V [A mg _{Pt} ⁻¹]	Ref.
PtNiMoRu NWs/C	0.885	1.04	This work
PtNiMo NWs/C	0.831	0.32	
PtNi NWs/C	0.853	0.61	
Pt NWs/C	0.825	0.51	
AuPt	0.87	0.31	1
Pt-Ni/C	0.873	0.64	2
Pt-Ni@PtD/G	0.829	0.06	3
Pt/TOMS	0.860	0.06	4
Pt/Nb-TiO ₂	0.854	0.28	5
Pt-SnO ₂ /C	0.875	0.46	6
Pt@Pt-SAC	0.877	0.33	7
PtMoCeO _x -NAs	0.884	0.39	8
PtZn-IMC@NC	0.847	0.81	9
O-PtCo-FeNC	0.86	1.34	10
PtCu NTs	0.864	0.105	11
O-PtMn ₃ /NCNT	0.88	0.22	12
Pt ₃ Fe/SWCNT	0.885	/	13
Pt/Fe, N-HG	0.88	0.208	14
Pt ₃ Fe/Fe ₃ C-NCB	0.887	0.97	15

Table S4. Peak power comparison of proton exchange membrane fuel cells using different Pt-based catalysts.

Catalysts	Anodic / Cathodic loading [$\text{mg}_{\text{Pt}} \text{ cm}^{-2}$]	Peak power density [W cm^{-2}]	Ref.
PtNiMoRu NWs/C	0.025/0.1	1.18	This work
commercial 20% Pt/C	0.025/0.1	1.14	
Pt-SnS ₂ /SnO ₂	0.025/0.1	0.7	[16]
Pt@Fe-N-OMC-2	0.2/0.2	1.05	[17]
Pt ₁ Fe ₁ @Fe _{0.5} NC-900	0.1/0.065	1.05	[18]
Pt-Ni UHT	0.16/0.066	0.79	[19]
Pt-Co UHT	0.16/0.066	0.77	[19]
PtFe-block copolymers	0.2/0.01	0.96	[20]
Pt-CNF/TiO ₂	0.4/0.4	0.99	[21]

Supplementary References

- [1] X. Weng, Y. Liu, K.-K. Wang, J.-J. Feng, J. Yuan, A.-J. Wang, Q.-Q. Xu, *Int. J. Hydrogen Energy* **2016**, 41, 18193.
- [2] W. Lei, M. Li, L. He, X. Meng, Z. Mu, Y. Yu, F. M. Ross, W. Yang, *Nano Res.* **2020**, 13, 638.
- [3] X. Lyu, Y. Jia, X. Mao, D. Li, G. Li, L. Zhuang, X. Wang, D. Yang, Q. Wang, A. Du, X. Yao, *Adv. Mater.* **2020**, 32, 2003493.
- [4] R. Alipour Moghadam Esfahani, I. I. Ebralidze, S. Specchia, E. B. Easton, *J. Mater. Chem. A.* **2018**, 6, 14805.
- [5] K.-J. Noh, I. Nam, J. W. Han, *Appl. Surf. Sci.* **2020**, 521, 146330.
- [6] J. Guan, Y. Zan, R. Shao, J. Niu, M. Dou, B. Zhu, Z. Zhang, F. Wang, *Small* **2020**, 16, 2005048.
- [7] B. Liu, R. Feng, M. Busch, S. Wang, H. Wu, P. Liu, J. Gu, A. Bahadoran, D. Matsumura, T. Tsuji, D. Zhang, F. Song, Q. Liu, *ACS Nano* **2022**, 16, 14121.
- [8] P. Wang, H. Cui, C. Wang, *Chem. Eng. J.* **2022**, 429, 132435.
- [9] P. Wang, K. Chen, J. Chen, G. Wang, W. Pan, Z. Wen, *Adv. Funct. Mater.* **2024**, 34, 2408267.
- [10] K. Chen, J. Huang, J. Chen, J. Gao, Z. Lu, X. Liu, S. Lan, G. Jia, S. Ci, Z. Wen, *Energy Environ. Sci.* **2025**, 18, 6732.
- [11] X. Du, S. Sun, G. Ma, H. Yu, M. Wang, Z. Lu, X. Yu, L. Li, X. Zhang, X. Yang, *Int. J. Hydrogen Energy* **2022**, 47, 6217.
- [12] B. Zhang, X. Zhou, Z. Wu, J. Huang, L. Bai, M. Sun, *ACS Appl. Nano Mater.* **2025**, 8, 10633.
- [13] J. He, C. Chen, H. Yu, Y. Zhao, M. Xu, T. Xiong, Q. Lu, Z. Yu, K. Tai, J. Tan, C. Liu, *J. Mater. Sci. Technol.* **2025**, 212, 139.
- [14] Z. Gao, Z. Chen, X. Zhan, L. Zhou, Y. Xie, X. Yang, J. Tian, G. Zhang, S. Sun, X. Tong, *ACS Appl. Nano Mater.* **2023**, 6, 10521.
- [15] N. Zhou, Y. Li, *Int. J. Hydrogen Energy* **2023**, 48, 13591.
- [16] Z. Lin, J. Liu, S. Li, J. Liang, X. Liu, L. Xie, G. Lu, J. Han, Y. Huang, Q. Li, *Adv. Funct. Mater.* **2023**, 33, 2211638.

- [17] K. Wang, H. Yang, Q. Wang, J. Yu, Y. He, Y. Wang, S. Song, Y. Wang, *Adv. Energy Mater.* **2023**, 13, 2204371.
- [18] Y. Wu, L. Chen, S. Geng, Y. Tian, R. Chen, K. Wang, Y. Wang, S. Song, *Adv. Funct. Mater.* **2024**, 34, 2307297.
- [19] J. Liu, S. Liu, F. Yan, Z. Wen, W. Chen, X. Liu, Q. Liu, J. Shang, R. Yu, D. Su, J. Shui, *J. Am. Chem. Soc.* **2022**, 144, 19106.
- [20] J. Choi, Y. J. Lee, D. Park, H. Jeong, S. Shin, H. Yun, J. Lim, J. Han, E. J. Kim, S. S. Jeon, Y. Jung, H. Lee, B. J. Kim, *Energy Environ. Sci.* **2020**, 13, 4921.
- [21] C. Wang, X. Chen, B. Wang, M. Huang, B. Wang, Y. Jiang, R. S. Ruoff, *ACS Nano* **2018**, 12, 5816.