

Liquid gallium-mediated vapor deposition induces strong metal-support interaction for ultrafine platinum nanocatalysts in high-current-density alkaline hydrogen evolution

Chunyan Yang^{1,2}, Yongyong Cao³(✉), Zheng Qin¹, Xu Han¹, Wenrui Yue¹, Hongwei Gu¹(✉), Jian-Ping Lang^{1,2}(✉)

¹ College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

² State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

³ College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing 314001, China

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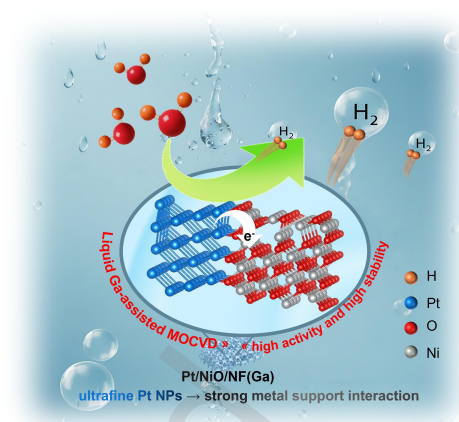
Liquid gallium-mediated vapor deposition induces strong metal-support interaction for ultrafine platinum nanocatalysts in high-current-density alkaline hydrogen evolution

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¹ College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

² State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.

³ College of Biological, Chemical Science and Engineering, Jiaying University, Jiaying 314001, China



A liquid gallium-mediated vapor deposition strategy enables the controlled growth of ultrafine Pt nanoparticles (1.77 nm) on a three-dimensional NiO/NF framework. The resulting strong metal-support interaction optimizes interfacial electronic structure, delivering exceptional alkaline hydrogen evolution performance and durable ampere-level operation in anion-exchange membrane water electrolysis.

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¹ College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

² State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

³ College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing 314001, China

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✉ Address correspondence to Jian-Ping Lang, jplang@suda.edu.cn; Hongwei Gu, hongwei@suda.edu.cn; Yongyong Cao, cyy@zjxu.edu.cn.

ABSTRACT

Engineering strong metal-support interaction (SMSI) is a powerful strategy for enhancing the activity and durability of platinum catalysts under industrial alkaline hydrogen evolution conditions, yet controllable fabrication of such interfaces remains challenging. Here, we report a liquid gallium-mediated vapor deposition approach that induces pronounced SMSI between ultrafine platinum nanoparticles and nickel oxide supported on nickel foam. The liquid Ga layer acts as a dynamic transport medium that regulates precursor diffusion and decomposition, enabling controlled nucleation of 1.77 nm Pt nanoparticles and promoting interfacial electronic coupling with the NiO support. Spectroscopic analysis and theoretical calculations reveal charge redistribution across the Pt-NiO interface, leading to modified hydrogen adsorption energetics and a reduced water dissociation energy barrier. The resulting catalyst achieves an overpotential of 20 mV at 10 mA cm⁻² and sustains stable operation for 800 h at 500 mA cm⁻² in alkaline electrolyte. When implemented in an anion-exchange membrane water electrolyzer, the catalyst maintains ampere-level current densities with excellent durability. This work demonstrates liquid metal-mediated vapor deposition as a versatile platform for inducing strong metal-support interaction in ultrafine electrocatalysts for high-current alkaline energy conversion.

KEYWORDS

liquid gallium, metal-organic chemical vapor deposition, alkaline hydrogen evolution reaction, strong metal-support interaction

1 Introduction

Platinum (Pt) remains the benchmark electrocatalyst for the hydrogen evolution reaction (HER) owing to its near-optimal hydrogen adsorption free energy ($\Delta G_{\text{H}^+} \approx 0$) [1, 2]. Nevertheless, its practical deployment in alkaline water electrolysis is restricted by high cost, limited elemental abundance, suboptimal alkaline kinetics, and structural degradation under prolonged high-current operation [3-5]. In particular, alkaline HER is kinetically hindered by the additional water dissociation step, making interfacial electronic structure and catalyst stability critical determinants of performance [6, 7]. Maximizing Pt utilization while maintaining long-term durability therefore represents a central challenge in catalyst design.

Reducing Pt to the nanoscale is an effective strategy to enhance atomic utilization and increase active-site density [8-10]. However, ultrafine Pt nanoparticles are thermodynamically prone to aggregation, Ostwald ripening, and surface reconstruction, especially under elevated temperature or high-current electrochemical conditions [11-13]. These phenomena diminish catalytic activity and stability over time [14, 15]. Beyond particle size control, engineering strong metal-support interaction (SMSI) has emerged as a powerful approach to stabilize nanoscale metals and modulate their electronic structure [16, 17]. Properly designed SMSI can suppress nanoparticle migration, alter charge

distribution at the interface, and optimize adsorption energetics of reaction intermediates [18, 19]. Achieving controllable SMSI formation during nanoparticle deposition, however, remains a significant materials engineering challenge.

Metal-organic chemical vapor deposition (MOCVD) offers precise control over vapor-phase precursor delivery and thin-film formation, making it an attractive method for preparing supported metal nanoparticles [20-22]. The technique allows relatively low deposition temperatures, uniform film growth and high reproducibility [23-27]. Nevertheless, conventional MOCVD processes often suffer from uncontrolled precursor transport, localized supersaturation, and rapid decomposition kinetics, which can result in uneven nucleation, particle coalescence, and weak metal-support coupling [28-30]. Moreover, achieving uniform deposition on complex three-dimensional substrates and inducing robust interfacial electronic interaction during growth are difficult to realize using traditional vapor deposition approaches.

Liquid metals offer a compelling strategy for regulating interfacial growth processes owing to their distinctive physicochemical properties. Among them, liquid gallium (Ga) exhibits high fluidity, excellent thermal conductivity, and the ability to form a self-limiting surface oxide layer [31-34]. The dynamic and adaptive surface of liquid Ga can modulate mass transport, confine precursor diffusion, and alter nucleation thermodynamics, thereby influencing crystal growth pathways.

Recent studies have demonstrated that liquid Ga can serve as a sealing layer to direct the formation of non-hollow carbon nanotubes on zeolitic imidazolate framework-67 (ZIF-67) [35] and as a growth platform for high-quality MoP single crystals [36]. These examples highlight its capability to regulate morphology and nucleation dynamics. Collectively, these characteristics suggest that liquid Ga may act as an effective mediator in vapor-phase deposition, enabling controlled nanoparticle nucleation and strengthened metal-support interactions.

Here, we report a liquid gallium-mediated MOCVD strategy to induce strong metal-support interaction between ultrafine Pt nanoparticles and nickel oxide supported on nickel foam (NiO/NF) (Figure 1). The liquid Ga layer acts as a dynamic transport-regulating medium that modulates precursor diffusion pathways and decomposition kinetics, enabling uniform nucleation of Pt nanoparticles with an average diameter of 1.77 nm. More importantly, this growth environment promotes pronounced interfacial electronic coupling between Pt and NiO, as evidenced by spectroscopic characterization and supported by density functional theory calculations. The induced SMSI leads to charge redistribution at the Pt-NiO interface, lowering the water dissociation energy barrier and optimizing hydrogen adsorption energetics. As a result, the Pt/NiO/NF(Ga) catalyst delivers an overpotential of 20 mV at 10 mA cm⁻² and sustains stable operation for extended periods under high-current conditions in alkaline electrolyte. When integrated into an anion-exchange membrane water electrolyzer, the catalyst maintains ampere-level current densities with excellent durability. This work establishes liquid metal-mediated vapor deposition as a versatile platform for controllably inducing strong metal-support interaction in ultrafine electrocatalysts, providing new insights into interface engineering for high-current alkaline energy conversion.

2 Experimental

2.1 Catalyst preparation

Synthesis of acid-etched NF: nickel foam (2 × 2 cm) was ultrasonically cleaned in acetone and ethanol, followed by chemical etching in 3 M HCl at 60 °C for 30 min. After etching, the foam was thoroughly rinsed with deionized water and dried at 60 °C for 12 h.

Synthesis of NiO/NF: the acid-etched NF was placed in a 5 mL crucible with a cover and calcined in a muffle furnace at 290 °C for 4 h under ambient air atmosphere. After natural cooling to room temperature, NiO/NF was obtained.

Synthesis of Pt/NiO/NF: 30 mg of Pt(acac)₃ was placed at the bottom of a 5 mL crucible, which was subsequently positioned inside a larger 10 mL crucible. The acid-etched NF was placed above the small crucible without direct contact with the precursor. The larger crucible was sealed with a lid and heated in a muffle furnace at 290 °C for 4 h under ambient air atmosphere, followed by natural cooling to room temperature to yield Pt/NiO/NF.

Synthesis of Pt/NiO/NF(Ga): 30 mg of Pt(acac)₃ was placed at the bottom of a 5 mL crucible. Liquid gallium (1 mL) was added to fully cover the precursor. The small crucible was then placed inside a 10 mL crucible, and the acid-etched NF was positioned above it. After sealing the outer crucible, the assembly was heated at 290 °C for 4 h in a muffle furnace under ambient air atmosphere and naturally cooled, affording Pt/NiO/NF(Ga).

Synthesis of Pt/NF(Ga): the same procedure as described above

was followed, except that untreated NF was used instead of NiO/NF. The obtained sample was denoted as Pt/NF(Ga).

Effect of gallium volume: to investigate the influence of gallium content, 30 mg of Pt(acac)₃ were covered with different volumes of liquid Ga (2 mL and 3 mL, corresponding to approximately 1.0 cm and 1.5 cm thickness, respectively). The subsequent thermal treatment procedure was identical to that described above. The resulting samples were labeled Pt/NiO/NF(Ga)-2 mL and Pt/NiO/NF(Ga)-3 mL.

Effect of Pt precursor mass: different amounts of Pt(acac)₃ (10, 20, and 40 mg) were used while maintaining 1 mL of liquid Ga. The remaining synthesis procedure was unchanged. The products were designated as Pt/NiO/NF(Ga)-10 mg, Pt/NiO/NF(Ga)-20 mg, and Pt/NiO/NF(Ga)-40 mg, respectively.

Effect of thermal treatment time: to study the influence of heating duration, the reaction temperature was maintained at 290 °C for 1, 2, 3, and 6 h using 30 mg Pt(acac)₃ and 1 mL Ga. All other conditions were identical. The samples were denoted as Pt/NiO/NF(Ga)-1 h, Pt/NiO/NF(Ga)-2 h, Pt/NiO/NF(Ga)-3 h, and Pt/NiO/NF(Ga)-6 h.

Synthesis of Pt/CC(Ga): carbon cloth (2 × 2 cm) was used as the substrate following the same Ga-mediated deposition procedure (30 mg Pt(acac)₃, 1 mL Ga, 290 °C for 4 h). The obtained material was denoted as Pt/CC(Ga).

Synthesis of Pt/Al₂O₃(Ga): Al₂O₃ ceramic plates were used as substrates under identical synthesis conditions (30 mg Pt(acac)₃, 1 mL Ga, 290 °C for 4 h). The resulting sample was denoted as Pt/Al₂O₃(Ga).

Recycling of gallium: the liquid gallium used in the above procedures was collected after cooling and can be recycled and reused without noticeable loss of performance.

2.2 Characterization instrument

Powder X-ray diffraction (PXRD) patterns were collected on an X'Pert-Pro MPD diffractometer (PANalytical, Netherlands) using Cu K α radiation ($\lambda = 1.540598$ Å) operated at 40 kV and 25 mA. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), high-angle annular dark-field scanning TEM (HAADF-STEM), selected area electron diffraction (SAED), and elemental mapping analyses were performed on a Talos F200X G2 field-emission transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images were obtained using a Regulus-8230 field-emission scanning electron microscope at an accelerating voltage of 15 kV. Thermogravimetric analysis (TGA) was conducted on an SDT Q600 thermogravimetric analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer. Raman spectra were recorded using a LabRAM Soleil confocal Raman microscope equipped with a 532 nm excitation laser. The contents of Ni and Pt were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian 710-ES instrument. Ni K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected using an EasyXAFS 300+ system equipped with a 1200 W X-ray tube.

2.3 Electrochemical measurement

Electrochemical measurements were performed using a CHI 660E electrochemical workstation (Chenhua Instruments, Shanghai, China) in 1 M KOH employing a standard three-electrode configuration. The as-prepared samples (0.5 × 0.5 cm²) were used directly as the working electrodes, while a Ag/AgCl (saturated KCl)

electrode and a carbon rod served as the reference and counter electrodes, respectively. After each experiment, the condition of the reference electrode was routinely checked by measuring the potential difference between the working Ag/AgCl reference electrode and a separate Ag/AgCl electrode. The latter was not used for any electrochemical measurements but served solely as a control to verify the stability of the reference electrode. No noticeable change in the potential difference was observed throughout the experiments, indicating that the reference electrode remained stable and showed no signs of degradation or damage. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale according to:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}$$

All potentials were corrected for iR compensation unless otherwise stated. The overpotential (η) was calculated using:

$$\eta = E_{\text{RHE}} - 1.023 \text{ V}$$

Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s^{-1} in 1 M KOH . Stability was evaluated by chronopotentiometry at a current density of 500 mA cm^{-2} . Electrochemical impedance spectroscopy (EIS) measurements were performed at the potential corresponding to a current density of 100 mA cm^{-2} using an AC perturbation amplitude of 5 mV over the frequency range from 100 kHz to 0.1 Hz . The electrochemically active surface area (ECSA) was estimated from the double-layer capacitance (C_{dl}), determined by cyclic voltammetry (CV) in the non-Faradaic potential region (-0.3 to -0.4 V vs. RHE). CV curves were recorded at scan rates of 10 , 20 , 40 , 60 , 80 , and 100 mV s^{-1} . The C_{dl} value was obtained from the slope of the linear fit of half the current density difference ($\Delta j/2$) at -0.35 V vs. RHE as a function of scan rate. The metal loading and molar amounts of Ni and Pt on the electrodes were calculated based on ICP-OES measurements.

2.4 Anion exchange membrane water electrolyzer (AEMWE) device and measurement

An AEMWE was employed to evaluate the electrocatalytic performance under practical operating conditions. The device consisted of end plates, stainless steel current collectors, NF, a membrane electrode assembly (MEA) support, and an anion exchange membrane (AEM, FAA-3-PK-130). The as-prepared Pt/NiO/NF(Ga) electrode was cut into $1 \times 1 \text{ cm}$ pieces (geometric area: 1 cm^2) and directly used as the cathode without additional binder treatment. The anode catalyst ink was prepared by dispersing 5 mg of IrO_2 and 5 mg of carbon powder in a mixed solvent containing $925 \mu\text{L}$ of isopropanol and $75 \mu\text{L}$ of Nafion solution ($5 \text{ wt}\%$), followed by ultrasonication for 1 h to obtain a homogeneous suspension. The resulting ink was uniformly drop-cast onto a $1 \times 1 \text{ cm}$ nickel foam substrate and dried under ambient conditions to form the anode catalyst layer. Prior to assembly, the AEM was pretreated in 1 M KOH solution to ensure complete ion exchange. The AEMWE cell was assembled in a sandwich configuration in the following order: end plate/current collector/anode/AEM/cathode/current collector/end plate, without hot-press treatment. Electrochemical measurements were conducted at 80°C using 1 M KOH as the electrolyte, which was continuously circulated at a flow rate of 20 mL min^{-1} . The cell was activated by performing 10 linear sweep voltammetry (LSV) cycles in the voltage range of 1.5 – 2.5 V , followed by potentiostatic operation at 1.85 V until the current variation was less than 2% per minute. Durability was evaluated by chronopotentiometry at a constant current density of $1,000 \text{ mA cm}^{-2}$ for an extended period,

and the corresponding cell voltage was recorded to assess operational stability.

2.4 Density Functional Theory (DFT) calculations

First-principles calculations were performed within the framework of density functional theory (DFT) using the Vienna ab initio Simulation Package (VASP) [37]. Core-valence interactions were described by the projector augmented-wave (PAW) method [38]. The exchange-correlation energy was treated using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [39, 40]. Long-range dispersion interactions were accounted for using Grimme's DFT-D3 correction scheme [41]. A plane-wave kinetic energy cutoff of 520 eV was employed. The electronic self-consistent field (SCF) calculations were converged to $1 \times 10^{-5} \text{ eV}$. Structural optimizations were performed until the residual forces on each atom were less than $0.05 \text{ eV \AA}^{-1}$. Brillouin-zone integrations were carried out using a $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh during geometry optimizations [42]. The k-point sampling and energy cutoff were verified to ensure adequate convergence of total energies. A vacuum region larger than $15 \text{ \AA}$ was introduced perpendicular to the slab surface to eliminate spurious interactions between periodic images. Transition states were identified using the climbing-image nudged elastic band (CI-NEB) method [43]. Multiple intermediate images were generated between the initial and final states to determine the minimum energy pathway, and the structures were optimized until the forces perpendicular to the reaction coordinate were sufficiently converged. Thermodynamic free energy changes for adsorption processes were evaluated using the computational hydrogen electrode (CHE) model [39]. Within this framework, the Gibbs free energy change was calculated as: $\Delta G = \Delta E + \Delta \text{EZPE} - T\Delta S$, where ΔE is the DFT-calculated adsorption energy, ΔEZPE is the zero-point energy correction, and ΔS represents the entropy contribution. The chemical potential of a proton-electron pair was referenced to one-half of that of molecular hydrogen under standard conditions.

3 Results and discussion

3.1 Liquid Ga-mediated vapor deposition and structural characterization

To investigate the regulatory effect of liquid Ga on the MOCVD process and the resulting material structure, two synthesis pathways were designed and compared. Initially, Pt/NiO/NF was prepared using conventional MOCVD. The platinum precursor, $\text{Pt}(\text{acac})_2$, was placed at the bottom of a small crucible, with acid-etched NF positioned above. This assembly was enclosed within a larger crucible, sealed with a lid, and subjected to thermal decomposition at 290°C (Figure S6b). Thermogravimetric analysis (TGA, Figure 2a) revealed that $\text{Pt}(\text{acac})_2$ undergoes significant mass loss between 160 – 270°C , forming metallic Pt and volatile decomposition products [21, 44, 45]. In this conventional setup, the gaseous species diffused in an uncontrolled manner, resulting in low transport efficiency and uneven deposition. The substrate exhibited nonuniform coverage, with large and irregular aggregates (Figures S8–S9), while substantial platinum and carbonaceous residues accumulated at the crucible bottom (Figures S10–S12). A pronounced “platinum mirror” appeared on the inner crucible wall, whereas no deposition occurred on the lid surface (Figure S7). These observations indicate that disordered vapor-phase transport in conventional MOCVD severely limits

uniform Pt deposition.

In contrast, introducing a liquid Ga layer as a physical confinement medium fundamentally altered the deposition process. By adding 1 mL of Ga (~0.5 cm thickness) onto Pt(acac)₂, while keeping other conditions unchanged, Pt/NiO/NF(Ga) was obtained (Figure 1a, Figure S6a). The liquid Ga layer creates a confined space and modifies gas flow dynamics, effectively restricting the escape of small molecules and generating a high-pressure environment that directs the decomposition products upward through the Ga layer [35, 46, 47]. Consequently, the transport of Pt species becomes more ordered, leading to uniform deposition. SEM images confirmed that Pt nanoparticles (NPs) on Pt/NiO/NF(Ga) are homogeneously distributed without noticeable agglomeration (Figure S15). Unlike the conventional process, no “platinum mirror” formed on the crucible wall; instead, a uniform and dense mirror appeared on the inner surface of the lid (Figure S14). These results demonstrate that the Ga layer not only regulates gas flow but also enhances Pt transport efficiency and deposition uniformity.

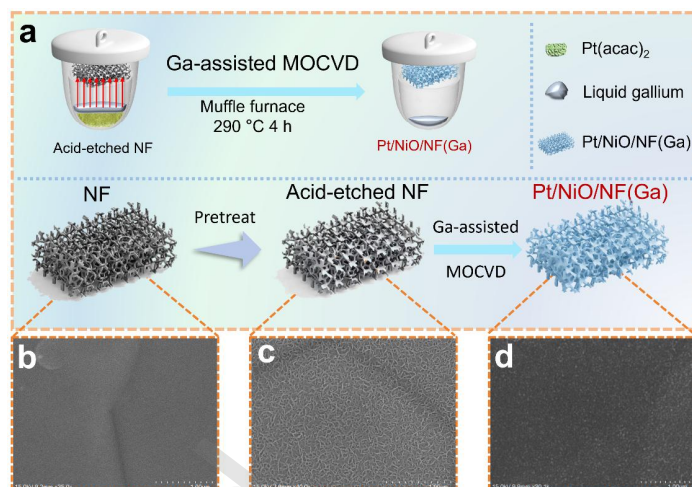


Figure 1 (a) Schematic illustration of the Ga-mediated MOCVD synthesis of Pt/NiO/NF(Ga). SEM images of (b) pristine NF, (c) acid-etched NiO/NF, and (d) Pt/NiO/NF(Ga) showing uniform deposition of Pt nanoparticles on the porous substrate.

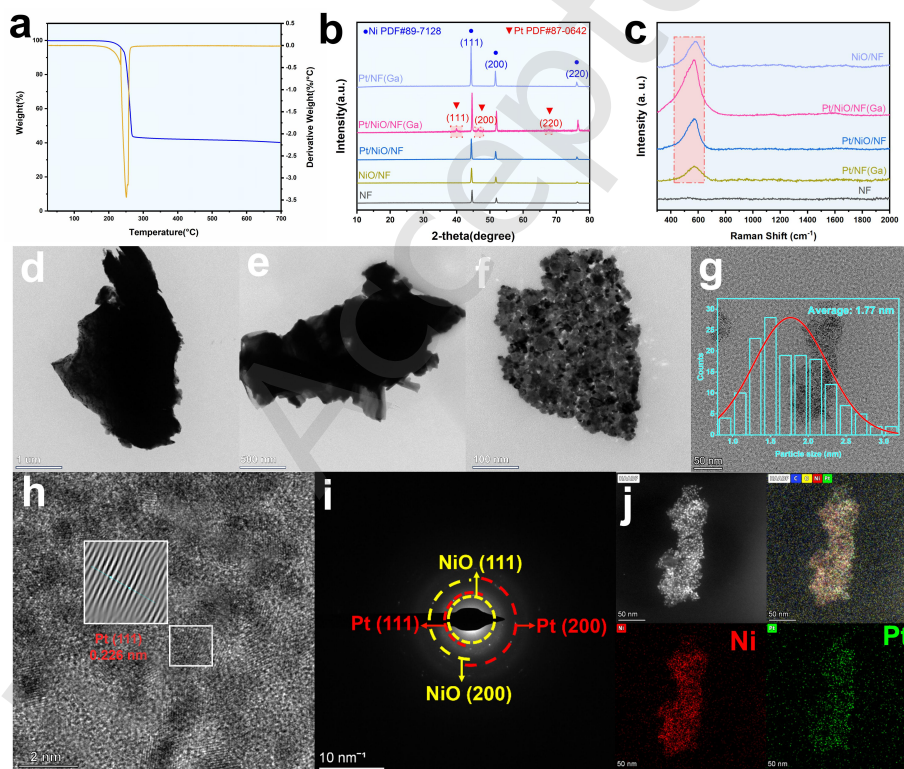


Figure 2 (a) TG and DTG curves of Pt(acac)₂. (b) PXRD patterns of NF, NiO/NF, Pt/NiO/NF, and Pt/NiO/NF(Ga). (c) Raman spectra highlighting NiO structural features. TEM images of (d) NF, (e) NiO/NF, (f) Pt/NiO/NF; (g) Pt/NiO/NF(Ga) with mean particle size distribution. (h) HR-TEM image of Pt/NiO/NF(Ga). (i) SAED pattern of Pt/NiO/NF(Ga). (j) EDS elemental maps of Pt/NiO/NF(Ga) for Ni, Pt, and O.

To optimize the Ga-mediated MOCVD process, key synthesis parameters were systematically evaluated. The thickness of the Ga layer was found to critically regulate precursor vapor transport. Increasing the thickness to 1.0 cm significantly reduced the intensity of the platinum mirror formed on the crucible lid (Figures S21–S24), indicating restricted mass transport. Further increasing the thickness to 1.5 cm effectively obstructed gas flow, completely suppressing Pt deposition (Figures S25–S29). The amount of Pt(acac)₂ precursor also affected outcomes: 10–20 mg produced similar morphologies with proportionally increased Pt loading (Figures S30–S35), whereas 40 mg induced agglomeration and

partial substrate detachment due to turbulent gas flow and excessive nucleation (Figures S36–S38). Deposition time was optimized at 4 h; Pt loading increased with time up to 4 h, but further extension to 6 h yielded minimal additional deposition (Figures S16, S39–S50). Notably, the Ga-mediated MOCVD strategy showed excellent reproducibility, as three independent synthesis batches consistently produced uniformly dispersed ultrafine Pt NPs (Figures S51–S52). The strategy was also readily extended to carbon cloth and Al₂O₃ substrates, demonstrating its broad applicability (Figures S53–S56).

Scanning electron microscopy (SEM) characterization illustrates

the impact of deposition strategy on morphology. Pristine NF surfaces were smooth and flat (Figure 1b, Figure S1), whereas acid etching produced rough, porous hierarchical structures with high specific surface area, favorable for metal NPs anchoring (Figure 1c, Figure S3). Conventional MOCVD resulted in uneven Pt NPs distribution with local agglomeration (Figure S8), whereas Ga-mediated MOCVD yielded dense, uniformly dispersed Pt NPs (Figure 1d, Figure S15), highlighting the role of Ga in regulating precursor transport and suppressing excessive particle growth.

Powder X-ray diffraction (PXRD) patterns confirmed successful deposition. All samples exhibited characteristic metallic Ni peaks (JCPDS No. 89-7128). Pt/NiO/NF(Ga) additionally displayed peaks at 39.6°, 46.0°, and 67.2° corresponding to Pt (JCPDS No. 87-0642, Figure 2b). Raman spectra (Figure 2c) showed characteristic NiO peaks in all samples except NF [48, 49]. Compared with NiO/NF, Pt/NiO/NF(Ga) exhibited asymmetric peak broadening and a slight red shift, consistent with modifications of the local lattice environment induced by strong Pt-NiO interfacial interactions. These spectral changes are also consistent with the formation of ultrafine Pt nanoparticles observed by TEM but should not be interpreted as a direct measure of particle size [50-52].

Transmission electron microscopy (TEM) and High-resolution-TEM (HR-TEM) images further elucidated structural details. NF consisted of large aggregates, while NiO/NF displayed flaky edge structures post-pretreatment (Figure 2d-e). Conventional Pt/NiO/NF contained large, uneven Pt NPs (Figure 2f), whereas Pt/NiO/NF(Ga) exhibited significantly smaller NPs (average diameter 1.77 nm, Figure 2g). HR-TEM revealed the Pt(111) lattice plane with 0.225 nm spacing, consistent with PXRD, and selected area electron diffraction (SAED) patterns displayed distinct Pt(111) and Pt(200) planes alongside NiO(111) and NiO(200) planes, confirming successful deposition (Figure 2h-i). Energy-dispersive X-ray spectroscopy (EDS) mapping demonstrated uniform elemental distribution of Ni, Pt, and O in Pt/NiO/NF(Ga) (Figure 2j), corroborating high dispersion of Pt NPs. Overall, these results demonstrate that Ga-mediated MOCVD provides precise control over gas flow and precursor transport, enabling uniform, nanoscale Pt deposition with broad substrate compatibility.

3.2 Evidence of strong metal-support interaction

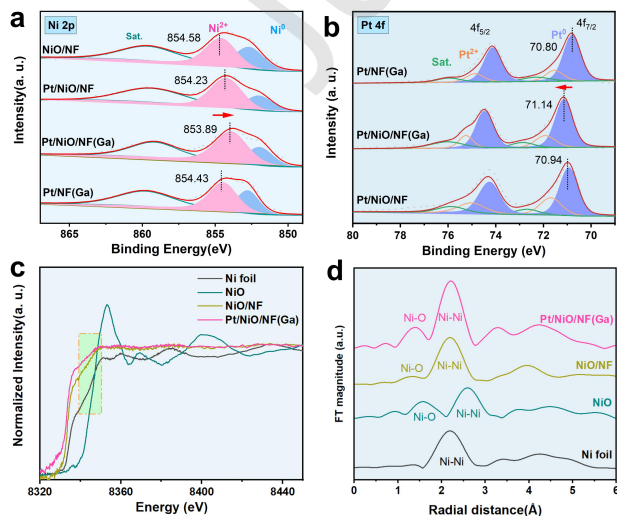


Figure 3 XPS spectra of (a) Ni 2p and (b) Pt 4f of samples. (c) Normalized Ni K-edge XANES spectra. (d) Fourier transform of Ni EXAFS in R-space, highlighting changes in Ni coordination.

X-ray photoelectron spectroscopy (XPS) was employed to probe changes in the surface chemical states and electronic structures of the samples. The Ni 2p spectrum (Figure 3a) can be deconvoluted into three components corresponding to NiO, Ni²⁺, and satellite peaks [53, 54]. In Pt/NiO/NF, the Ni 2p_{3/2} binding energy shifted approximately 0.35 eV lower relative to NiO/NF, indicating increased electron density around NiO. For Pt/NiO/NF(Ga), this peak further shifted to 855.94 eV, suggesting a substantial enhancement in NiO electron density due to strong interaction with Pt. The Pt 4f spectra (Figure 3b) were deconvoluted into metallic Pt⁰ and surface Pt²⁺ components together with weak satellite features [55-57]. Compared with Pt/NF(Ga), the Pt 4f_{7/2} peak gradually shifted toward higher binding energy from 70.80 to 70.94 and finally to 71.14 eV after introducing the NiO support. This positive shift indicates a decrease in the electron density of Pt nanoparticles, suggesting interfacial charge redistribution between Pt and NiO. The ultrafine Pt nanoparticles produced via the Ga-mediated MOCVD process exhibited the largest positive shift, implying a stronger electronic interaction at the Pt/NiO interface.

To further investigate the electronic structure and local coordination environment of Ni, X-ray absorption near-edge structure (XANES) spectroscopy was performed. As shown in Figure 3c, the Ni K-edge XANES spectrum of Pt/NiO/NF(Ga) exhibits a slight negative shift in the absorption edge relative to that of NiO/NF, indicating an increase in electron density around Ni and a corresponding decrease in its effective oxidation state. Extended X-ray absorption fine structure (EXAFS) analysis provides further insight into the local atomic structure. The Fourier-transformed Ni K-edge EXAFS spectra in R space (Figure 3d) reveal a shortened Ni–O bond distance together with an enhanced Ni–O coordination peak intensity for Pt/NiO/NF(Ga) compared with NiO/NF, indicating modifications of the local coordination environment that are consistent with strong Pt-NiO interfacial coupling.

These complementary structural and spectroscopic results also provide important insight into the role of liquid Ga during the MOCVD process. Rather than participating directly in the final catalyst, liquid Ga functions as a transient transport and growth medium, regulating precursor diffusion and decomposition while suppressing nanoparticle migration and coalescence. This controlled growth environment promotes homogeneous nucleation, leading to the formation of ultrafine and uniformly dispersed Pt nanoparticles and thereby substantially increasing the effective Pt-NiO interfacial area.

The resulting intimate Pt-NiO interface facilitates coupled structural and electronic evolution, as evidenced by the positive shift of the Pt 4f binding energy together with the XANES- and EXAFS-derived changes in the local electronic and coordination environments of Ni. Combined with the differential charge density and Bader charge analyses discussed below, these independent experimental and theoretical results consistently support the establishment of a strong metal-support interaction (SMSI) at the Pt/NiO interface. The resulting interfacial electronic coupling modulates the electronic structure of the Pt active sites, thereby optimizing the adsorption behavior of HER intermediates and contributing to the enhanced catalytic activity.

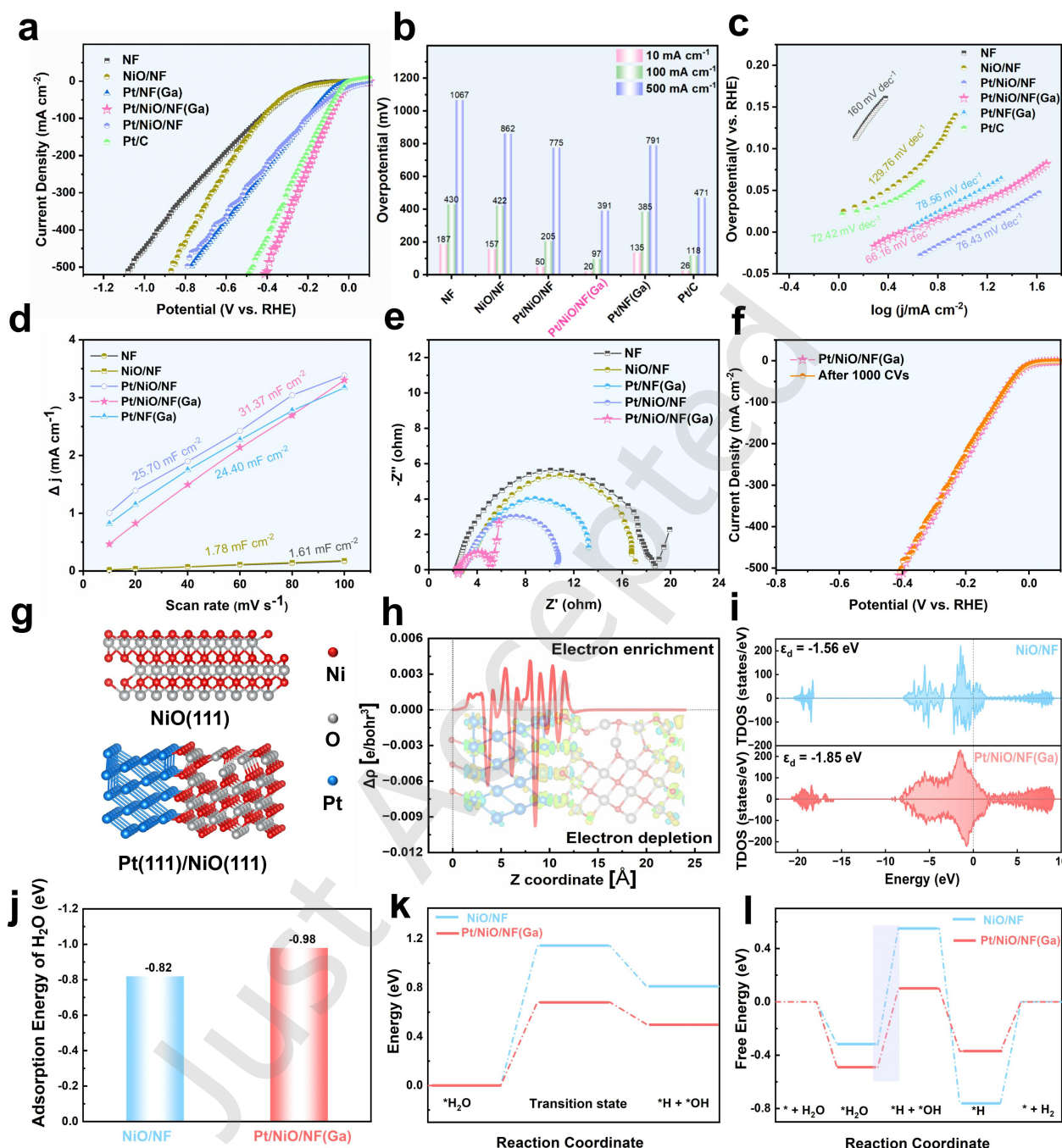


Figure 4 Electrochemical and theoretical analysis of HER activity. (a) LSV curves of each sample in 1 M KOH. (b) Overpotential comparison at various current densities. (c) Tafel plots. (d) Double-layer capacitance (C_{dl}) of the samples. (e) Electrochemical impedance spectra (EIS). (f) LSV curves after 1,000 CV cycles, demonstrating durability. (g) Optimized structural models of NiO/NF and Pt/NiO/NF(Ga) used for DFT calculations. (h) Differential charge density (DCD) of Pt/NiO/NF(Ga) (yellow: electron accumulation; blue: electron depletion). (i) Partial density of states (PDOS) for NiO/NF and Pt/NiO/NF(Ga), indicating d-band center and Fermi level positions. (j) Adsorption free energies of H_2O molecules on NiO/NF and Pt/NiO/NF(Ga). (k) Gibbs free energy profiles for the H_2O dissociation (Volmer) step. (l) Free energy diagram of HER at $U = 0$ V for Pt/NiO/NF(Ga) and reference samples. The red, grey, white, and blue balls represent O, Ni, H, and Pt atoms, respectively.

3.3. Electrochemical performance and kinetics

The electrocatalytic activity of Pt/NiO/NF(Ga) toward the hydrogen evolution reaction (HER) was evaluated in a standard three-electrode configuration in 1 M KOH and compared with NF,

NiO/NF, Pt/NiO/NF, and commercial Pt/C under identical conditions. As shown in Figure 4a, Pt/NiO/NF(Ga) exhibited the most remarkable HER performance among all tested samples. At a current density of 10 mA cm^{-2} , an overpotential of only 20 mV was

required, which is substantially lower than those of Pt/NiO/NF and commercial Pt/C. Notably, inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Table S3) revealed a Pt loading of 3.25 wt% in Pt/NiO/NF(Ga), significantly lower than that of commercial Pt/C (20 wt%), highlighting the high mass-specific catalytic efficiency of the Ga-mediated system. Across a broad current density range (Figure 4b), Pt/NiO/NF(Ga) consistently delivered lower overpotentials, further confirming its superior intrinsic activity. The enhanced HER performance is attributed to the uniform dispersion of ultrafine Pt NPs and the SMSI between Pt and NiO, which collectively promote efficient exposure of active sites and facilitate interfacial charge transfer. Such interfacial coupling likely optimizes proton adsorption and accelerates electron transport kinetics during HER.

To quantify reaction kinetics, Tafel analysis was performed (Figure 4c). Pt/NiO/NF(Ga) exhibited a Tafel slope of 66.16 mV dec⁻¹, lower than NF (160 mV dec⁻¹), NiO/NF (129.76 mV dec⁻¹), Pt/NiO/NF (76.43 mV dec⁻¹), and Pt/C (72.42 mV dec⁻¹), indicating accelerated HER kinetics and superior catalytic efficiency. The electrochemical surface area (ECSA) of the catalysts, estimated from double-layer capacitance (C_{dl}) using cyclic voltammetry (CV) at different scan rates (Figure S58), provides insight into the number of accessible active sites [58]. Pt/NiO/NF(Ga) exhibited the largest C_{dl} value of 31.37 mF cm⁻², significantly higher than Pt/NiO/NF (25.70 mF cm⁻²), indicating a higher density of electrochemically active sites (Figure 4d) [59].

Electrochemical impedance spectroscopy (EIS) (Figures 4e and S59a) revealed that Pt/NiO/NF(Ga) had the smallest semicircle radius, corresponding to the lowest charge-transfer resistance and enhanced electron transfer kinetics. Furthermore, long-term stability tests demonstrated excellent durability; the linear sweep voltammetry (LSV) curves of Pt/NiO/NF(Ga) remained nearly unchanged after 1000 cycles in 1 M KOH (Figure 4g), highlighting its robust performance under harsh alkaline conditions. Overall, these results demonstrate that Ga-mediated MOCVD enables the formation of highly dispersed ultrafine Pt NPs with SMSI, which collectively enhance HER activity, accelerate reaction kinetics, increase electrochemically active surface area, and ensure long-term stability.

3.4 DFT analysis of interfacial electronic modulation

To gain atomic-level insight into the electronic interactions between Pt NPs and NiO and their influence on HER activity, density functional theory (DFT) calculations were performed. Structural models of NiO(111) and Pt(111)/NiO(111) were optimized (Figure 4g). Differential charge density (DCD) analysis revealed pronounced interfacial electron redistribution between Pt and NiO (Figure 4h), which agreed well with the positive shift of the Pt 4f XPS spectra and the Ni K-edge XANES results. Bader charge analysis indicated a transfer of 3.82 e⁻ from Pt to NiO, consistent with the experimental XPS and XANES results, confirming the presence of SMSI. This charge transfer effectively modulates the electronic structure of the interface, enhancing catalytic activity.

According to d-band center theory, the affinity of metal sites for reaction intermediates decreases as the d-band center (ϵ_d) shifts away from the Fermi level [60–62]. The density of states (DOS) analysis showed that the ϵ_d of Pt/NiO/NF(Ga) is -1.85 eV, lower than -1.56 eV for NiO/NF (Figure 4i). This negative shift indicates that Pt NPs optimize the adsorption strength of H*, a key intermediate in the HER, facilitating improved catalytic efficiency.

Water adsorption, a critical step in alkaline HER, was further analyzed. The adsorption free energy of H₂O on Pt/NiO was calculated as -0.98 eV, slightly stronger than -0.82 eV on NiO alone (Figure 4j), suggesting that Pt sites promote more favorable H₂O adsorption. The dissociation of H₂O (Volmer step), often the rate-determining step in alkaline HER, was evaluated by calculating the energy barriers. For NiO, the H₂O dissociation barrier was 1.14 eV, whereas for Pt/NiO/NF(Ga), it decreased to 0.68 eV (Figure 4k), indicating that the presence of Pt significantly facilitates water splitting.

The Gibbs free energy profiles for HER on both NiO/NF and Pt/NiO/NF(Ga) were also calculated (Figure 4l). The potential-determining step (PDS) is H₂O dissociation in both cases. The diffusion barrier for H* migration on NiO/NF was 0.87 eV, while it decreased to 0.59 eV on Pt/NiO/NF(Ga). This reduction demonstrates that Pt not only promotes H₂O dissociation but also accelerates the migration and desorption of intermediates, enhancing H₂ evolution kinetics. Overall, the DFT results reveal that the outstanding HER activity of Pt/NiO/NF(Ga) originates from the unique electronic structure modulation induced by Ga-mediated deposition. The interfacial charge transfer, optimized d-band center, and reduced energy barriers for H₂O dissociation and H* migration collectively facilitate efficient adsorption, reaction, and desorption of intermediates, providing a mechanistic explanation for the superior catalytic performance.

3.5 Long-term stability and device-level performance

Compared with commercial Pt/C and recently reported platinum-based electrocatalysts for alkaline HER, Pt/NiO/NF(Ga) exhibits outstanding electrocatalytic performance, achieving an overpotential as low as 20 mV at a current density of 10 mA cm⁻² (Figure 5a). Long-term operational stability is a critical metric for practical applications. Remarkably, after 800 h of continuous operation, Pt/NiO/NF(Ga) showed only ~5% activity loss (Figure 5b), demonstrating excellent durability under alkaline conditions.

To further evaluate the structural and chemical stability of the catalyst, comprehensive post-operando characterization was conducted after 800 h of continuous cycling. Elemental mapping (Figure S63a and S63b) confirmed that Pt, Ni, and O remained homogeneously distributed throughout the catalyst, indicating excellent compositional uniformity after prolonged electrolysis. ICP-OES analysis (Table S6) revealed negligible changes in the Pt and Ni contents before and after the durability test, while no detectable Pt or Ni species were found in the electrolyte, demonstrating the absence of measurable metal leaching. XPS analysis (Figure S64a and S64b) showed that the chemical states of both Pt and Ni remained essentially unchanged after long-term operation. In addition, the PXRD patterns and Raman spectra (Figure S64c and S64d) exhibited no discernible changes relative to those of the fresh catalyst, indicating that the crystal structure of the Pt/NiO/NF(Ga) catalyst and the NiO support remained well preserved throughout the durability test. TEM analysis further revealed only slight particle coarsening, with the average Pt nanoparticle size increasing modestly from 1.77 to 2.07 nm (Figure S63c), suggesting minimal nanoparticle migration or aggregation during prolonged electrolysis. These results demonstrate the excellent structural, compositional, and chemical stability of Pt/NiO/NF(Ga) under extended alkaline HER conditions. The outstanding durability can be attributed to the Ga-mediated vapor deposition strategy, which produces uniformly dispersed ultrafine Pt nanoparticles with strong interfacial coupling

to the NiO support, thereby effectively suppressing nanoparticle aggregation and preserving the active interfacial structure during long-term operation.

The practical applicability of Pt/NiO/NF(Ga) was further evaluated in an anion exchange water electrolyzer (AEM) device, paired with commercial IrO₂ as the anode. For comparison, a Pt/C||IrO₂ device was also assembled and tested under identical conditions. At 80 °C, the Pt/NiO/NF(Ga)||IrO₂ system achieved a

current density of 1 A cm⁻² at a cell voltage of 1.80 V, consistently lower than that of Pt/C||IrO₂ (Figure 5c). Long-term stability testing at 80 °C in 1 M KOH at 1 A cm⁻² revealed that Pt/NiO/NF(Ga)||IrO₂ operated stably for 1,500 h, with a minimal degradation rate of 7.78% (Figure 5d). These results demonstrate that Pt/NiO/NF(Ga) combines low overpotential, exceptional durability, and excellent device-level performance, underscoring its promise for practical alkaline water electrolysis applications.

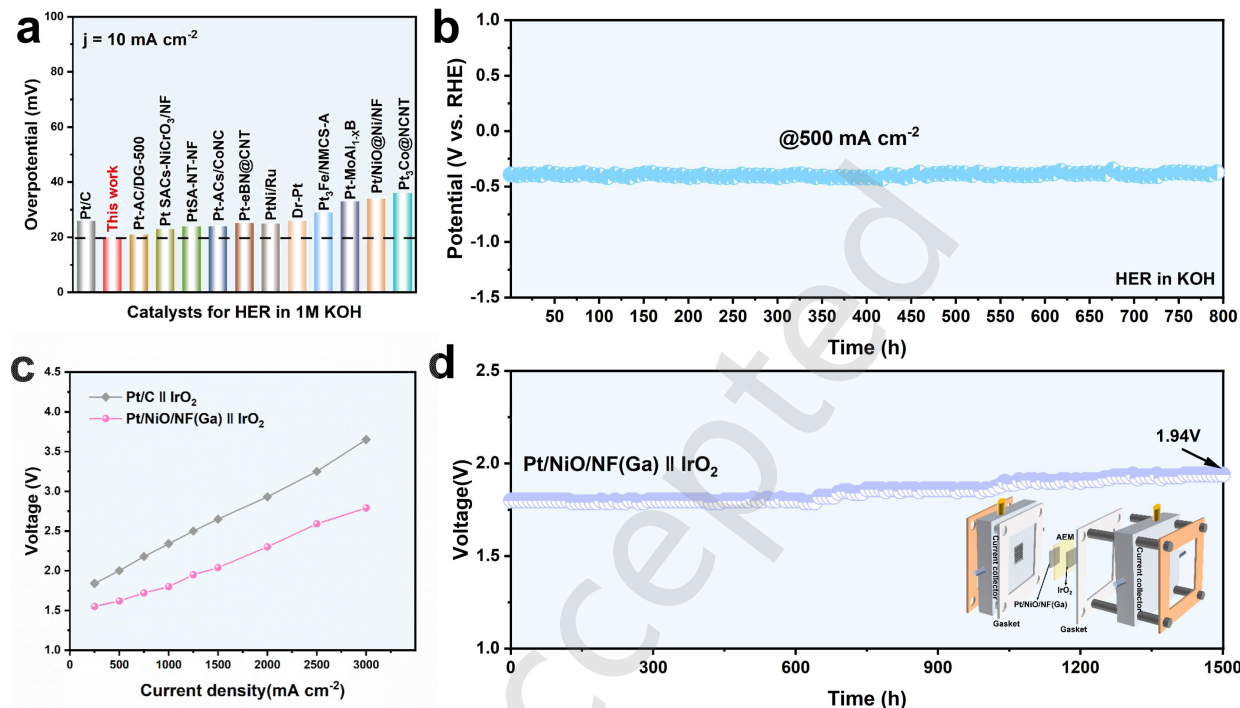


Figure 5 (a) Comparison of overpotentials at 10 mA cm⁻² for Pt/NiO/NF(Ga) and representative state-of-the-art platinum-based catalysts (Table S4). (b) Long-term HER stability of Pt/NiO/NF(Ga) in 1 M KOH at 500 mA cm⁻². (c) Polarization curves of AEMWEs using Pt/NiO/NF(Ga) and commercial Pt/C as cathodes. (d) Chronopotentiometry of Pt/NiO/NF(Ga)||IrO₂ at 1 A cm⁻², showing sustained stability over 1500 h.

4 Conclusions

In summary, we have developed a liquid gallium-mediated vapor deposition strategy that enables controlled nucleation of ultrafine Pt NPs and induces strong electronic metal-support interaction with a NiO/NF substrate. The liquid Ga layer functions as a dynamic transport mediator that regulates precursor diffusion and decomposition, thereby suppressing vapor-phase supersaturation and promoting uniform growth of 1.77 nm Pt NPs across a three-dimensional porous framework. This confined growth environment enhances interfacial contact and facilitates electronic coupling between Pt and NiO. Spectroscopic analyses and theoretical calculations reveal that the Ga-mediated growth process induces interfacial charge redistribution, resulting in electron transfer from Pt to NiO and modulation of the Pt d-band structure. This electronically mediated SMSI optimizes hydrogen adsorption energetics and lowers the energy barrier for water dissociation, thereby accelerating alkaline hydrogen evolution kinetics. As a consequence, the Pt/NiO/NF(Ga) catalyst delivers an overpotential of 20 mV at 10 mA cm⁻² and maintains stable operation for 800 h at 500 mA cm⁻² in alkaline electrolyte. When integrated into an anion-exchange membrane water electrolyzer, the catalyst sustains ampere-level current densities for 1,500 h, demonstrating durability under industrially relevant conditions. Beyond

performance metrics, this work establishes liquid metal-mediated vapor deposition as a versatile platform for inducing SMSI during nanoparticle growth rather than through post-synthetic treatments. The strategy provides a scalable pathway for constructing electronically engineered noble-metal catalysts with minimized loading and enhanced stability, offering new opportunities for high-current-density alkaline energy conversion.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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.

Author contribution statement

Chunyan Yang: Writing - original draft, Software, Methodology, Investigation, Conceptualization. **Yongyong Cao:** Theoretical calculation, Supervision. **Zheng Qin:** Investigation. **Xu Han:** Investigation. **Wenrui Yue:** Investigation. **Hongwei Gu:** Writing - review & editing, Supervision, Resources, Funding acquisition, Data curation, Conceptualization. **Jian-Ping Lang:** Writing - review & editing, Supervision, Resources, Funding acquisition, Data curation, Conceptualization.

Use of AI statement

None.

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Electronic Supplementary Material

Liquid gallium-mediated vapor deposition induces strong metal-support interaction for ultrafine platinum nanocatalysts in high-current-density alkaline hydrogen evolution

Chunyan Yang^{1,2}, Yongyong Cao³ (✉), Zheng Qin¹, Xu Han¹, Wenrui Yue¹, Hongwei Gu¹ (✉), and Jian-Ping Lang^{1,2} (✉)

¹ College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

² State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

³ College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing 314001, China

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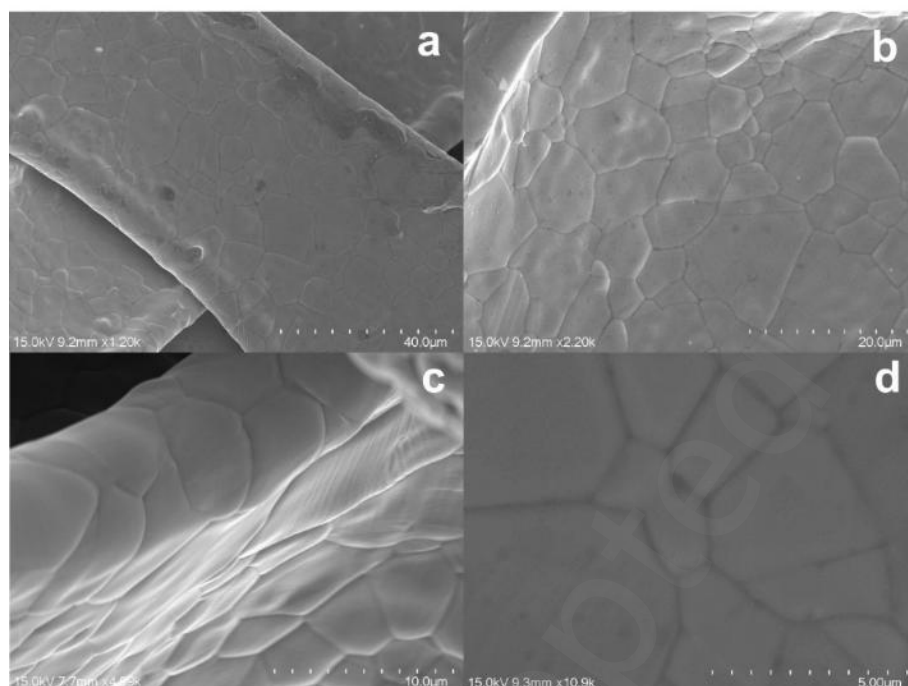


Figure S1 (a-d) SEM images of NF.

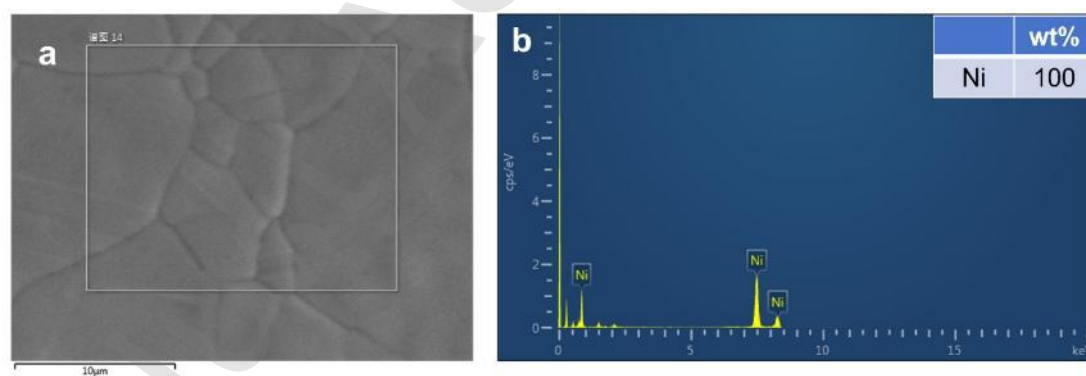


Figure S2 (a, b) EDX spectra of NF.

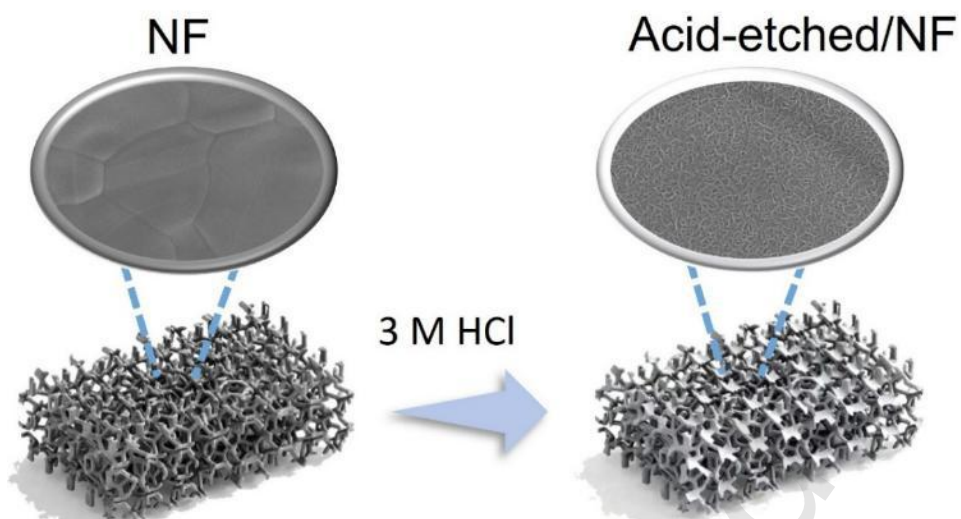


Figure S3 SEM mages showing the surface morphology evolution of NF after acid etching treatment.

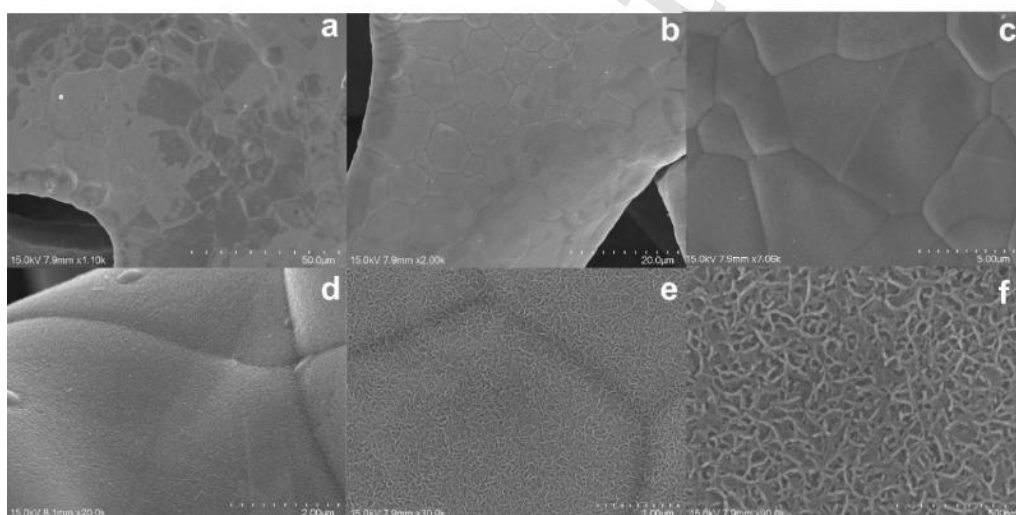


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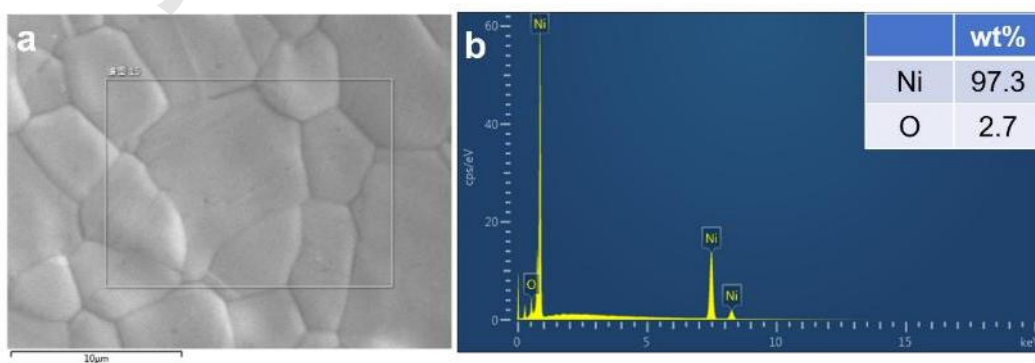


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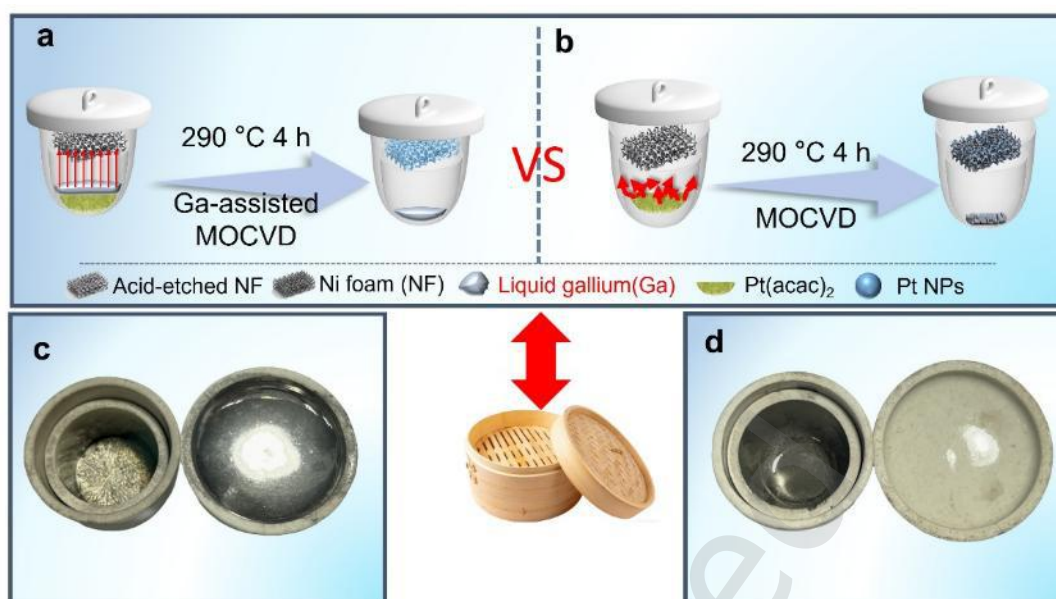


Figure S6 Comparison of synthetic configurations. (a) Schematic for Ga-assisted deposition for Pt/NiO/NF(Ga). (b) Schematic of Ga-free deposition for Pt/NiO/NF. (c) Digital photograph of the crucible setup for Pt/NiO/NF(Ga). (d) Digital photograph of the crucible setup for Pt/NiO/NF.

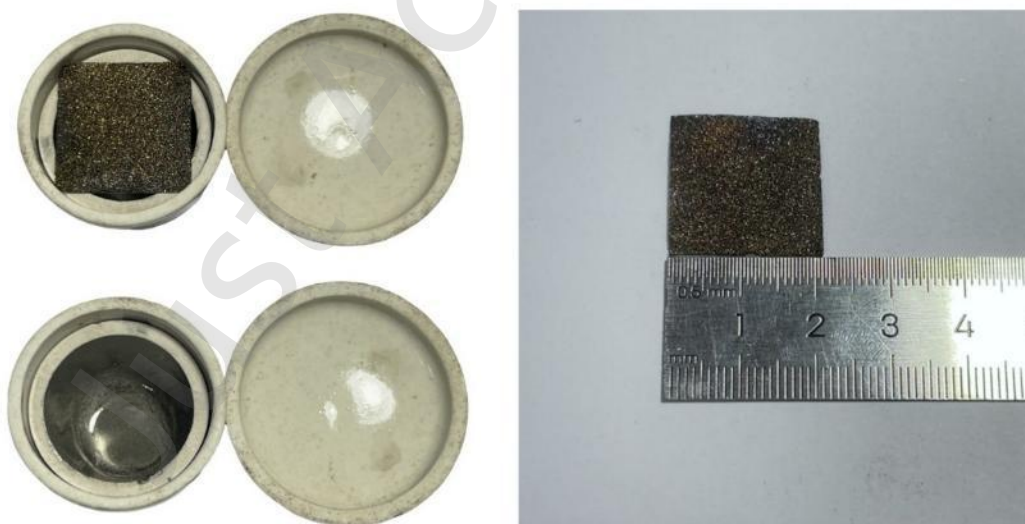


Figure S7 Digital photographs of the crucible configuration used for the synthesis of Pt/NiO/NF.

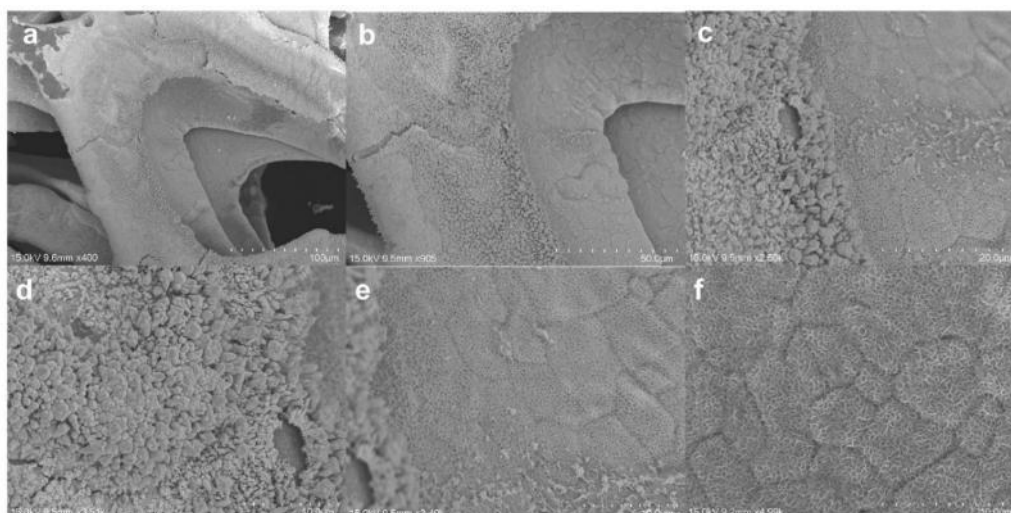


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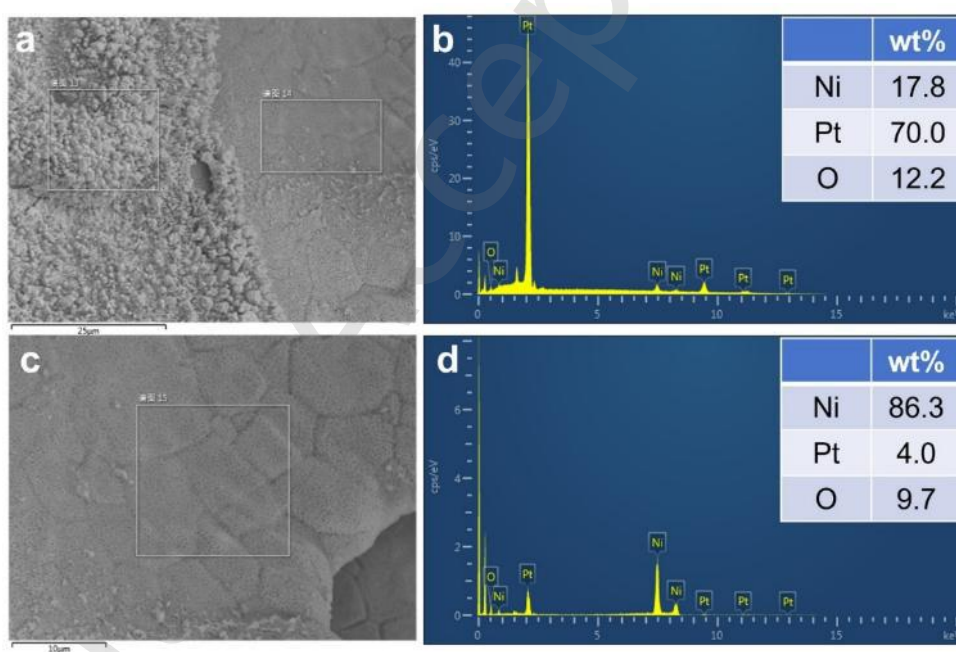


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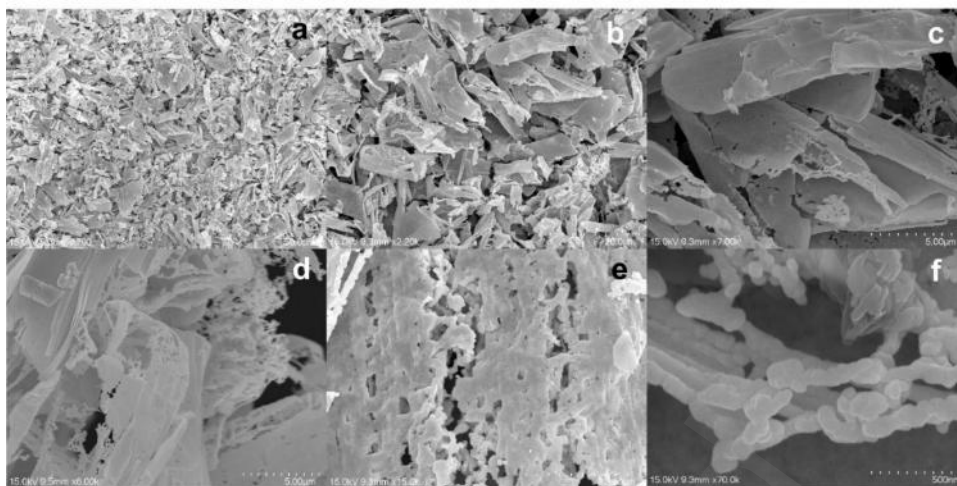


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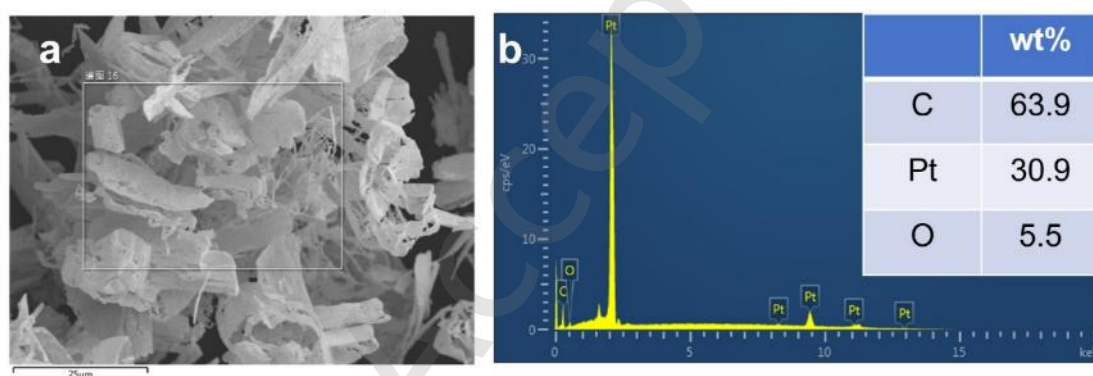


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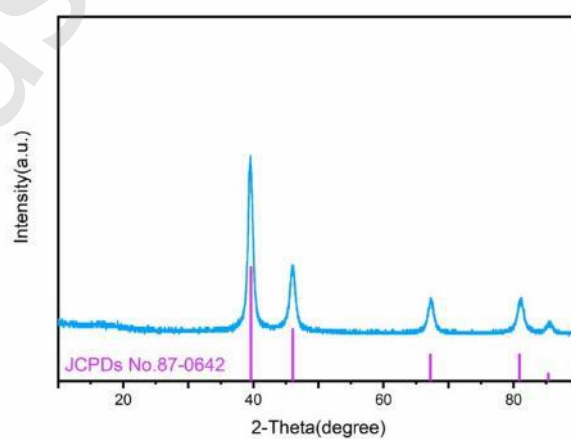


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Figure S14 Digital photographs of the crucible used for Pt/NiO/NF(Ga) synthesis (30 mg $\text{Pt}(\text{acac})_2$, 1 mL Ga, deposition height: 2 cm).

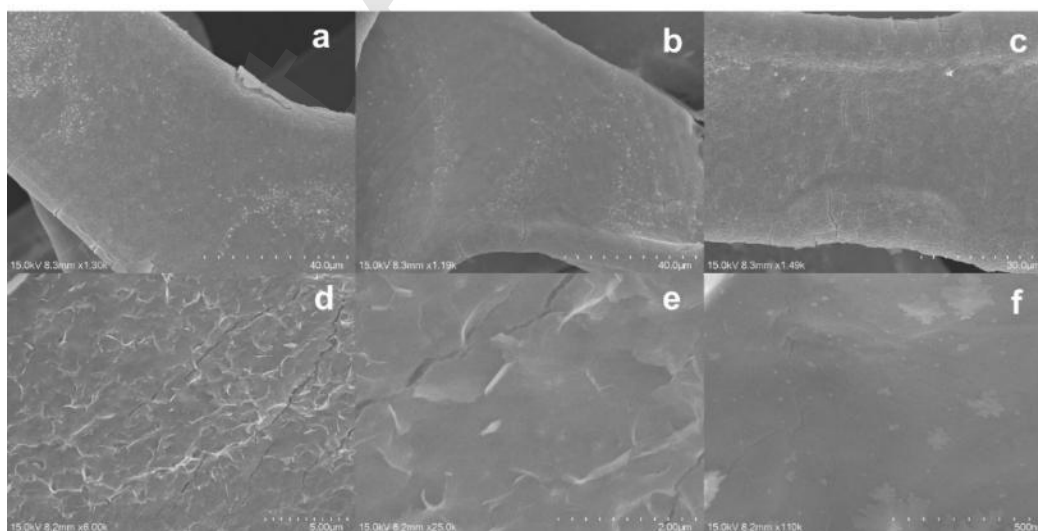


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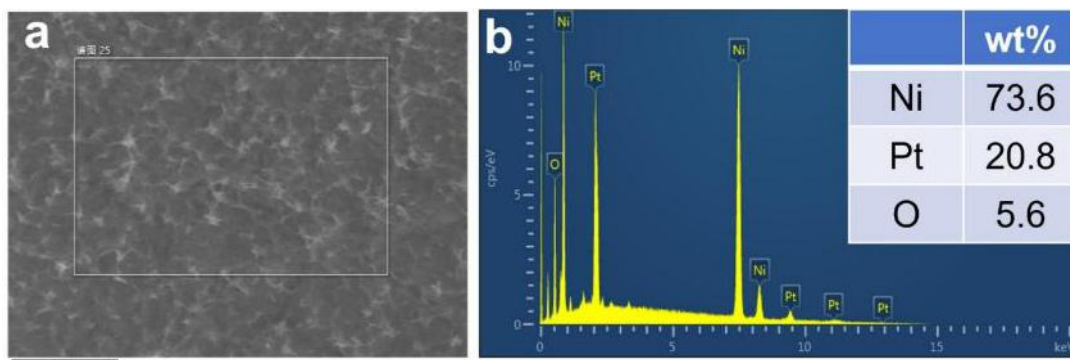


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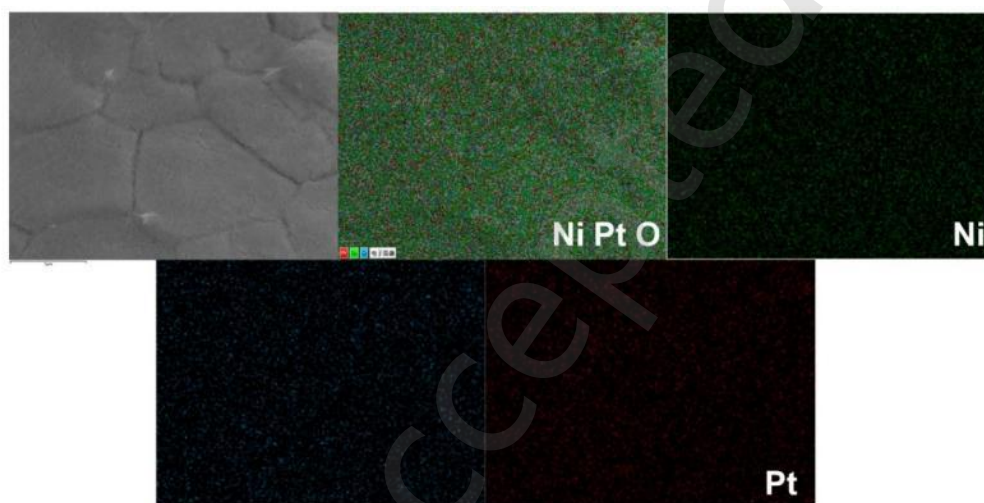


Figure S17 Element mapping (Ni, Pt, O) of Pt/NiO/NF (Ga).

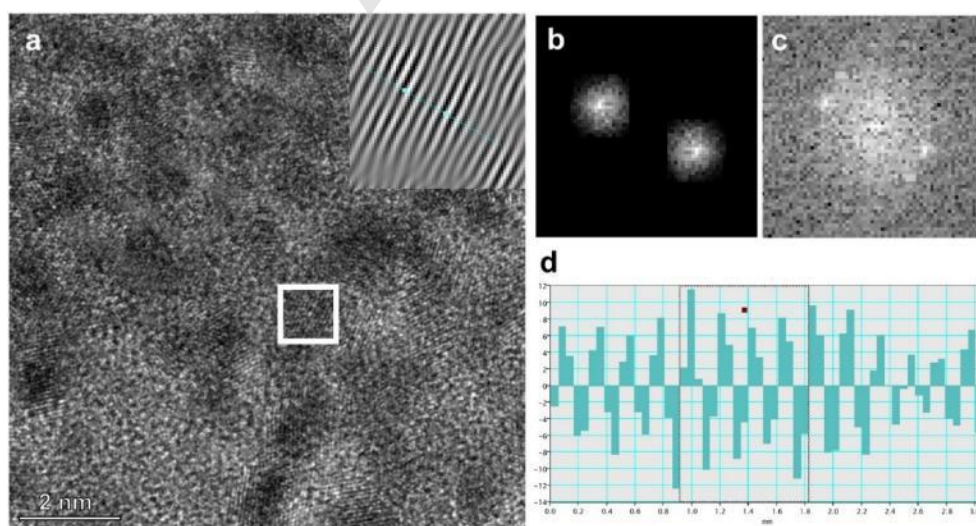


Figure S18 (a) HR-TEM image of Pt/NiO/NF (Ga); (b–d) corresponding interplanar spacing analysis and statistical distribution.

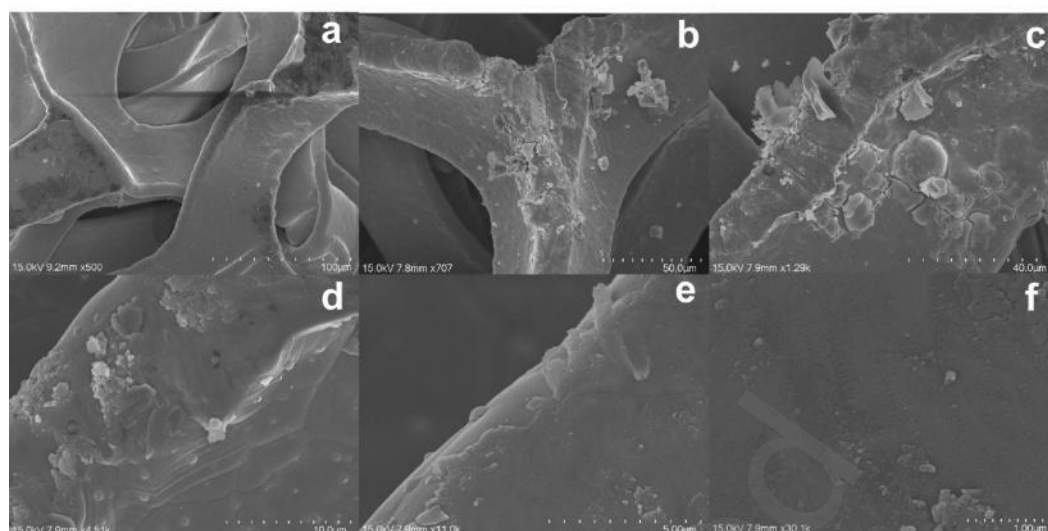


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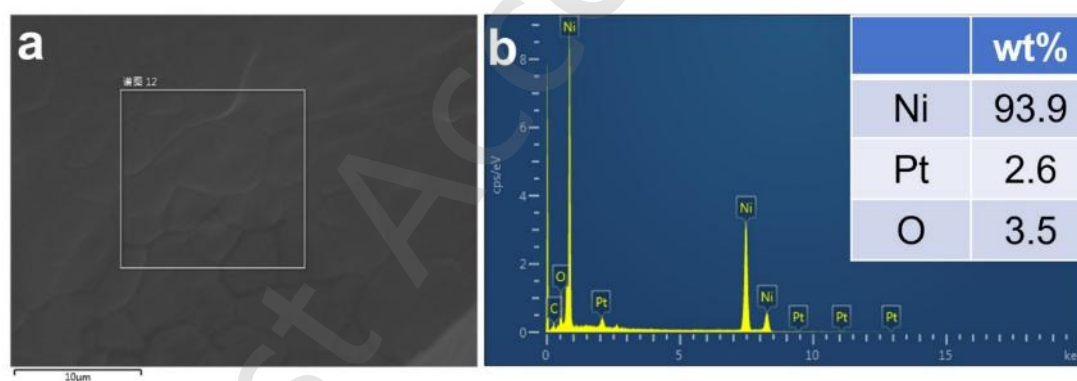


Figure S20 (a, b) EDX spectra of Pt/NF(Ga).

Note: Platinum was directly deposited onto untreated NF via Ga-assisted MOCVD, resulting in non-uniform Pt nanoparticle distribution and low loading (see also Figs. S19–S20). These results highlight the necessity of acid etching for achieving high dispersion and effective Pt loading.

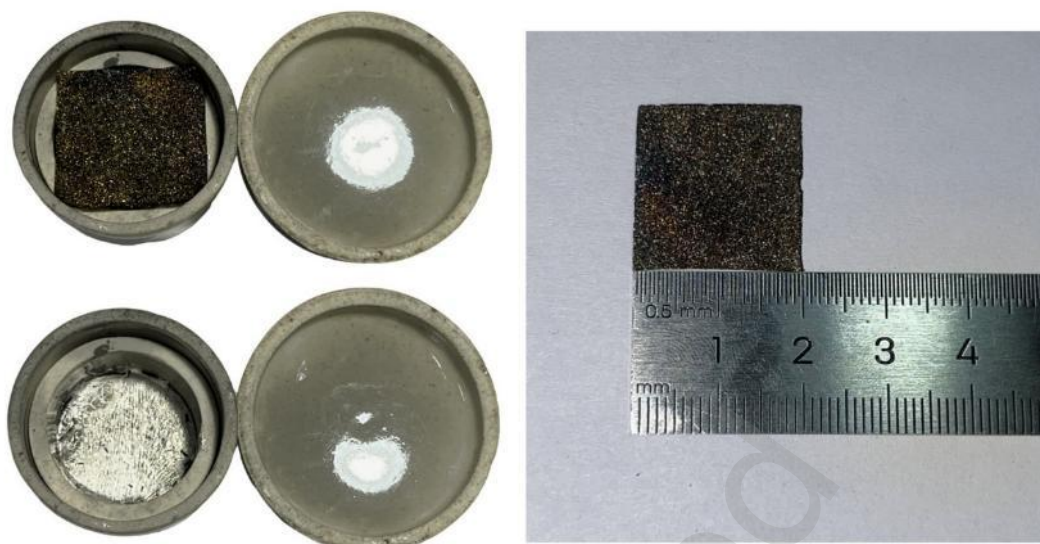


Figure S21 Digital photographs of the crucible used for the synthesis of Pt/NiO/NF(Ga-2 ml).

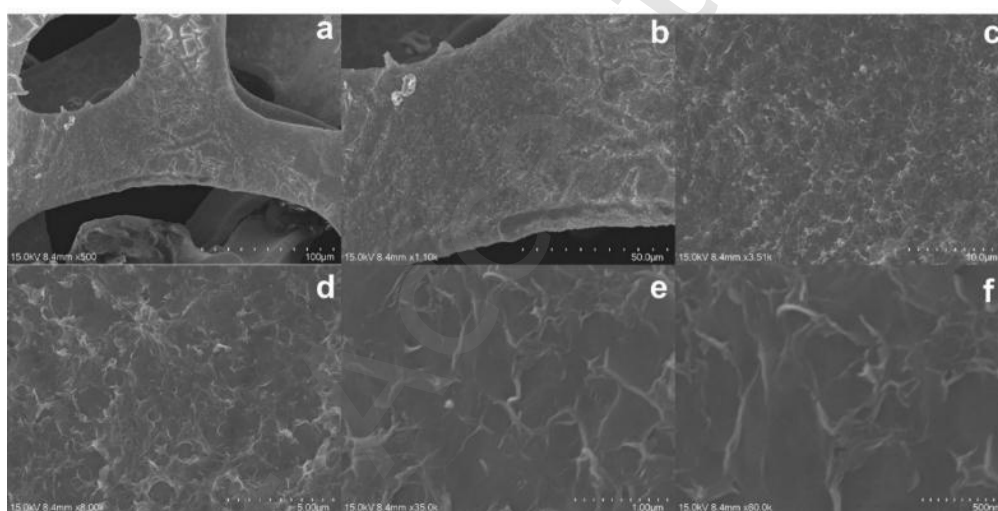


Figure S22 (a-f) SEM image of Pt/NiO/NF(Ga-2 ml).

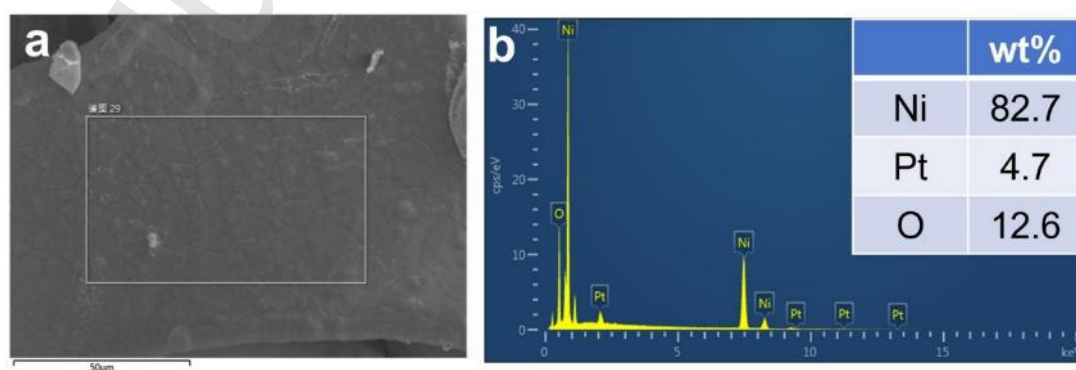


Figure S23 (a, b) EDX spectra of Pt/NiO/NF(Ga-2 ml).

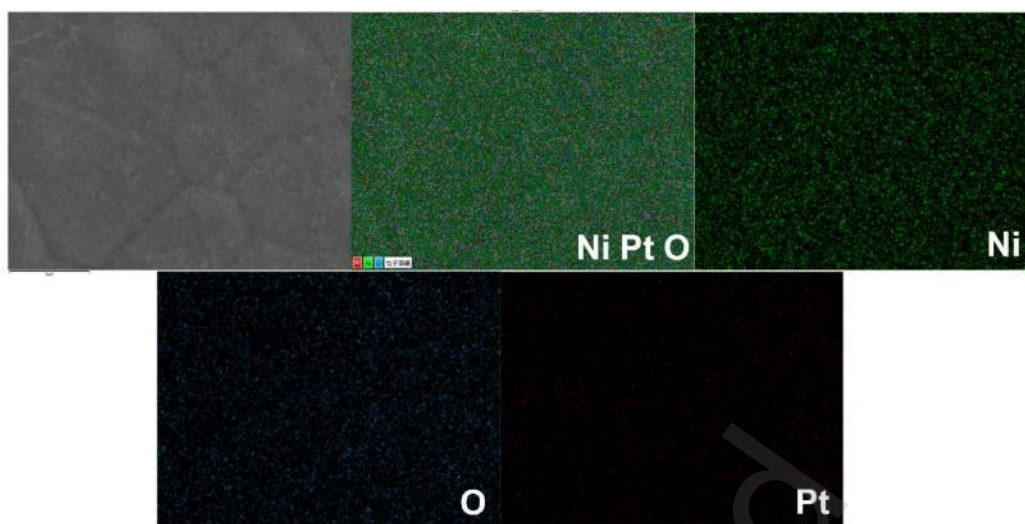


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Figure S25 Digital photographs of the crucible used for the synthesis of Pt/NiO/NF(Ga-3 ml).

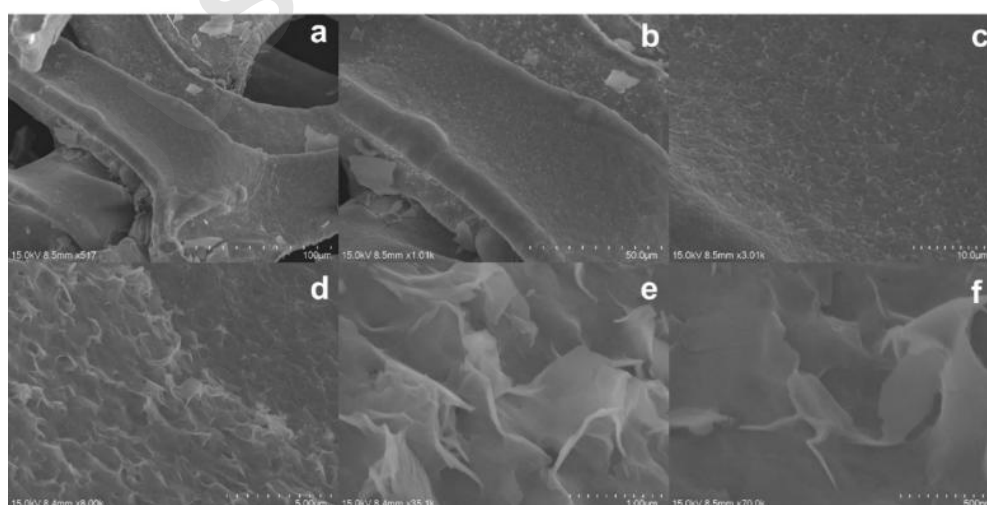


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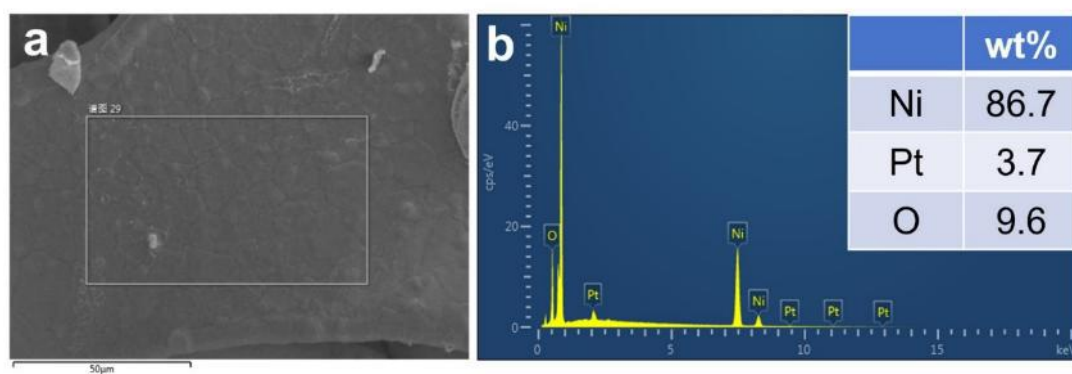


Figure S27 (a, b) EDX spectra of Pt/NiO/NF(Ga-3 ml).

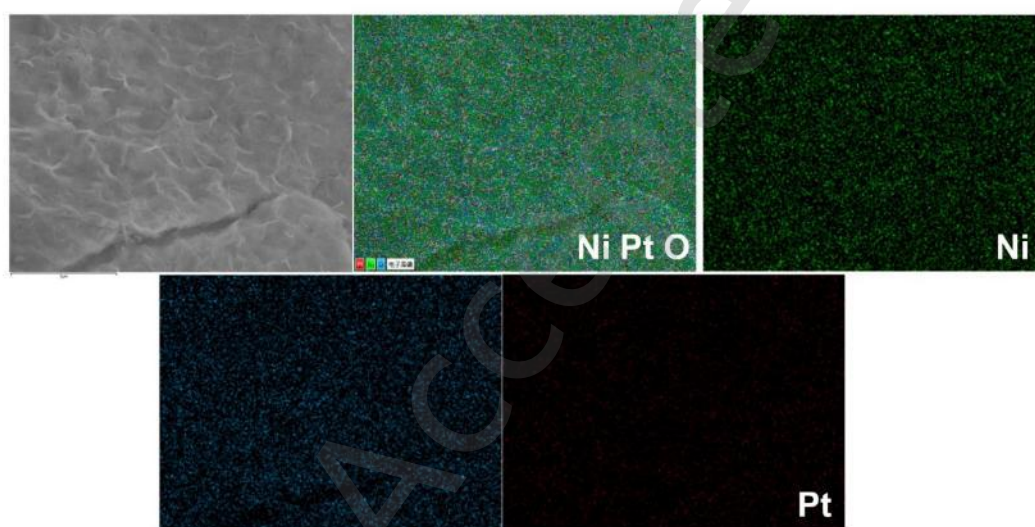


Figure S28 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga-3 ml).

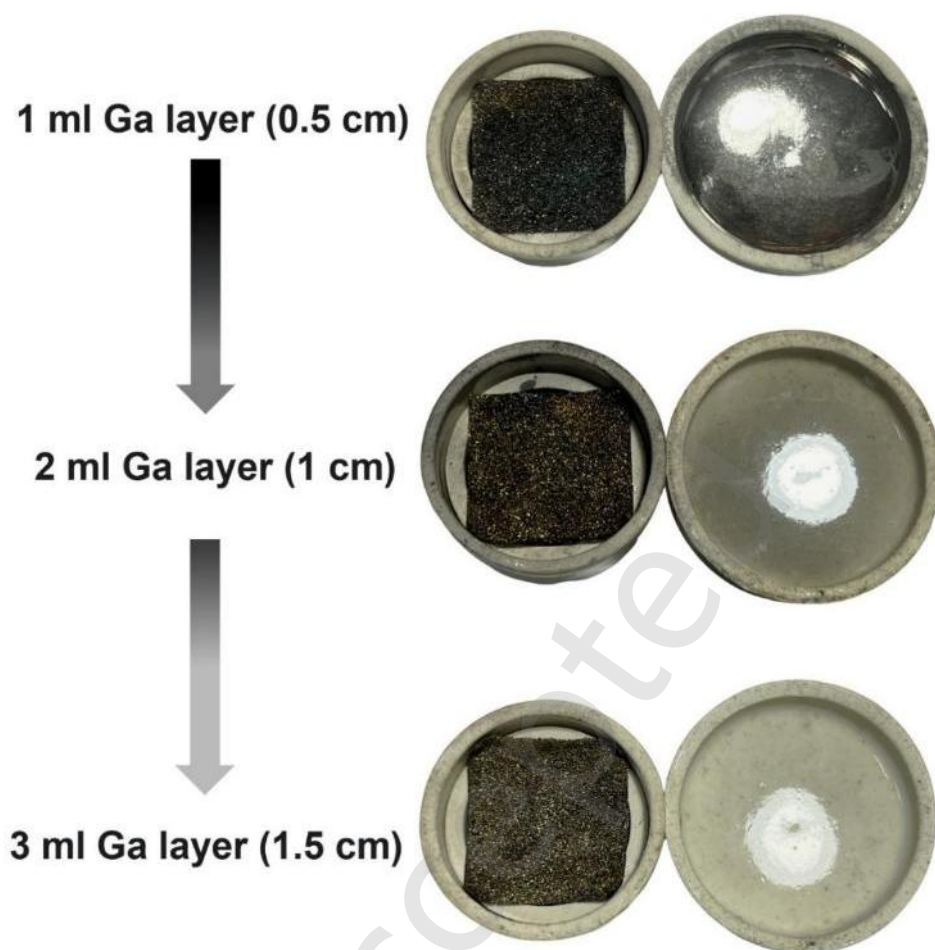


Figure S29 Digital photographs of crucibles corresponding to samples prepared with different Ga layer thicknesses.

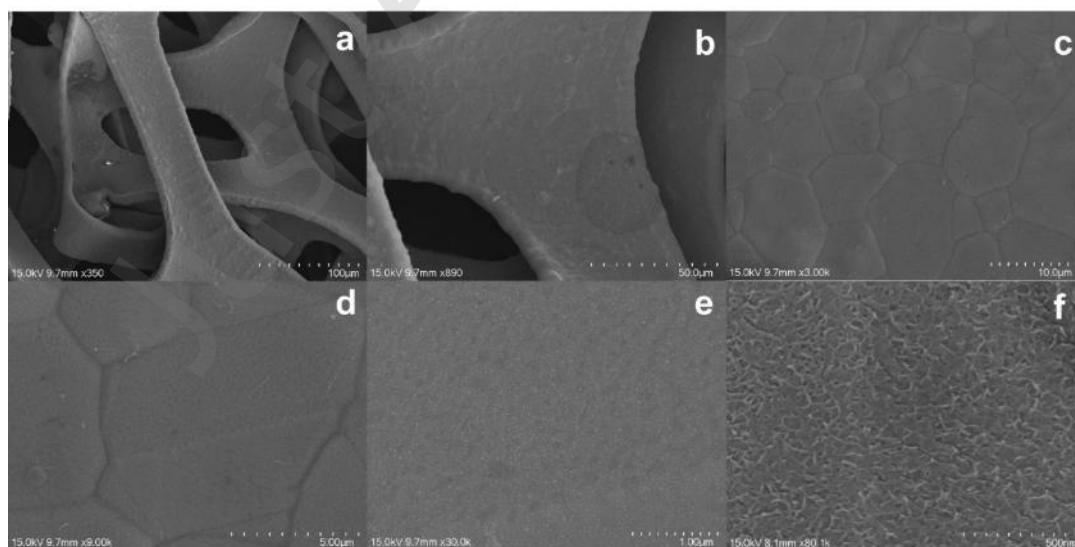


Figure S30 (a-f) SEM images of Pt/NiO/NF(Ga)-10 mg.

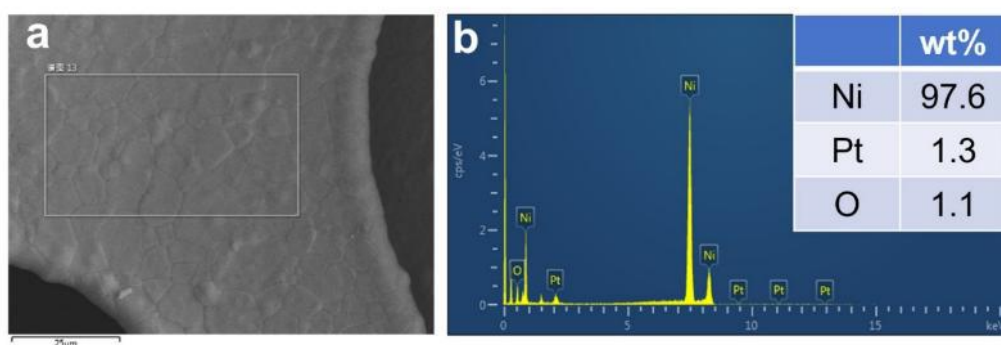


Figure S31 (a, b) EDX spectra of Pt/NiO/NF(Ga)-10 mg.

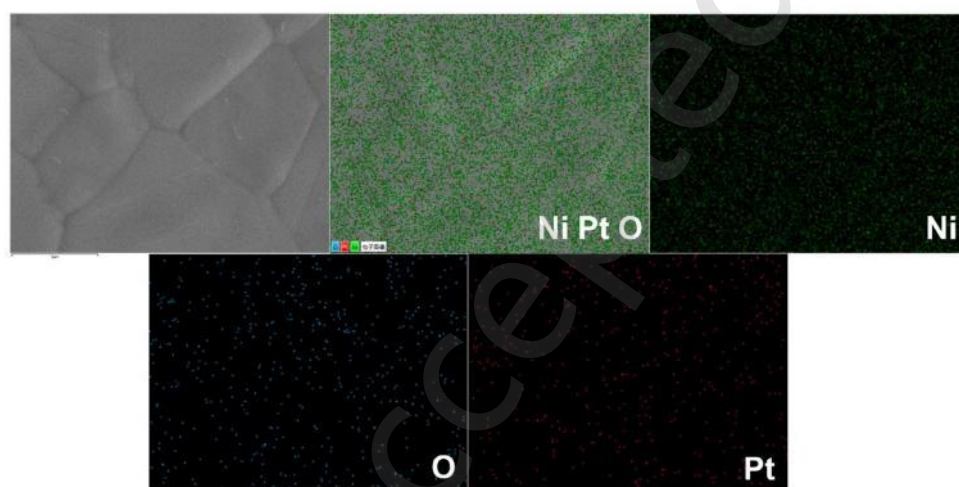


Figure S32 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-10 mg.

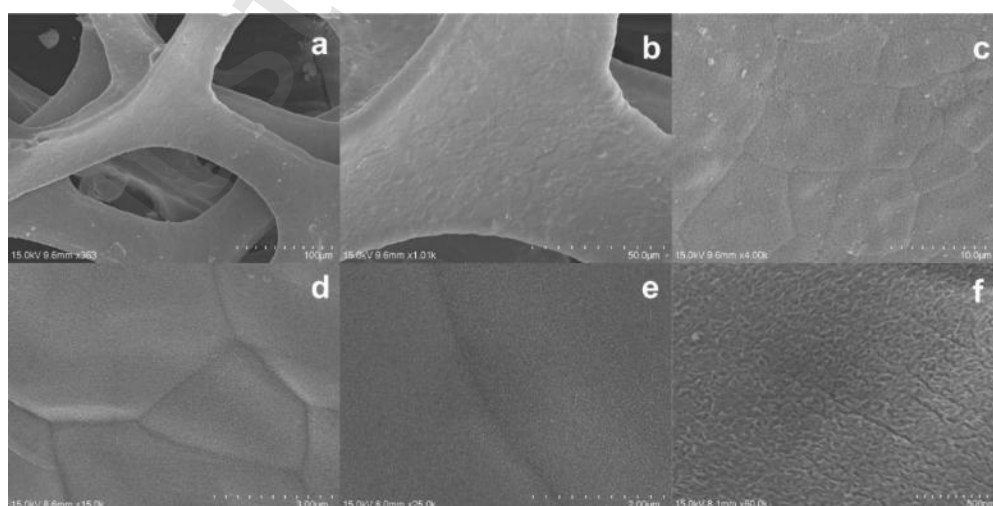


Figure S33 (a-f) SEM images of Pt/NiO/NF(Ga)-20 mg.

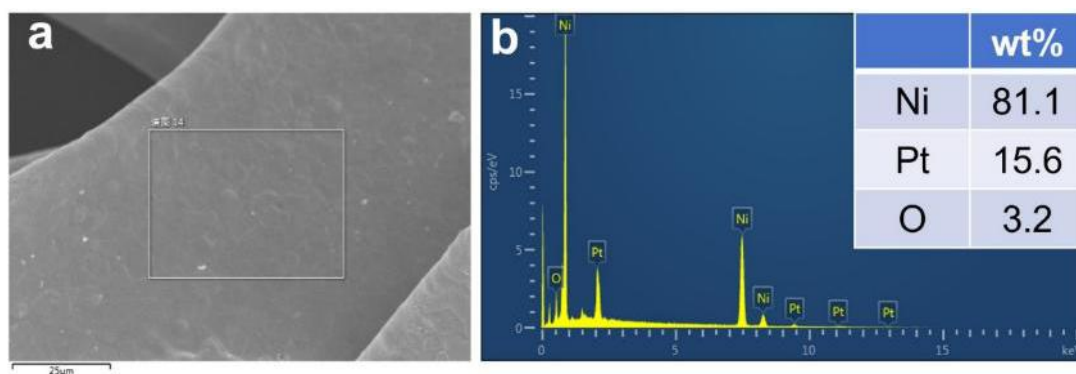


Figure S34 (a, b) EDX spectra of Pt/NiO/NF(Ga)-20 mg.

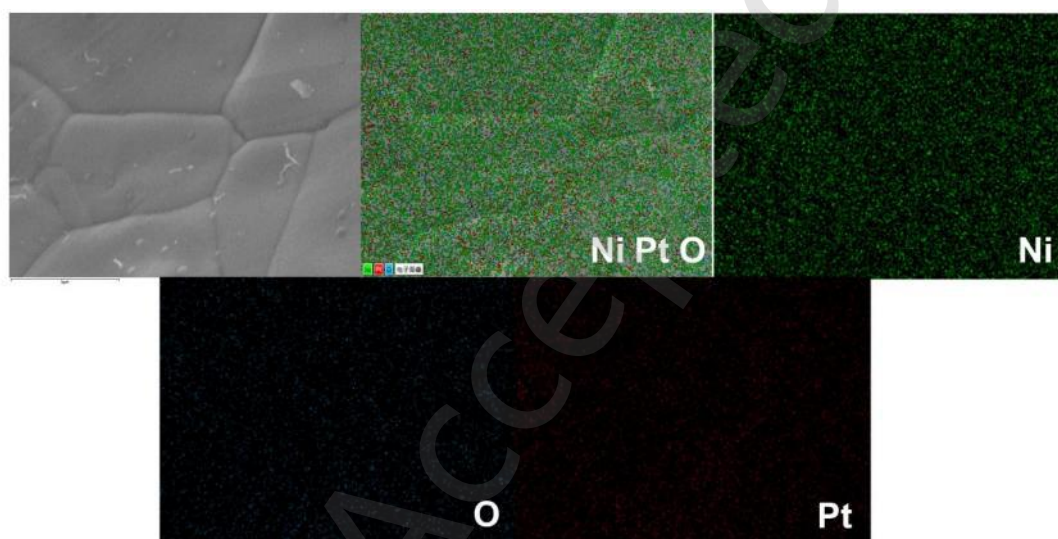


Figure S35 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-20 mg.

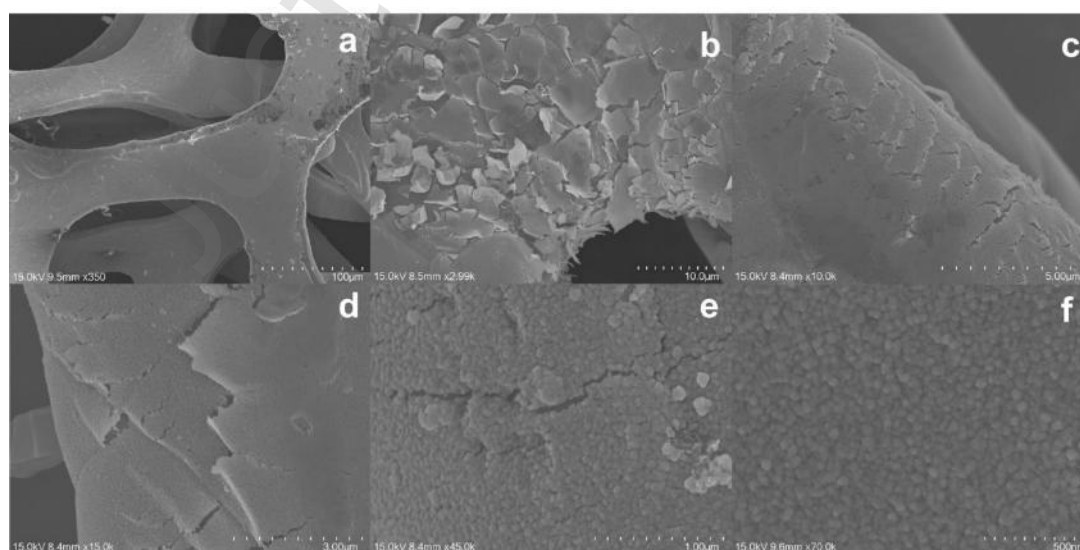


Figure S36 (a-f) SEM images of Pt/NiO/NF(Ga)-40 mg.

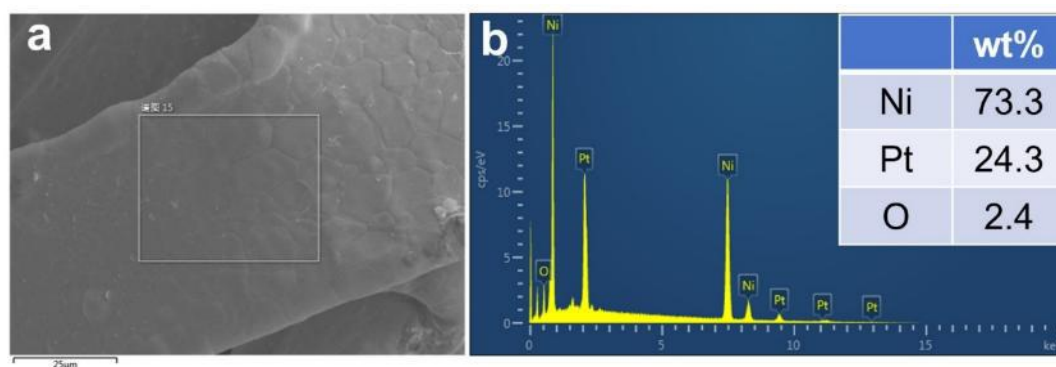


Figure S37 (a, b) EDX spectra of Pt/NiO/NF(Ga)-40 mg.

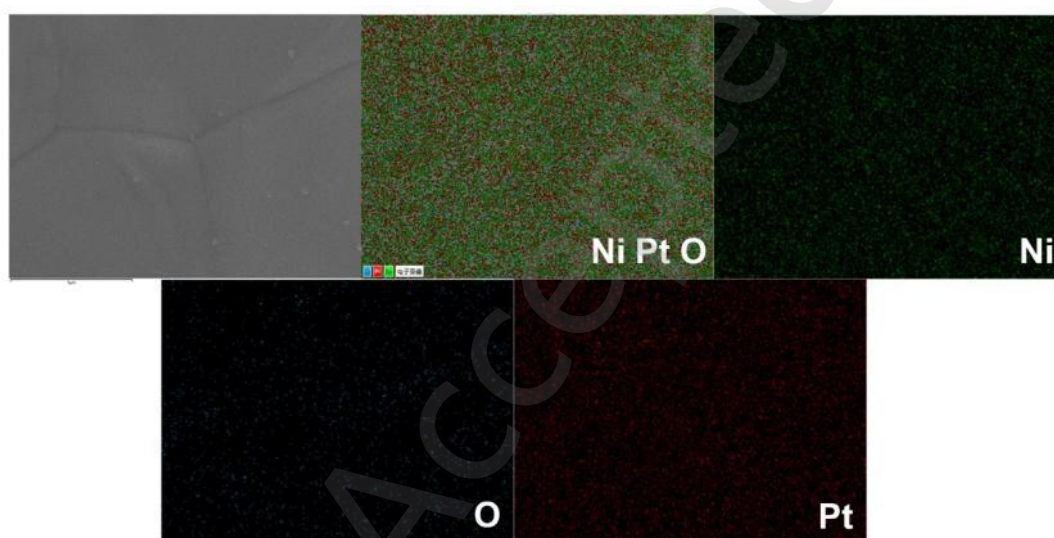


Figure S38 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-40 mg.

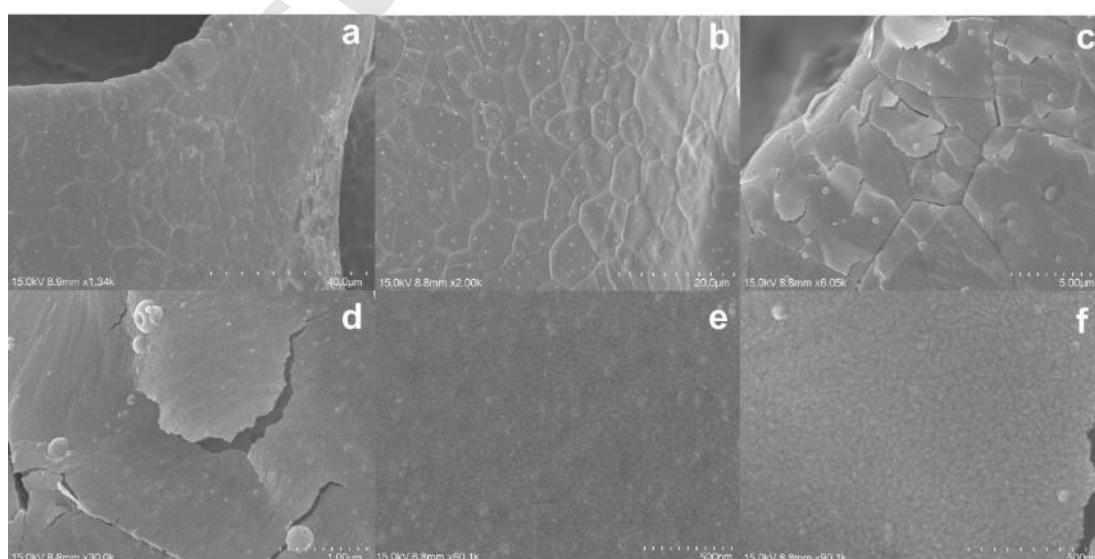


Figure S39 (a-f) SEM images of Pt/NiO/NF(Ga)-1h after 1 h deposition.

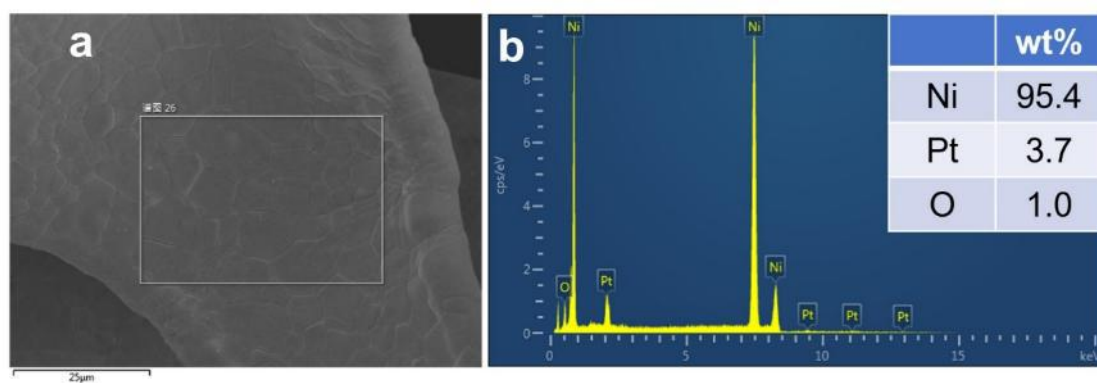


Figure S40 (a, b) EDX spectra of Pt/NiO/NF(Ga)-1h after 1 h deposition.

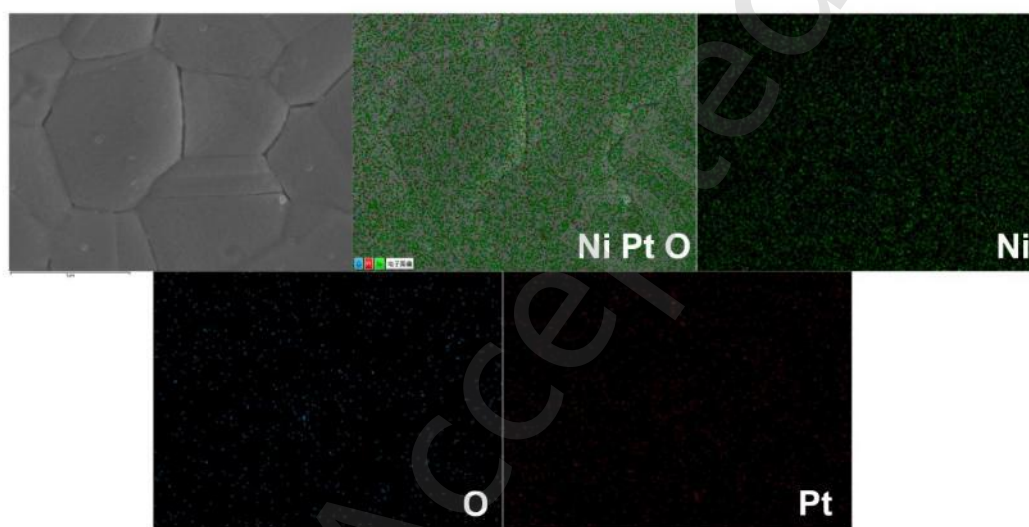


Figure S41 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-1h after 1 h deposition.

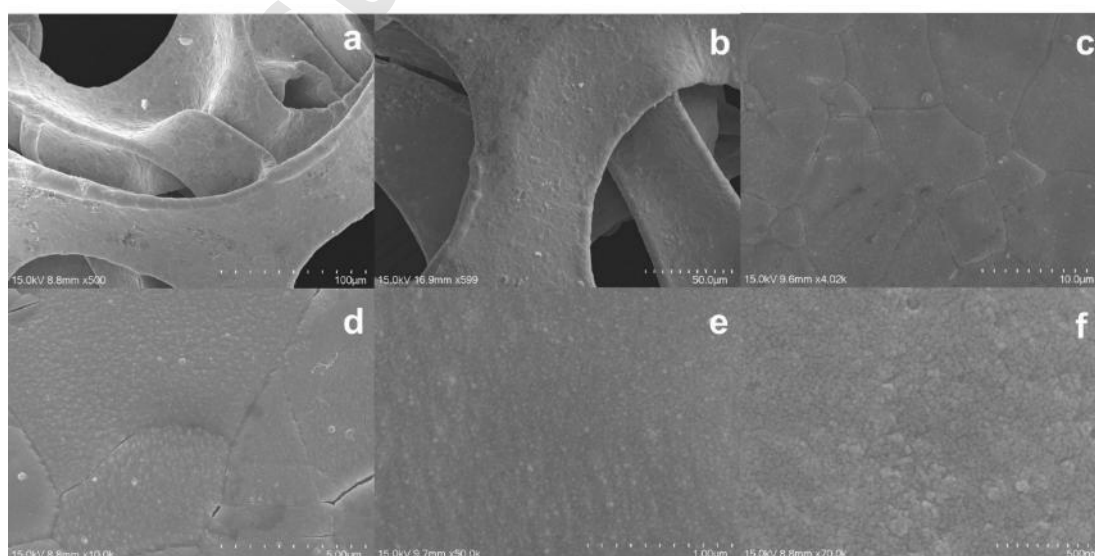


Figure S42 (a-f) SEM images of Pt/NiO/NF(Ga)-2 h after 2 h deposition.

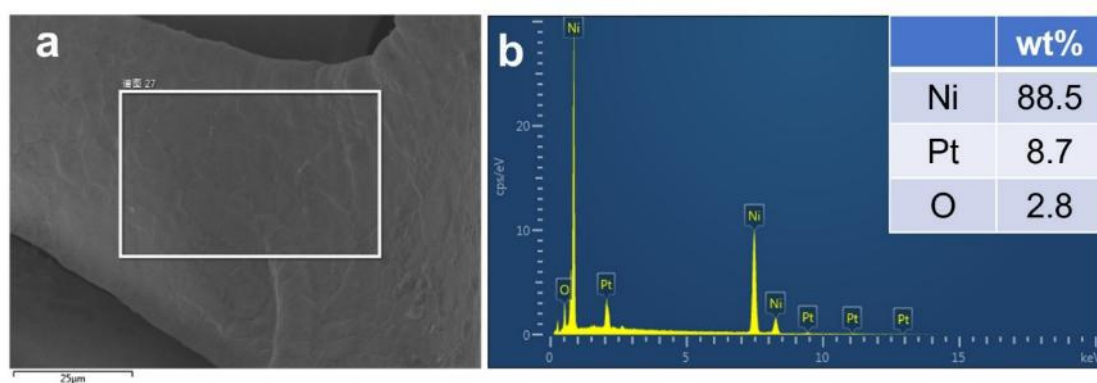


Figure S43 (a, b) EDX spectra of Pt/NiO/NF(Ga)-2 h after 2 h deposition.

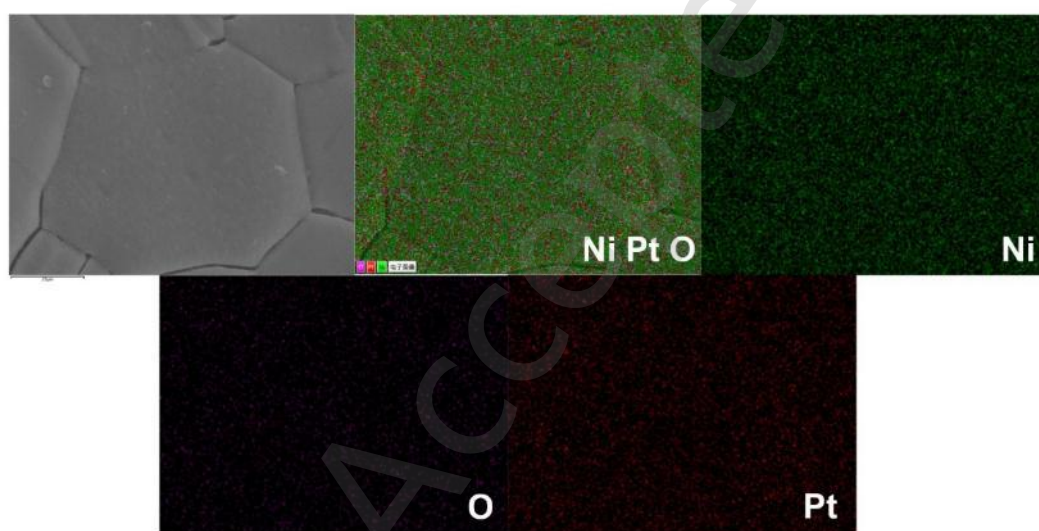


Figure S44 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-2h after 2 h deposition.

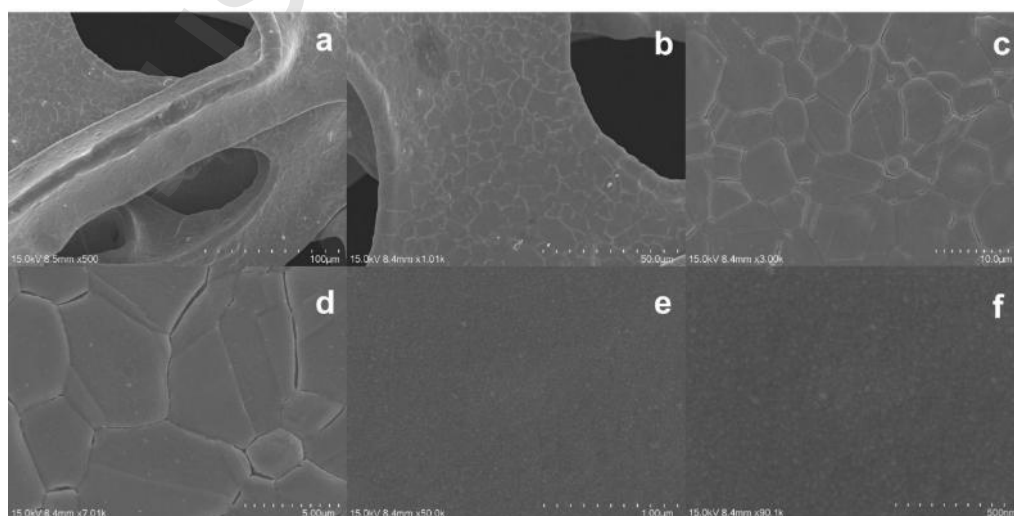


Figure S45 (a-f) SEM images of Pt/NiO/NF(Ga)-3 h after 3 h deposition.

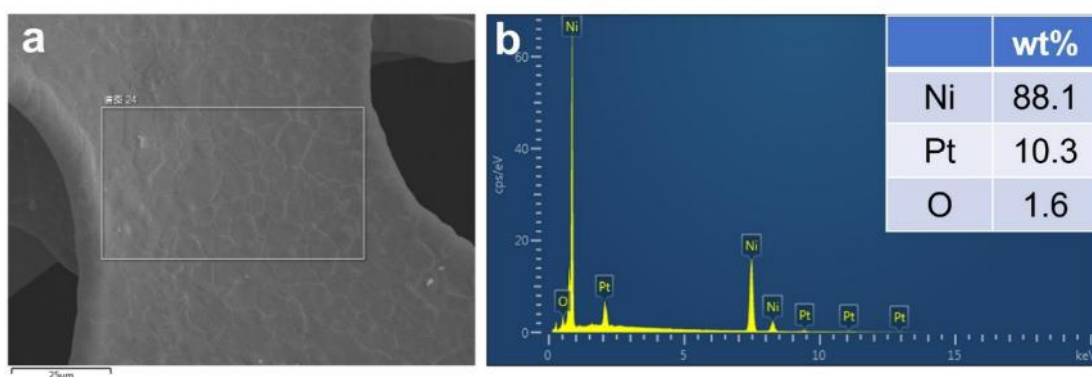


Figure S46 (a, b) EDX spectra of Pt/NiO/NF(Ga)-3 h after 3 h deposition.

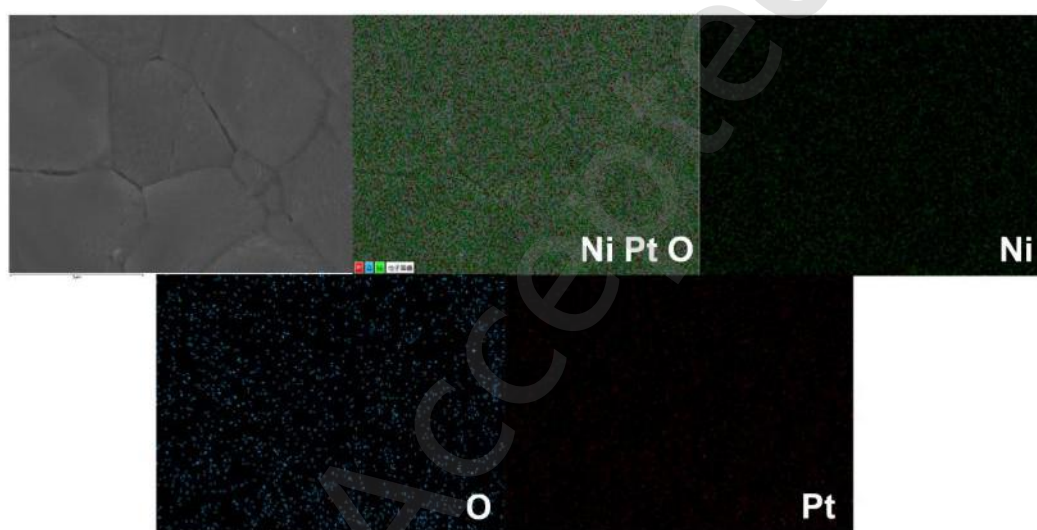


Figure S47 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-3 h after 3 h deposition.

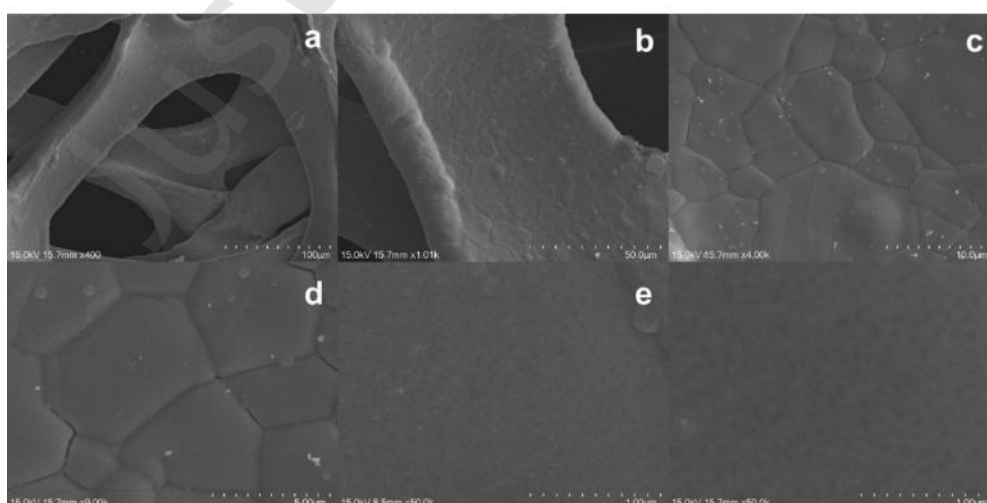


Figure S48 (a-f) SEM images of Pt/NiO/NF(Ga)-6 h after 6 h deposition.

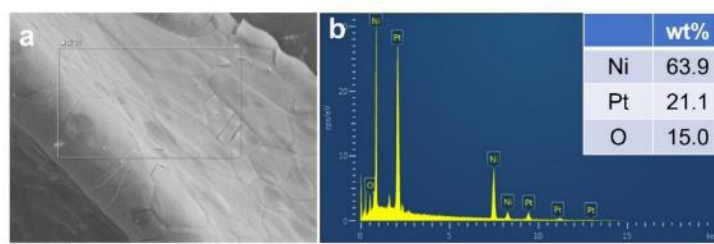


Figure S49 (a, b) EDX spectra of Pt/NiO/NF(Ga)-6 h after 6 h deposition.

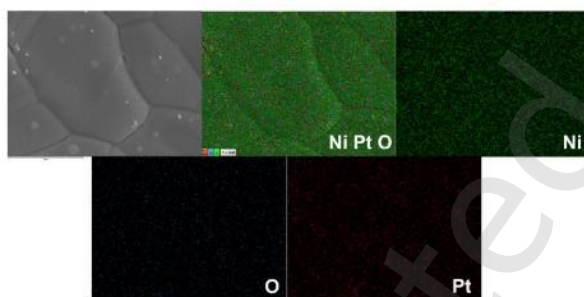


Figure S50 Element mapping (Ni, Pt, O) of Pt/NiO/NF(Ga)-6 h after 6 h deposition.



Figure S51 Digital photos of three independent Pt/NiO/NF (Ga) synthesized crucibles under the same experimental conditions.

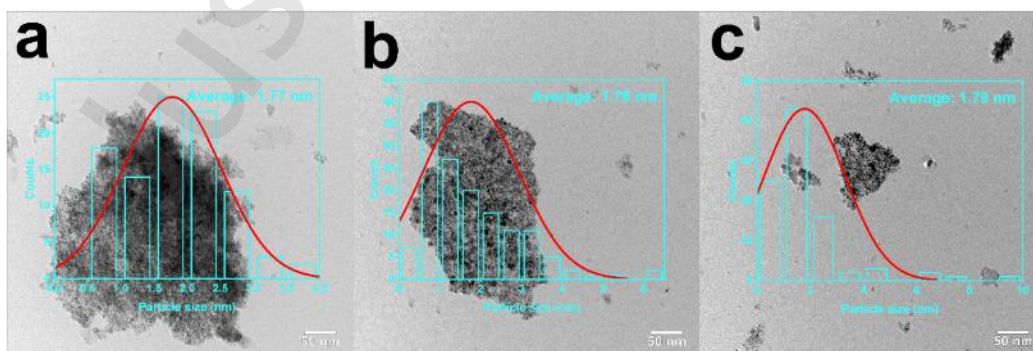


Figure S52 TEM images and average particle size distribution of three independently prepared Pt/NiO/NF (Ga) batches.

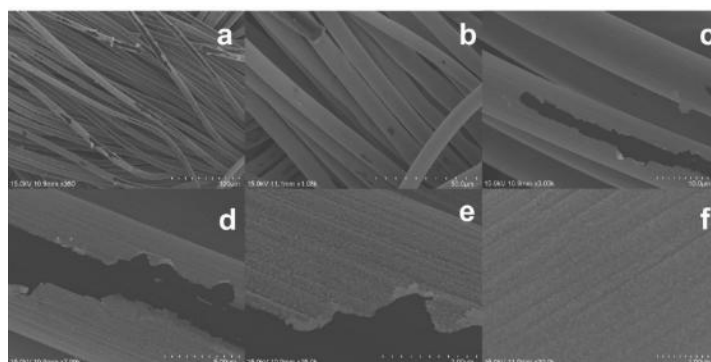


Figure S53 (a-f) SEM images of Pt/CC(Ga).

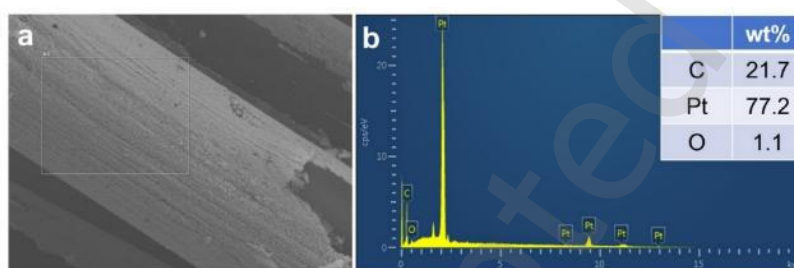


Figure S54 (a, b) EDX spectra of Pt/CC(Ga).

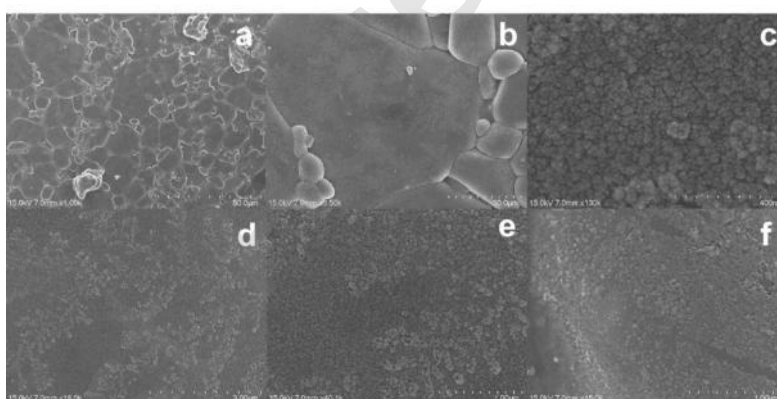


Figure S55 (a-f) SEM images of Pt/Al₂O₃(Ga).

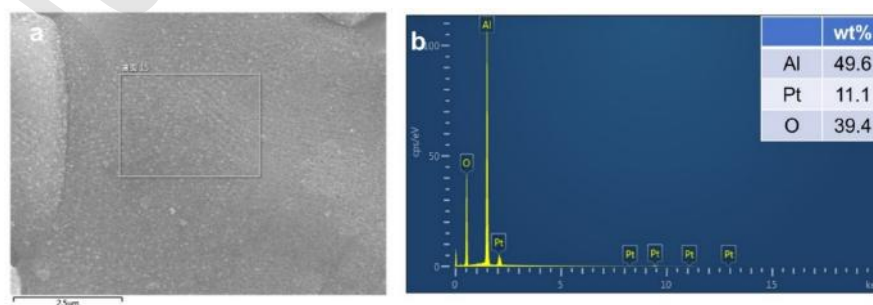


Figure S56 (a, b) EDX spectra of Pt/Al₂O₃(Ga).

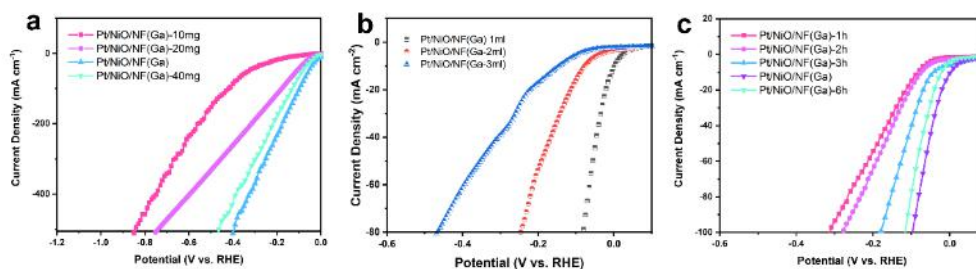


Figure S57 (a) LSV curves of catalysts prepared with different Pt precursor masses (10, 20, 30, and 40 mg) in 1 M KOH. (b) LSV curves of catalysts prepared with different Ga volumes (1, 2, and 3 mL). (c) LSV curves of catalysts prepared with different deposition times (1, 2, 3, 4, and 6 h)

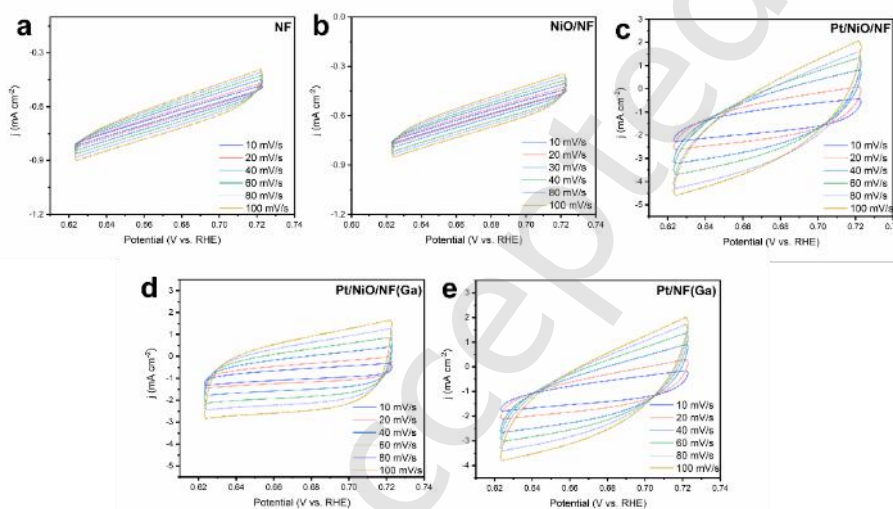


Figure S58 CV curves of (a) NF, (b) NiO/NF, (c) Pt/NiO/NF, (d) Pt/NiO/NF(Ga) and (e) Pt/NF(Ga) recorded at different scan rates in 1 M KOH for double-layer capacitance analysis.

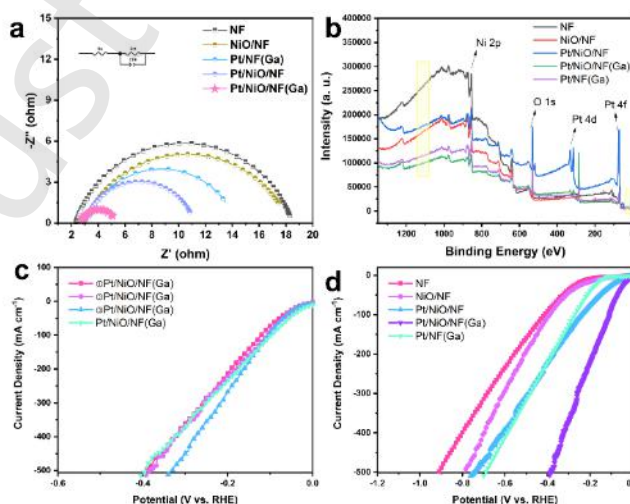


Figure S59 (a) EIS fitting curve. (b) XPS survey spectrum of the sample. (c) LSV curves of three independently prepared batches of Pt/NiO/NF(Ga) in 1 M KOH under the same experimental conditions. (d) LSV curve of Hg/HgO electrode as reference electrode in 1 M KOH.

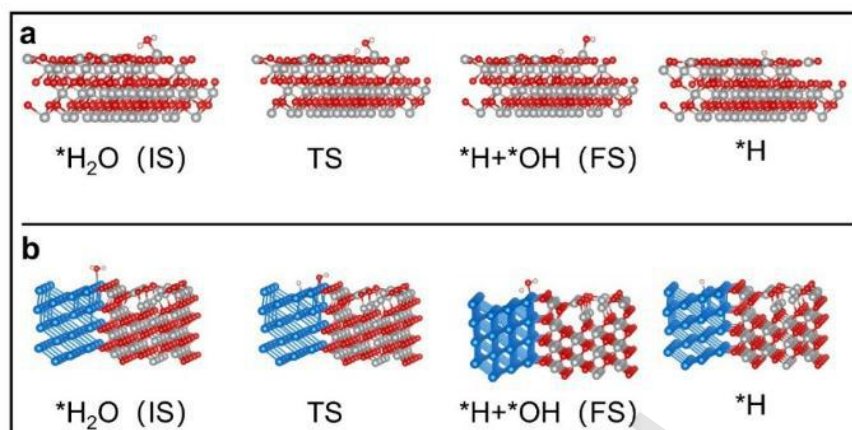


Figure S60 Side-view structural models for H_2O dissociation into H^* and OH^* on (a) NiO/NF and (b) $\text{Pt}/\text{NiO}/\text{NF}(\text{Ga})$. Red, gray, white, and blue spheres represent O, Ni, H, and Pt atoms, respectively.

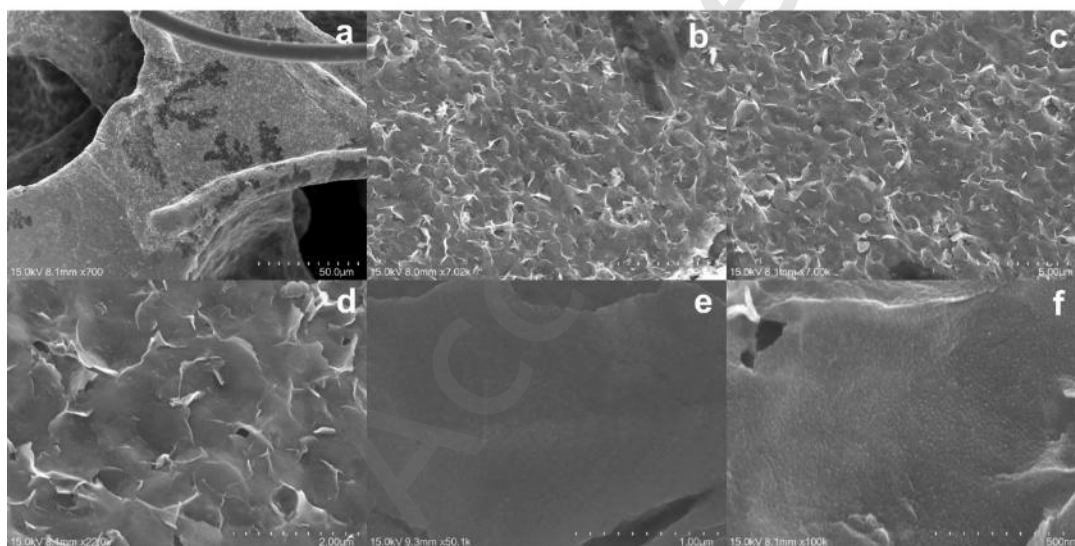


Figure S61 (a-f) SEM image of $\text{Pt}/\text{NiO}/\text{NF}(\text{Ga})$ after long-term HER testing.

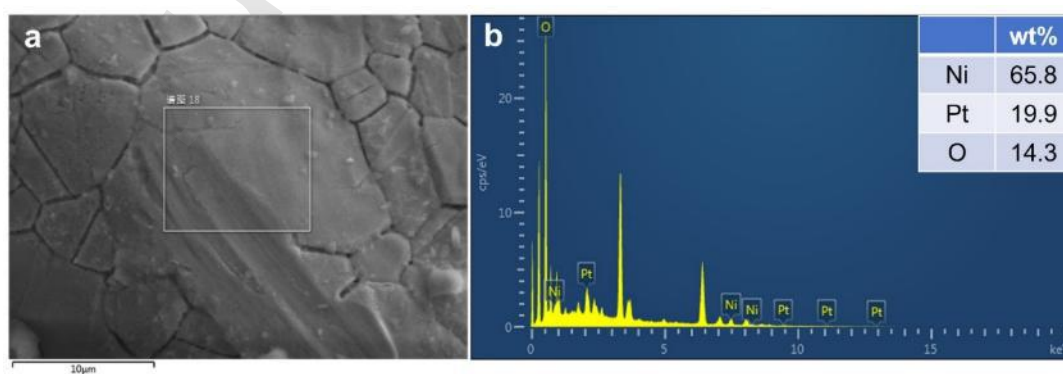


Figure S62 (a, b) EDX spectra of $\text{Pt}/\text{NiO}/\text{NF}(\text{Ga})$ after HER stability testing.

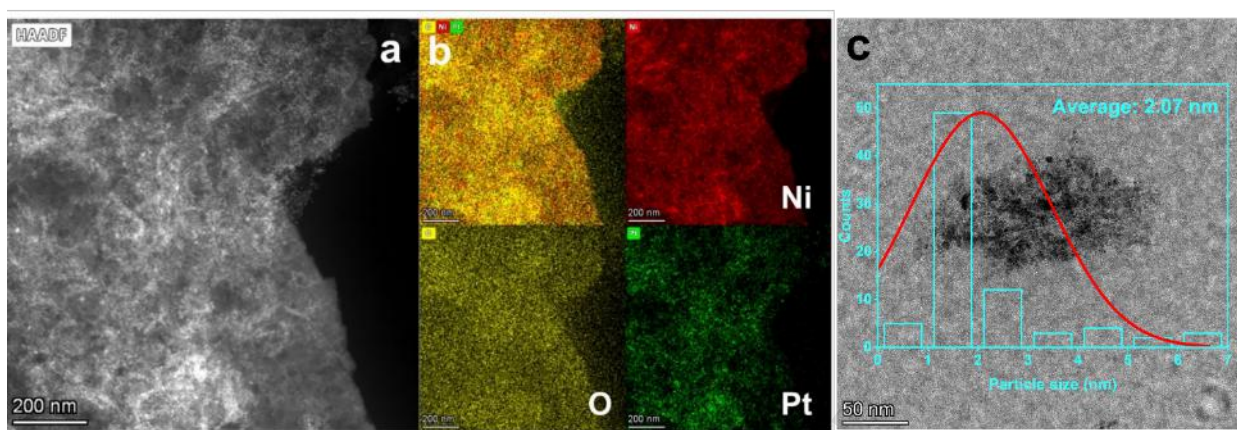


Figure S63 (a, b) Elemental mapping (Ni, Pt, O) and (c) TEM with particle size distribution of Pt/NiO/NF(Ga) after HER stability testing.

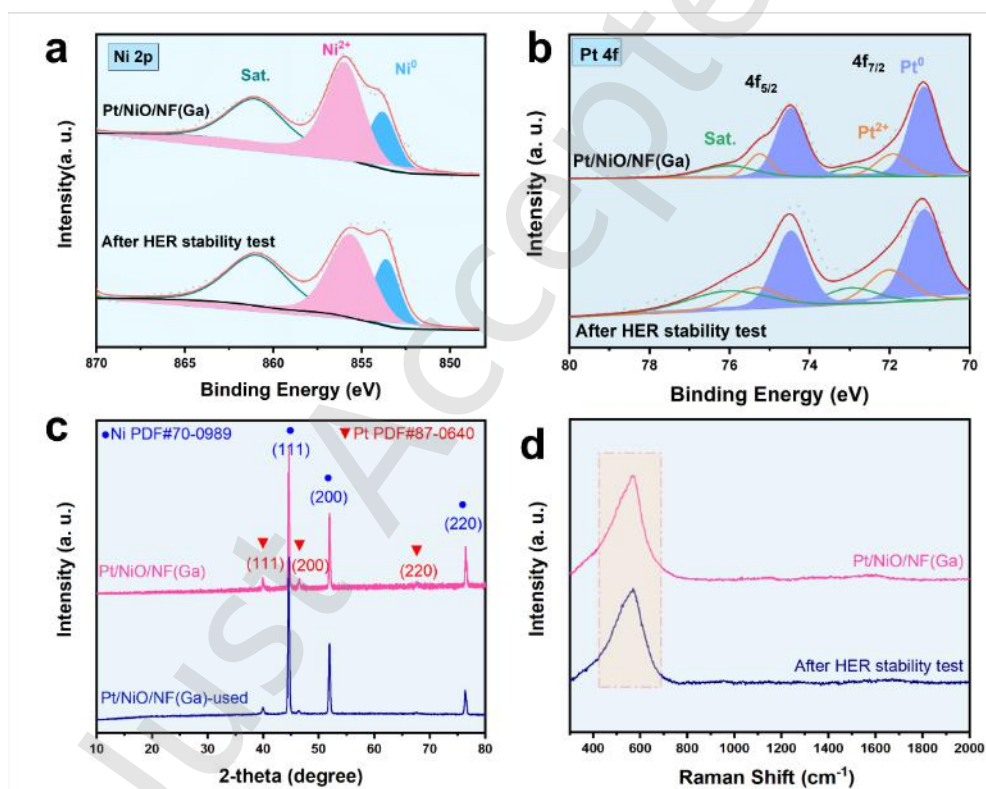


Figure S64 Pt/NiO/NF(Ga) after HER stability testing: (a) Ni 2p spectrum; (b) Pt 4f spectrum; (c) PXRD pattern; (d) Raman spectra.

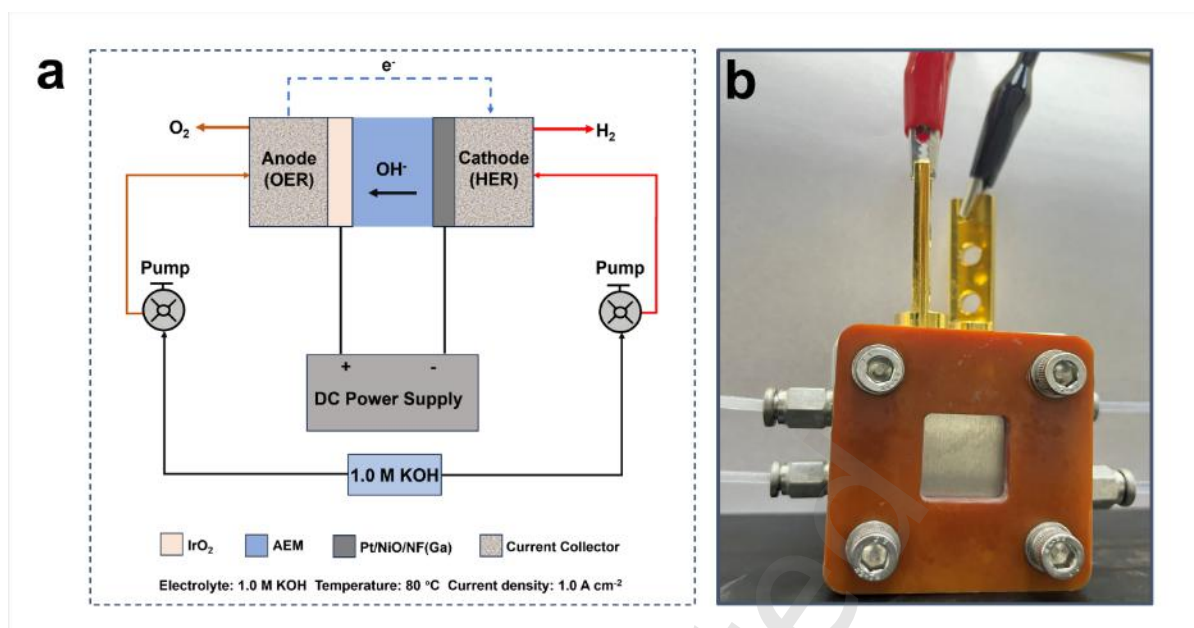


Figure S65 (a) Schematic diagram and (b) image of anion-exchange membrane water electrolyzer (AEMWE).

2. Supplementary Tables

Table S1 XPS fitting parameters of Ni 2p spectra for the investigated samples.

Samples	Ni ⁰ Position(eV)	Ni ⁰ (%)	Ni ²⁺ Position(eV)	Ni ²⁺ (%)
NiO/NF	853.39	44.13	855.29	55.86
Pt/NiO/NF	853.68	33.18	855.63	66.82
Pt/C	-	-	-	-
Pt/NiO/NF(Ga)	853.80	30.79	855.94	69.21
Pt/NF(Ga)	853.54	47.47	855.59	52.52

Table S2 XPS fitting parameters of Pt 4f spectra for the investigated samples.

Samples	Pt 4f _{7/2} Position(eV)		Pt 4f _{5/2} Position(eV)	
	Pt ⁰	Pt ²⁺	Pt ⁰	Pt ²⁺
Pt/NiO/NF	70.94	71.69	74.27	75.02
Pt/NiO/NF(Ga)	71.14	71.92	74.47	75.25
Pt/NF(Ga)	70.80	71.54	74.13	74.87

Table S3 Metal contents of all samples determined by ICP-OES.

Sample	Ni (wt%)	Pt (wt%)	Ga (wt%)
NiO/NF	63.65	< 0.001	< 0.001
Pt/NiO/NF	48.22	1.60	< 0.001
Pt/C	< 0.001	20	< 0.001
Pt/NiO/NF(Ga)	47.86	3.25	< 0.001
Pt/NF(Ga)	47.93	0.67	< 0.001

Table S4 Performance comparison of representative platinum-based electrocatalysts for the HER in alkaline media.

Number	Electrocatalyst	Electrolyte	η_{10} (mV)	Ref.
1	Pt/NiO/NF(Ga)	1 M KOH	20	This work
2	Pt ₃ Co@NCNT	1 M KOH	36	[1]
3	Pt/NiO@Ni/NF	1 M KOH	34	[2]
4	Pt-MoAl _{1-x} B	1 M KOH	33	[3]
5	Pt ₃ Fe/NMCS-A	1 M KOH	29	[4]
6	Dr-Pt	1 M KOH	26	[5]
7	PtNi/Ru	1 M KOH	25	[6]
8	Pt - eBN@CNT	1 M KOH	25.1	[7]
9	Pt-ACs/CoNC	1 M KOH	24	[8]
10	PtSA-NT-NF	1 M KOH	24	[9]
11	Pt SACs-NiCrO ₃ /NF	1 M KOH	23	[10]
12	Pt-AC/DG-500	1 M KOH	21	[11]
13	Pt@MTO-S	1 M KOH	73	[12]
14	Pt/WO ₃	1 M KOH	39	[13]
15	Pt-PMo/ZIF-67-800	1 M KOH	26	[14]
16	PtCu/NC	1 M KOH	23.5	[15]

Table S5 Mass activity of Pt/NiO/NF(Ga) and Pt/C.

Catalyst	Pt content (wt%)	Overpotential@ 100 mA cm ⁻² (mV)	Pt loading (mg cm ⁻²)	Mass activity@ 100 mA cm ⁻² (mA mg _{Pt} ⁻¹)
Pt/NiO/NF(Ga)	3.25	97	1.08	92.68
Pt/C	20.00	118	6.88	14.53

Table S6 Metal contents of Pt/NiO/NF(Ga) after long-term durability testing and the corresponding metal concentrations in the post-test electrolyte, determined by ICP-OES.

Sample	Ni (wt%)	Pt (wt%)	Ga (wt%)
Pt/NiO/NF(Ga)	47.86	3.25	< 0.001
After HER stability test	47.87	3.22	< 0.001
the electrolyte after durability test	< 0.001	< 0.001	< 0.001

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