

Engineering a dual-oxide/alloy interface for synergistically enhanced oxygen reduction reaction

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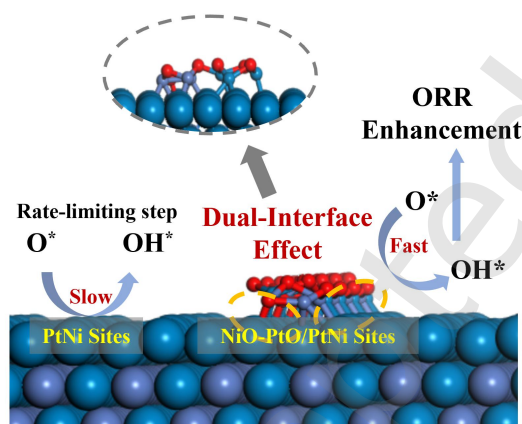
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NiO-PtO/PtNi dual-oxide/alloy interface sites were successfully constructed, which demonstrated superior oxygen reduction reaction (ORR) performance with mass activity of 3.2 A/mg_{Pt}, representing a 9.2-fold enhancement compared to commercial Pt/C. Moreover, the catalyst exhibited remarkable durability, with negligible activity decay after 50,000 cycles.

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ABSTRACT: Rational engineering of metal-oxide interfaces presents a powerful avenue for tailoring the catalytic properties of metal nanoparticles. However, the strategy of focusing on a single interface offers limited scope for tuning the performance. Herein, we transcend this limitation by constructing a dual-oxide/alloy interface to concurrently boost the activity and stability of oxygen reduction reaction (ORR) catalysts. Using a PtNi alloy as a model system, we demonstrate that the synergistic interplay between two distinct oxides (PtO and NiO) and the PtNi alloy creates a uniquely tailored interfacial microenvironment (NiO-PtO/PtNi) which can improve the kinetics of the ORR. The stability of the NiO-PtO/PtNi dual-oxide/alloy interface structure during the actual ORR operation conditions is confirmed by in situ Raman spectra. The resulting catalyst exhibits exceptional performance, achieving a half-wave potential of 0.97 V, with mass and specific activities of 3.2 A/mg_{Pt} and 5.3 mA/cm², 9.2 and 4.4 times greater than commercial Pt/C (40 wt%), respectively, alongside outstanding durability (negligible decay after 50,000 cycles). A combination of in situ infrared spectroscopy and first-principles calculations reveals that this multi-component interface optimizes the Pt d-band center, thereby regulating the adsorption of oxygen-containing intermediates and altering the rate-determining step of the ORR. This study underscores the profound potential of multi-component interface engineering for advancing the design of high-performance Pt-based electrocatalysts.

KEYWORDS: interface, alloy, oxygen reduction reaction, platinum, structure-performance relationship

1 Introduction

The rational design of active sites governed by the local coordination environment and electronic structure, is central to advancing heterogeneous catalysis [1-4]. Toward this end, engineering precisely controlled heterointerface has emerged as a pivotal strategy for accessing novel catalytic active sites unattainable in single-phase materials [5-7]. The interface formed between metals and oxides is particularly noteworthy [8-10], as it not only secures active metal nanoparticles but also creates a unique interfacial microenvironment governed by strong metal-support interactions (SMSI) [11, 12], electronic metal-support interactions (EMSI) [13], and direct orbital overlap at metal-metal contacts [14]. These effects exert a profound influence on key catalytic parameters by reshaping the electronic density of states at active sites, enabling efficient charge flow, and reinforcing the catalyst's architecture [15-17]. This versatile mechanism underpins their successful application across a diverse catalytic spectrum, ranging from traditional thermal conversions like Fischer-Tropsch synthesis [18-21] and selective hydrogenation [22-24] to modern electrochemical energy technologies [25-27].

Build on this foundation, the exploration of alloy-oxide

interface represents a significant leap forward, leveraging the synergistic interplay between the alloy and the interface to achieve superior tunability of catalytic properties [28-31]. For instance, PdAu/CeO₂ interfaces harness concerted alloy-support interactions to dramatically boost both selectivity and stability in methanol synthesis [32]. Similarly, Pt₃Co/CoO interfaces leverage synergistic effects between the alloy and oxide to accelerate B-H bond cleavage and water activation, enabling efficient ammonia borane hydrolysis [33]. These advancements underscore a key principle: multi-component interfacial engineering enables multifaceted catalytic enhancement. However, the intrinsic limitations of a single-oxide support—constrained by its fixed chemical and electronic properties—often impede the simultaneous and independent optimization of multiple performance descriptors, such as activity, selectivity, and stability [34-36]. To overcome this limitation, we propose a novel interfacial architecture: the dual-oxide/alloy interface. This design aims to decouple the interfacial environment by employing two distinct oxides, each providing independent yet cooperative functions. To demonstrate the power and versatility of this strategy, we selected the oxygen reduction reaction (ORR) as a critical testbed, a pivotal process in renewable energy technologies that places stringent and concurrent demands on

both catalyst activity and durability [37–40]. Recent efforts have focused on enhancing the ORR kinetics through various strategies, including morphological design [41], electronic structure modulation via interstitial or substitutional microalloying [42,43], and the construction of novel metal–oxide heterojunctions [44]. Although these approaches have achieved notable success, our proposed dual-oxide/alloy architecture offers a more comprehensive platform for the simultaneous optimization of this complex interfacial microenvironment.

Herein, we construct a model dual-oxide/alloy interface (NiO–PtO/PtNi) by a modified ion-exchange inverse loading (IEIL) method [45]. This tailored architecture not only creates synergistic active sites for exceptional ORR activity but also effectively anchors and stabilizes the alloy nanoparticles, resulting in unprecedented durability. The optimized catalyst (PtNi-500) achieves a remarkable half-wave potential of 0.97 V, significantly outperforming commercial Pt/C catalyst (0.88 V). In addition, PtNi-500 has excellent durability, with activity remaining virtually unchanged after 50,000 cycles of stability testing. This work not only presents a superior ORR electrocatalyst but, more importantly, validates the dual-oxide/alloy interface as a general and powerful design strategy for next-generation heterogeneous catalysts.

2 Results and Discussion

2.1 Structure and chemical state of PtNi catalysts

The PtNi sample without reduction thermal treatment is named as PtNi-MMH, while those reduced at the temperature ranging from 100 to 700 °C are denoted as PtNi-r ($r = 100, 300, 500$ and 700). The X-ray diffraction (XRD) patterns of the PtNi-MMH and PtNi-r samples are presented in Fig. 1. PtNi-MMH exhibits distinct $\text{Ni}(\text{OH})_2$ diffraction peaks, confirming its presence in the composite. Conversely, signals for $\text{Pt}(\text{OH})_4$ are absent, likely due to its amorphous state formed via surface ion exchange. In addition to the persistent signals characteristic of $\text{Ni}(\text{OH})_2$, the PtNi-100 sample exhibits distinct diffraction peaks corresponding to the (111), (200), and (220) planes of Pt, indicating the formation of a face-centered cubic platinum phase. In contrast to standard Pt, PtNi-100 displays a discernible shift of its diffraction peaks to higher 2θ angles, which could be a sign of the formation of a PtNi alloy. Upon increasing the reduction temperature, the $\text{Ni}(\text{OH})_2$ signal disappears for PtNi-300. A slight positive shift of the Pt diffraction peaks is observed, coupled with the appearance of new reflections corresponding to a crystalline NiO phase. The larger values of 2θ for PtNi-300 in comparison to those for the standard NiO can be attributed to the interaction with the PtNi alloy. The XRD patterns for PtNi-500 and PtNi-700 are dominated by peaks corresponding to a PtNi alloy. The progressive sharpening and intensification of these peaks at higher reduction temperatures reflect concurrent enhancements in the alloying degree and an increase in nanoparticle size due to sintering.

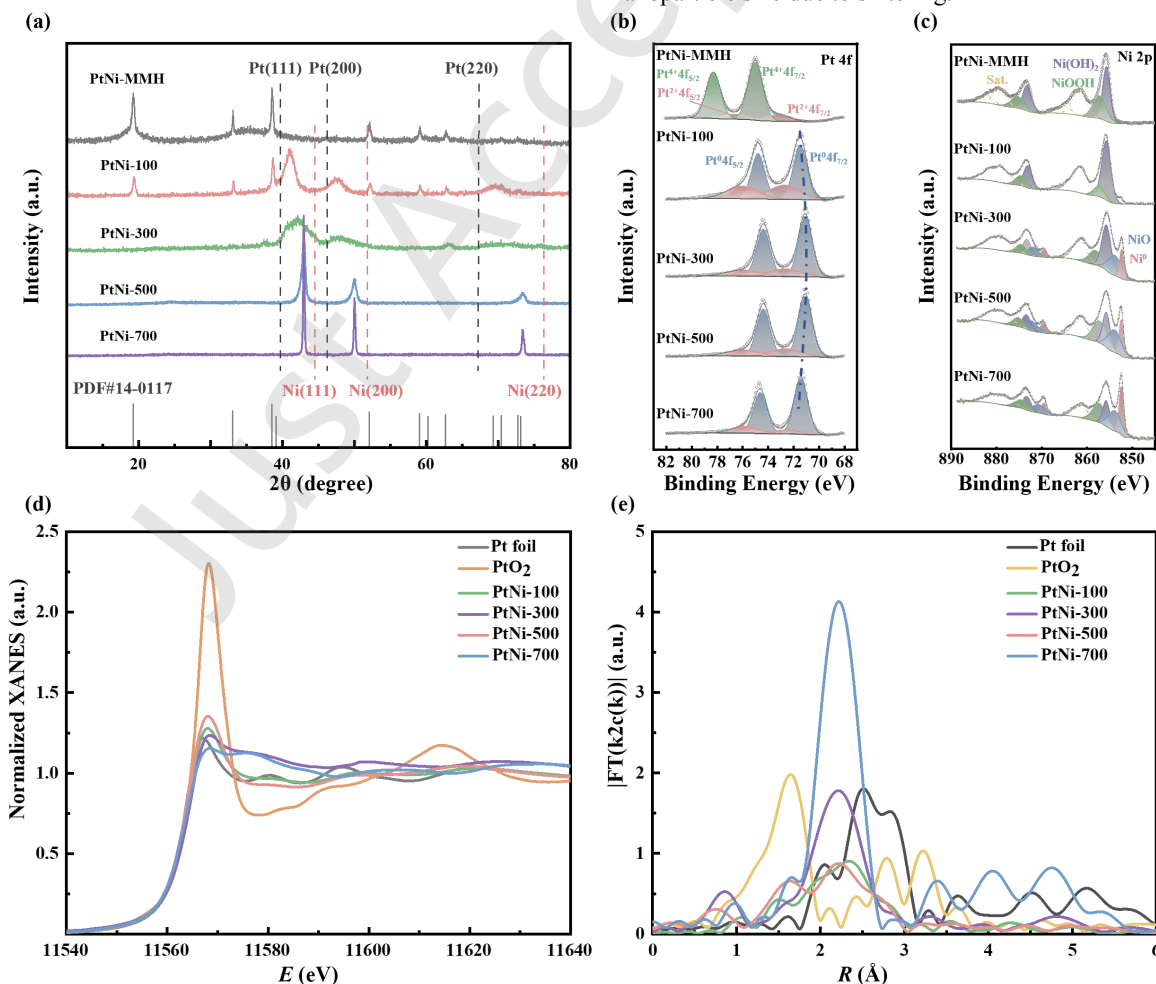


Figure 1 (a) XRD patterns. (b–c) XPS spectra of Pt 4f and Ni 2p. (d) XANES spectra of Pt L₃-edge. (e) Pt L₃-edge k³-weighted FT-EXAFS spectra.

The chemical states of the samples were characterized by X-ray photoelectron spectroscopy (XPS). As illustrated in Fig. 1b,

the Pt4f XPS spectra of PtNi-MMH exhibit Pt4f_{5/2} and Pt4f_{7/2} at 78.31 and 75.01 eV, respectively, each peak was deconvoluted into two peaks attributed to Pt⁴⁺ and Pt²⁺. It is notable that the content of Pt⁴⁺ is considerably larger than Pt²⁺. For PtNi-100, the binding energies of Pt 4f_{7/2} and Pt 4f_{5/2} are shifted to 71.5 eV and 74.5 eV, respectively. Deconvolution of the Pt 4f spectra yields two doublets: a dominant one attributed to Pt⁰ (71.5 and 74.8 eV) and a secondary one corresponding to Pt²⁺ (72.7 and 76.0 eV), indicating the partial reduction of Pt⁴⁺ from PtNi-MMH. With the increase in the reduction temperature, the proportion of Pt⁰ first rises and then declines. This variation trend is further corroborated by the X-ray absorption near-edge structure (XANES) results (Fig. 1d).

The Ni 2p spectra of PtNi-MMH, PtNi-100, PtNi-300, PtNi-500 and PtNi-700 are presented in Fig. 1c. The PtNi-MMH sample displays well-resolved Ni 2p peaks with binding energies of 855.7 eV (Ni 2p_{3/2}) and 873.3 eV (Ni 2p_{1/2}). The observed spin-orbit splitting of 17.6 eV is in excellent agreement with the reference value for Ni(OH)₂, corroborating the XRD findings. Considering the satellite peak, the Ni2p_{3/2} peak of PtNi-100 could be decomposed into two peaks at 855.7 and 857.3 eV, which are closely related to the Ni(OH)₂ and NiOOH, respectively. For PtNi-300, a strong shake-up satellite signal at high binding energy close to the main peak of the Ni 2p core level spectrum is indicative of a multi-modal adsorption pattern. This phenomenon can be explained by electron excitation. Deconvolution of the Ni 2p_{3/2} XPS spectrum for PtNi-300 reveals four distinct components: Ni⁰ (852.3 eV), NiO (853.9 eV), Ni(OH)₂ (855.7 eV), and NiOOH (857.3 eV). The

identification of NiO by XPS is in good agreement with its detection in the corresponding XRD pattern. Relative to the standard value of Ni⁰ 2p_{3/2} (852.6 eV), the binding energy of PtNi-300 is shifted by 0.3 eV, which could arise from electron transfer either due to interaction with nickel oxide or as a consequence of PtNi alloy formation. Quantitative analysis of XPS data reveals that Ni⁰/Ni²⁺ increases gradually with rising reduction temperature. Meanwhile, as the calcination temperature increases, the amount of Ni(OH)₂ gradually decreases. In contrast, the proportion of NiOOH exhibits a progressive increase with temperature, eventually reaching a plateau after 500 °C.

The surface morphology of the samples, as characterized by transmission electron microscopy (TEM), is shown in Figure 2, Fig. S1 and Fig. S2. PtNi-MMH is composed of spherical nanoparticles of 1-2 nm in diameter. XRD and XPS results suggest that the particles are Pt/Ni(OH)_x composites, wherein Pt⁴⁺ are partially substituted for Ni²⁺ within the Ni(OH)₂ lattice. The bulk of PtNi-100 remains as Ni(OH)₂, while all surface Pt⁴⁺ cations are reduced to Pt²⁺ and Pt⁰. As the reduction temperature increases, the core of PtNi-300 undergoes a phase transition from Ni(OH)₂ to NiO. The presence of a crystalline NiO phase in PtNi-300 is confirmed (d = 0.22 nm in Fig. 2b), and is fully consistent with the XRD and XPS results. PtNi-500 and PtNi-700 are highly alloyed, and the particle size of PtNi-700 is much larger than PtNi-500. A small amount of NiO can be observed on the surface of PtNi-500. This is corroborated by the electron energy loss spectroscopy (EELS) mapping showing oxygen enrichment at the surface of the catalyst (Fig. 2h).

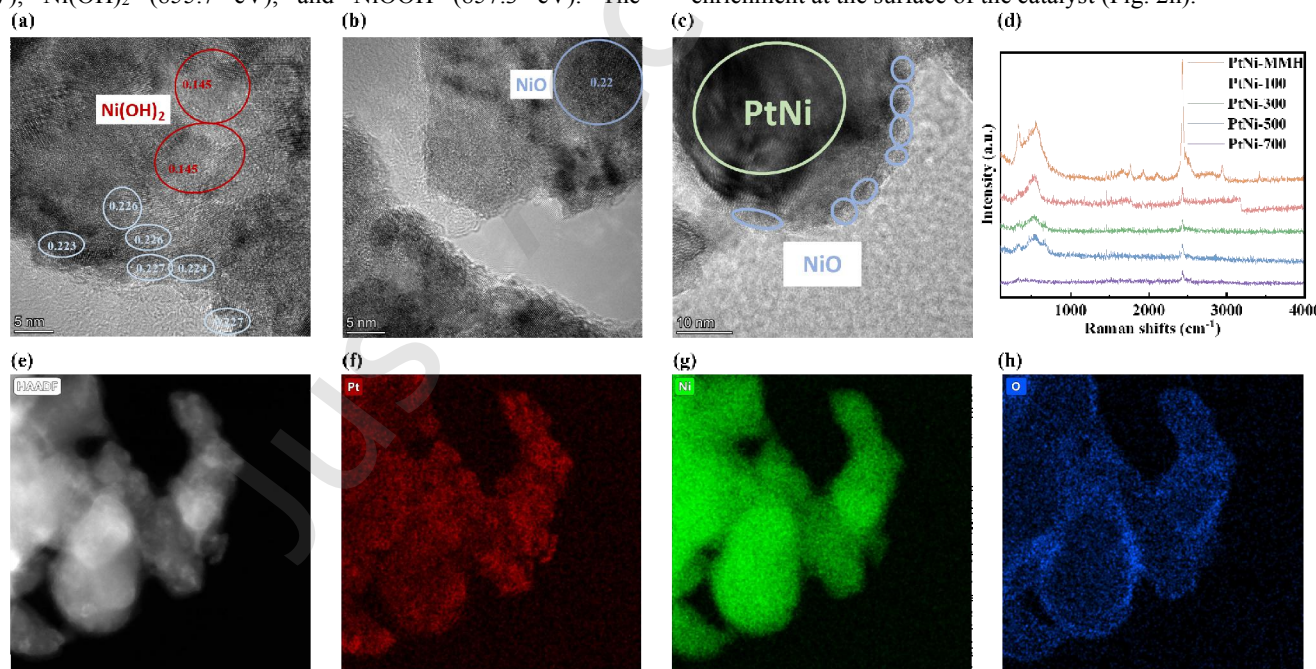


Figure 2 HRTEM images of PtNi-100 (a), PtNi-300 (b) and PtNi-500 (c). (d) Raman spectroscopy. HAADF-STEM image of PtNi-500 (d) and the corresponding EELS elemental mappings of Pt(f), Ni(g) and O(h).

The Raman spectra of PtNi catalysts are shown in Fig. 2d. The broad peak observed for PtNi-MMH at 567 cm⁻¹ is a convolution of two peaks at 450 cm⁻¹ and 570 cm⁻¹, which are assigned to the Ni-O stretching mode of Ni(OH)₂ and Pt-OH vibrations, respectively [46]. The appearance of Pt-OH vibrational modes is indicative of a surface substitution reaction during ion exchange, wherein Pt⁴⁺ replaces Ni²⁺ in the Ni(OH)₂ lattice. Two additional Raman peaks at 338 and 3580 cm⁻¹ are

attributed to the E-type vibrational mode of Ni-OH and the symmetric stretching of hydroxyl groups, respectively [47]. These peaks, along with the Ni-O signal observed at 450 cm⁻¹, further confirm the existence of Ni(OH)₂ in PtNi-MMH. The bending and stretching modes of H₂O are also present in the signals at 1650 cm⁻¹ and 3400 cm⁻¹, respectively.

The Raman peaks characteristic of Ni(OH)₂ are notably diminished in the PtNi-100 spectrum. Meanwhile, the

disappearance of the Pt-OH Raman peak in PtNi-100 confirms the reduction of Pt^{4+} . The featureless Raman spectrum of PtNi-700 is consistent with a high degree of reduction, leading to a surface dominated by a metallic PtNi alloy phase. A new peak at 667 cm^{-1} for PtNi-300 and PtNi-500 is assigned to B_{1g} mode of PtO [48, 49], which is more obvious for PtNi-500. Quantitative structural parameters for the local atomic coordination, derived from fitting the extended X-ray absorption fine structure (EXAFS) spectra (Fig. 1e and S3), are presented in Table S1. The average Pt-O coordination number of PtNi-500 is 1.6. This value is consistent with the local structure expected for a PtO phase, providing strong evidence for its presence in the catalyst. The standard NiO spectra feature a prominent band at approximately 500 cm^{-1} , a shoulder peak near 390 cm^{-1} , along with broad second-order bands located around 680 and 1046 cm^{-1} [50-52]. In contrast to the standard NiO spectrum, the primary Raman bands for PtNi-300 and PtNi-500 are up-shifted to approximately 535 cm^{-1} , while the second-order broad bands become indistinguishable. These spectral modifications suggest that the Ni-O lattice vibrations are perturbed by strong interfacial coupling between the PtNi alloy and the NiO cluster. Based on complementary analyses from XRD, XPS, TEM, Raman, XANES, and EXAFS, it is evident that a PtNi-NiO/PtO dual oxide-metal interface is established in the catalysts following reduction at 300°C and 500°C .

2.2 ORR Performance

Fig. 3a presents cyclic voltammetry (CV) results for the PtNi-r catalysts recorded in an N_2 -saturated 0.1 M HClO_4 solution. According to the hydrogen underpotential deposition (HUPD) analysis, the electrochemically active surface area (ECSA) of PtNi-100, PtNi-300, PtNi-500 and PtNi-700 are 11.4, 53.8, 62.5 and $21.6\text{ m}^2/\text{g}_{\text{Pt}}$, respectively. PtNi-500 shows the highest ESCA, indicating that it possesses the greatest number of accessible reactive sites. The low ESCA of PtNi-100 is owing to its low reduction degree, which yields primarily inactive Pt^{2+} species. Despite being almost completely reduced, PtNi-700 exhibits a low ECSA due to its substantially larger particle size, as observed by TEM. This suggests that an excessively high reduction temperature, while ensuring full reduction, can lead to an over-sintering of the nanoparticles, thereby compromising the exposure of active sites. In general, the ECSA exhibits a volcanic trend with increasing reduction temperature, initially increasing and then decreasing after reaching a maximum at 500°C .

The ORR polarization curves in Figure 3b reveal that PtNi-500 achieves a remarkable half-wave potential of 0.97 V , surpassing those of the $20\text{ wt}\%$ (0.88 V) and $40\text{ wt}\%$ (0.92 V) commercial Pt/C catalysts and many state-of-the-art Pt-Ni catalysts (Table S2), underscoring its superior ORR activity. PtNi-300 also demonstrates favorable ORR activity, as shown by its polarization curve. In contrast, PtNi-100 and PtNi-700 exhibit much lower limiting current densities, which can be ascribed to their insufficient reduction and excessive metallization/sintering, respectively. Crucially, PtNi-500 delivers a mass activity (MA) of $3.40\text{ A}/\text{mg}_{\text{Pt}}$ and a specific activity (SA) of $5.43\text{ mA}/\text{cm}^2$, which are 9.2 and 4.4 times higher than those of the $40\text{ wt}\%$ commercial Pt/C catalyst ($0.37\text{ A}/\text{mg}_{\text{Pt}}$ and $1.23\text{ mA}/\text{cm}^2$), respectively. This outstanding performance underscores that PtNi-500 is the most active ORR catalyst among all the samples studied. Koutecky-Levich (K-L) analysis

reveals an average electron transfer number of approximately 3.8 for the PtNi-r catalysts. This value closely approaches the theoretical value of 4.0 for a direct four-electron ORR pathway, suggesting that the reaction proceeds efficiently via the direct reduction of O_2 to H_2O with minimal peroxide formation.

The stability of PtNi-500 was further assessed through accelerated durability test (ADT) in an O_2 -saturated 0.1 M HClO_4 solution, with potential cycling between 0.6 and 1.1 V vs. RHE at a scan rate of 50 mV/s . Following 50,000 ADT cycles, PtNi-500 demonstrated exceptional durability, exhibiting only a minimal 1 mV negative shift in its half-wave potential and negligible ECSA loss (Fig. 3e). Remarkably, it retained a high specific activity of $5.3\text{ mA}/\text{cm}^2$ and mass activity of $3.2\text{ A}/\text{mg}_{\text{Pt}}$, corresponding to degradations of merely 3.6% and 6.7% , respectively, relative to its initial performance. Conversely, the commercial $40\text{ wt}\%$ Pt/C catalyst showed a marked degradation after the ADT, with its half-wave potential shifting negatively by 26 mV . This comparison further underscores the superior electrochemical stability of PtNi-500.

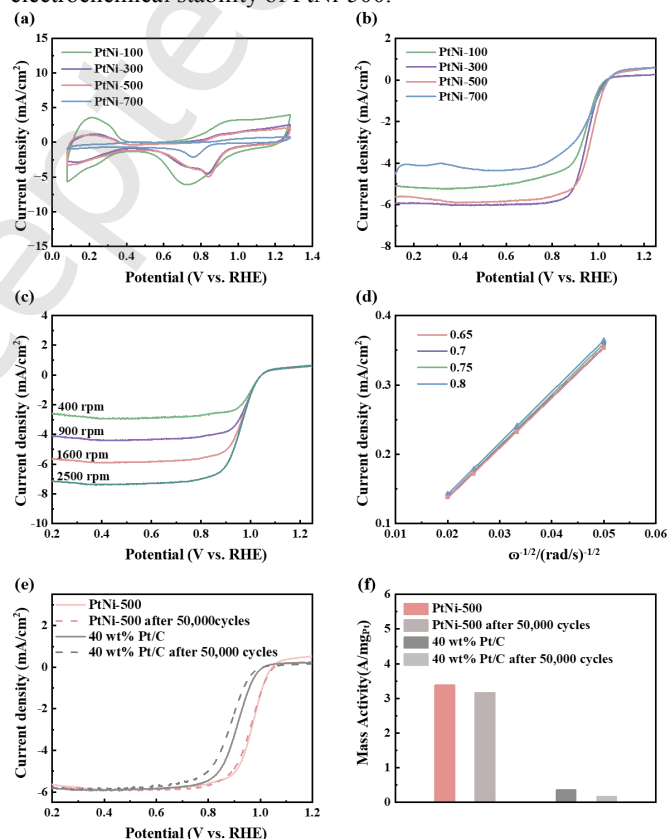


Figure 3 (a-b) CV and polarization curves of the PtNi-r catalysts. (c) Current-potential curves of PtNi-500 depending on rotating speed. (d) The Koutecky-Levich plots of PtNi-500 at different potentials. (e) Polarization curves of PtNi-500 and $40\text{ wt}\%$ Pt/C before and after 50,000 ADT cycles. (f) MA of PtNi-500 and $40\text{ wt}\%$ Pt/C before and after 50,000 ADT cycles.

2.3 The origin of the enhanced ORR performance

To elucidate the presence of surface oxides during the ORR and their influence on the ORR performance of the PtNi-r catalysts, the surface evolution of PtNi-300 and PtNi-500 catalysts under ORR conditions was monitored using in situ Raman spectroscopy. As shown in the in situ Raman spectrum of PtNi-300 (Fig. 4a), distinct Ni-O vibrational bands were observed at 340 cm^{-1} and 490 cm^{-1} [51, 53], along with a weaker Pt-O signal near 570 cm^{-1} , indicating the coexistence of both NiO and PtO surface species on the catalyst under ORR conditions.

Meanwhile, the Raman spectrum of PtNi-500 (Fig. 4b) exhibited a dominant Pt-O vibration peak at 580 cm^{-1} [54, 55], while the Ni-O signals at 340 and 480 cm^{-1} were relatively weak, consistent with the XRD results. Notably, previous studies have suggested that oxides are difficult to stabilize under the ORR conditions. However, the in situ Raman spectroscopy in our work revealed that both PtO and NiO species remain stable even

after 10,000 cycles under the actual ORR conditions (Fig. S4), confirming the exceptional stability of the NiO-PtO/PtNi dual-oxide/alloy interface on this catalyst. For both PtNi-300 and PtNi-500, a vibrational feature associated with the OOH* intermediate was detected around 700 cm^{-1} , with the signal being more pronounced for PtNi-500, revealing an OOH*-mediated reaction pathway for the ORR on these catalysts [56].

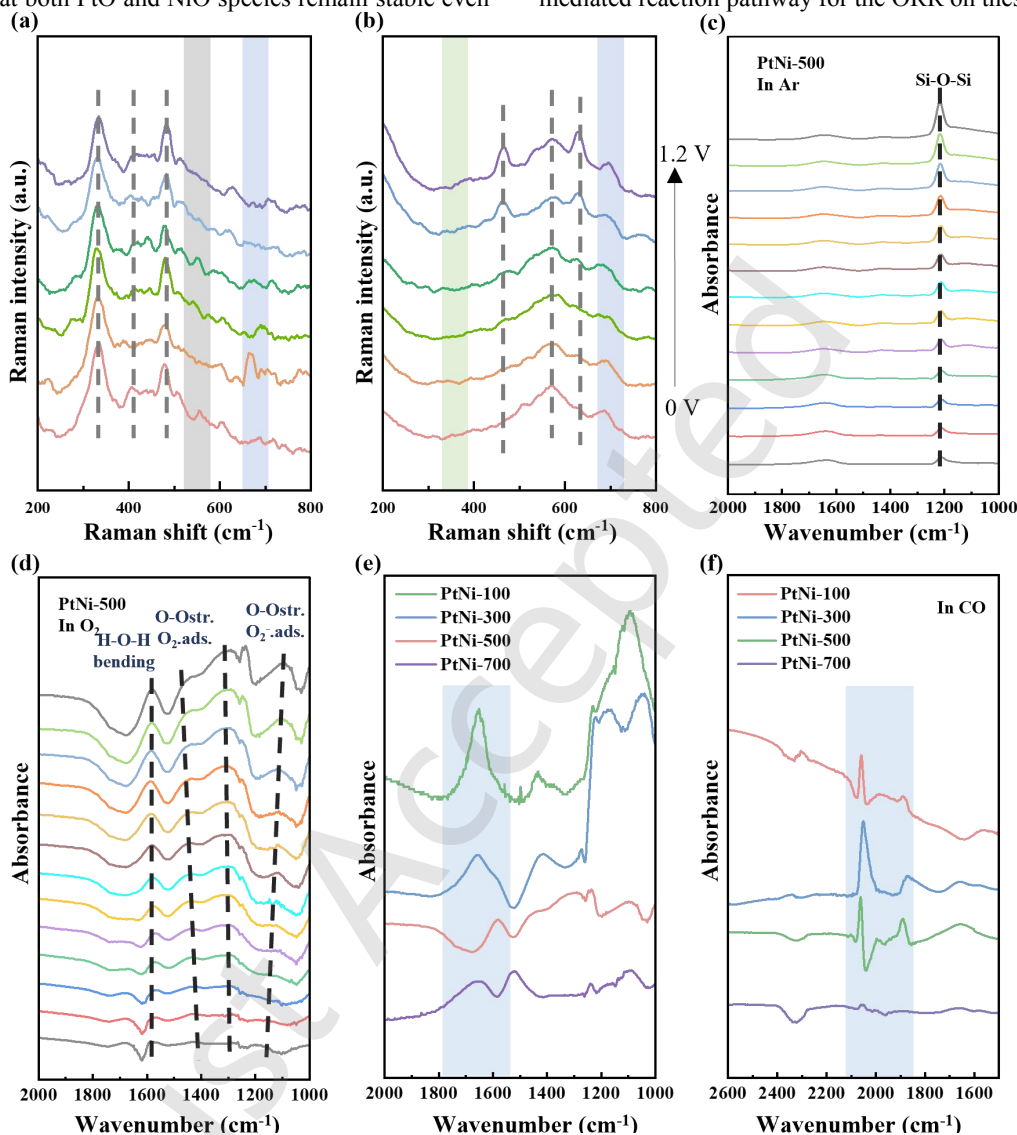


Figure 4 In situ Raman spectra of (a)PtNi-300 and (b)PtNi-500 during ORR. In situ FTIR spectra during ORR of PtNi-500 in presence (c) and absence (d) of O₂ gas in 0.1M HClO₄. (e) In situ FTIR spectra obtained during ORR reaction at 0.8 V in O₂. (f) In situ FTIR spectra obtained from CO adsorption on PtNi samples.

In situ Fourier transform infrared (FTIR) spectroscopy was employed to elucidate the catalytic mechanism by real-time monitoring the ORR reaction process at the liquid/solid interface and obtaining valuable information on the reactants, adsorbed species, and reaction intermediates involved. Figures 4c and 4d show the in situ FTIR spectra of the PtNi-500 surface recorded in 0.1 M HClO₄ solutions under N₂-saturated and O₂-saturated conditions, respectively, as a function of the applied potential. Both plots exhibit a discernible potential-dependent peak at 1226 cm^{-1} , corresponding to the Si-O-Si stretching mode of the Si ATR prism [57, 58]. The peak in the $1600\text{--}1800\text{ cm}^{-1}$ region is attributed to the bending vibration of O-H in crystalline water molecule [59]. A comparative analysis of the spectra at 0.8 V, summarized in Figure 4e, reveals a clear trend that with increasing reduction temperature, the characteristic peak

position shifts progressively to lower wavenumbers. A reduction in the O-H vibration frequency suggests an increase in the population of crystalline water and an enhancement in the strength of hydrogen bonding between these molecules. The signals near 1429 and 1080 cm^{-1} in Fig. 4d, corresponding to the O-O stretching of O₂ and O₂²⁻ adsorbed on the catalyst surface, exhibit potential-dependent shifts, suggesting a continuous modulation of the O-O bond strength during the ORR process. The synergistic effects of strong adsorption and charge polarization at the active site can facilitate the cleavage of O-O bond, thereby accelerating the reaction process. The observed shift and intensification of the O-O stretching bands at 1429 and 1080 cm^{-1} suggest either a change in the adsorption strength of oxygen species or an accumulation of O₂ reactants at the interface, or a combination of both [60]. Furthermore, the shift

of the O-O bending mode observed in the 1050-1080 cm^{-1} region also indicates the presence of interactions between Pt and Ni atoms, which result in charge transfer. The bending mode of the reaction intermediate OOH^* adsorbed on the catalyst surface is also evident at 1270 cm^{-1} in the spectra of both PtNi-300 and PtNi-700, with the signal intensity is weaker for PtNi-700.

In situ FTIR spectroscopy of the CO oxidation reaction is a valuable tool for understanding surface chemistry of the catalyst by providing information about CO adsorption. However, deconvoluting the contributions from Pt- and Ni-bound CO in the low-frequency region is complicated by the significant overlap of their respective vibrational bands. The signals in this region are therefore considered collectively in the following analysis. Fig. 4f illustrates the FTIR spectra of the PtNi-r catalysts at the same potential. The band observed in the 2050-2080 cm^{-1} region is associated with linearly adsorbed CO on Pt. The feature typically observed around 1860 cm^{-1} corresponds to bridge-bonded CO [61-64]. A comparison of the spectra in Figure 4f reveals that, with the exception of PtNi-700, all catalysts (PtNi-100, -300, and -500) exhibit clear spectroscopic signatures for both linearly and bridge-adsorbed CO on their surfaces. Furthermore, the linear-CO band shifts from 2065 cm^{-1} for PtNi-100 to 2076 cm^{-1} for PtNi-500 with increasing reduction temperature, indicating an increase in the C-O stretching frequency. Generally, the reduction in the chemisorption energy of CO weakens the metal-carbon bond, which in turn strengthens the C-O bond and leads to an increase in its stretching frequency [65]. Fundamentally, this weakened CO binding essentially reflects a downshift of the Pt d-band center, which weakens the adsorption strength not only for CO but also for other oxygenated intermediates [66, 67]. Therefore, the reduced CO chemisorption energy directly correlates with a weakened adsorption of the reaction intermediate OOH on PtNi-500. This optimally weakened binding of OOH is beneficial for the ORR, as it facilitates the desorption of intermediates and helps prevents active site poisoning. The signal at 1902 cm^{-1} in the PtNi-700 spectrum, assigned to bridge-adsorbed CO on (111)/(100) alloy facets, corroborates the high degree of alloying achieved in this catalyst [68].

To gain deeper insight into the role of the NiO and PtO phases and their interplay with the PtNi alloy in enhancing the ORR, we performed density functional theory (DFT) calculations on a series of model systems representing the catalyst's surface. Given the thermodynamic tendency for Pt to segregate to the surface, we modeled the catalyst as a single Pt monolayer on top of the PtNi alloy to simulate the Pt-rich skin structure (Fig. S5). The synergistic effect of the dual-oxide interface was investigated by placing NiO and PtO clusters on the Pt-skin model surface to simulate their interaction with the PtNi alloy (Fig. S6-S8). Fig. 5a and Fig. S9 compares the Gibbs free energy of the ORR on different PtNi-oxide interfaces, where the largest uphill change in free energy (Fig. S9) represents the overpotential of the ORR reaction. The overpotentials of Pt(111), PtNi, NiO/PtNi, PtO/PtNi and NiO-PtO/PtNi are 0.91 V, 0.77 V, 0.53 V, 0.48 V and 0.39 V, respectively. It is evident that the rate-limiting step for Pt(111) and PtNi is the third step, involving the transition from O^* to OH^* . In contrast, for the oxide-modified surfaces (NiO/PtNi, PtO/PtNi and NiO-PtO/PtNi), the rate-limiting step shifts to the final reduction stage, from OH^* to H_2O . This change in the potential-determining step is

attributed to the modified surface chemistry induced by the oxide phases.

Previous research has demonstrated that introducing a secondary metal into Pt-based alloys causes a downward shift of the Pt d-band center, thereby reducing the adsorption of oxygen intermediates and consequently enhancing the ORR performance. Despite having the lowest d-band center (-2.34 eV), PtO/PtNi does not exhibit the lowest overpotential; instead, the NiO-PtO/PtNi dual-oxide interface achieves the smallest overpotential of 0.39 eV. The overpotential follows a volcanic trend with respect to the d-band center, initially decreasing and then increasing after reaching an optimum [66, 69]. The calculated oxygen adsorption energies for PtNi, NiO/PtNi, PtO/PtNi and NiO-PtO/PtNi are 1.9, 1.77, 1.56, and 1.98 eV, respectively, all exceeding the 1.25 eV value for pure Pt. In comparison to PtNi, the incorporation of NiO-PtO/PtNi dual-oxide/alloy interface results in a reduction in the adsorption energy of O, which is the origin of the enhanced performance for ORR.

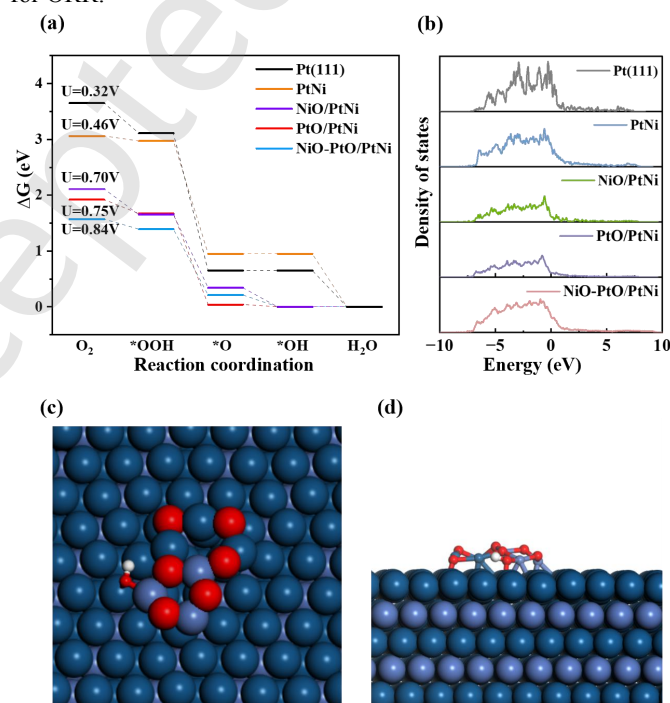


Figure 5 (a) Free energy diagrams for ORR on Pt(111), PtNi, NiO/PtNi, PtO/PtNi and NiO-PtO/PtNi at the corresponding thermodynamic limiting potential. (b) Density of states for the surface Pt layer. Top (c) and side (d) views of OH surface species on NiO-PtO/PtNi.

3 Conclusions

In conclusion, this work demonstrates the exceptional efficacy of a dual-oxide/PtNi alloy interface, synthesized via an improved IEIL method, in achieving unprecedented ORR performance. Precise control over the reduction temperature enabled the evolution of gradient NiO-PtO/PtNi alloy architectures. The optimally configured PtNi-500 catalyst exhibits a high half-wave potential of 0.97 V and delivers mass and specific activities at 0.9 V that are 9.2 and 4.4 times higher than those of 40 wt% commercial Pt/C, respectively. Its robustness is equally impressive, showing negligible activity decay after 50,000 ADT cycles, which places it at the forefront of documented durable electrocatalysts. We attribute these exceptional properties to the synergistic effects originating from

the unique dual-oxide/alloy interface, which cooperatively optimizes the electronic structure for enhanced activity and reinforces the catalyst for superior durability. This work opens a new avenue for refining the surface structure of Pt-alloys through multi-component interface engineering, offering a transformative strategy for the advancement of catalyst design.

Electronic Supplementary Material: Supplementary material (the Experimental section, supplementary Figures and Tables) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908638>.

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.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

W.Z.W.: Conceptualization, experimental design, data curation, validation, writing original draft. Y.Y.C.: data curation, software. P.F.T.: Project administration, funding acquisition, supervision, manuscript revision. W.L.: Data curation, manuscript revision. J.X.: Supervision, manuscript revision. M.L.Z.: Conceptualization. F.Z.X.: Project administration, funding acquisition, manuscript revision. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Engineering a dual-oxide/alloy interface for synergistically enhanced oxygen reduction reaction

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3. Supplementary Tables

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Table S2. Comparison of ORR performance of PtNi-based catalysts in 0.1M HClO₄ solution.

4. References

1. Experimental Section

1.1 Preparation of PtNi catalysts

The initial stage of the synthesis process entailed the dissolution of 14.5 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of deionized water, followed by the addition of 1.6 g of MgO . After stirring continuously for 48 h at 30 °C, the resulting solid was collected by centrifugation (washed eight times) and then dried in an oven at 60 °C, yielding a light-green powder identified as $\text{Ni}(\text{OH})_2$.

10.8 g of PtCl_4 was dissolved in 60 mL of deionized water with continuous stirring. Subsequently, 1.8 g of previously prepared $\text{Ni}(\text{OH})_2$ was added, and the mixture was stirred thoroughly. The resulting suspension was transferred to an autoclave, sealed, and heated to 120 °C for 4 h with stirring at 500 rpm. After cooling to room temperature, the solid product was collected by centrifugation, washed repeatedly, and dried in an oven at 60 °C. This product was denoted as PtNi-MMH. Finally, to obtain the gradient-structured catalysts, PtNi-MMH was reduced for 2 h at 100, 300, 500, and 700 °C under a 5% H_2 / N_2 atmosphere. The resulting materials were denoted as PtNi-r, where r represents the reduction temperature (100, 300, 500, and 700).

1.2 Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2550 diffractometer using $\text{Cu-K}\alpha$ radiation, operated at an accelerating voltage of 40 kV and a detector current of 100 mA. Data were collected over a 2θ range of 10–80° at a scan rate of 10°/min with a step size of 0.02°.

X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Thermo Scientific K-Alpha spectrometer using a monochromatic $\text{Al-K}\alpha$ X-ray source ($h\nu = 1486.6$ eV) operated at 12 kV and 6 mA. The analysis chamber vacuum was maintained below 5.0×10^{-7} mbar. Spectra were acquired with a spot size of 400 μm , with high-resolution spectra recorded at 50 and 100 eV and survey spectra at steps of 0.1 and 1 eV. All binding energies were calibrated using the C 1s peak at 284.8 eV as a reference.

X-ray absorption spectroscopy (XAS) spectra, including both X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra, at the Pt L_3 -edge were acquired at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The storage ring was operated in "top-up" mode with an electron beam energy of 3.5 GeV and a current of 220 mA. A fixed-exit monochromator equipped with two flat Si(311) crystals was used for energy selection. Data for the catalysts and a Pt foil reference were collected in transmission mode using Oxford ion chambers at room temperature. The acquired data were processed and analyzed using the Athena and Artemis software packages.

Transmission electron microscopy (TEM) images were obtained on a ThermoFisher Talos F200X microscope operated at an accelerating voltage of 200 kV. Samples for analysis were prepared by dispersing the catalyst powder in ethanol via ultrasonication. A small drop of the resulting suspension was then deposited onto a carbon-coated copper grid and allowed to dry in air before being inserted into the microscope.

In situ electrochemical Fourier-transform infrared (FTIR) spectroscopy measurements were performed on a PerkinElmer spectrometer equipped with a liquid-nitrogen-cooled MCT detector. A gold nanofilm was chemically deposited onto a Si prism, which was then coated with the catalyst to serve as the working electrode. A Pt wire and an Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. Spectra were collected at a resolution of 4 cm^{-1} with 64 scans.

Raman spectra under ambient conditions were acquired using a LabRAM HR (Horiba Jobin Yvon) microconfocal Raman spectrometer with a 532 nm laser source. The setup was equipped with an interference filter and an Edge Rayleigh filter specific to the 532 nm laser, enabling a low wavenumber cutoff below 50 cm^{-1} .

In situ Raman spectra were collected using the same spectrometer with the 532 nm laser source. To prevent laser-induced thermal damage to the catalyst or signal saturation, the laser power was appropriately attenuated using neutral density filters, ensuring stable and reproducible spectral acquisition. A custom-designed three-electrode electrochemical cell with a quartz window was employed for the in situ measurements. The working electrode was prepared by drop-casting 615 μL of catalyst ink (the entire volume obtained from one preparation) onto a 0.5×1 cm carbon paper substrate, followed by drying at the room temperature. All experimental conditions for the in situ Raman measurements, including the catalyst ink composition, electrode preparation, electrolyte, gas purging, potential control, electrochemical workstation, and the counter/reference electrodes, were identical to those used for the electrochemical performance tests described in Section 1.3 of the Supporting Information.

1.3 Electrochemical measurement

Electrochemical tests were conducted using a three-electrode configuration, in which the reference electrode is Ag/AgCl with saturated KCl, the counter electrode is a platinum wire, and the working electrode is a platinum-carbon rotating disc electrode with catalyst ink deposited on the surface, with a diameter of 5 mm. The inks were ultrasonically mixed with 5 mg catalyst, 2 mg carbon black, 300 μL isopropanol, 300 μL ethanol and 15 μL 5 wt% Nafion solution.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves were performed in a 0.1 M HClO_4 with constant bubbling of O_2 , and the polarization curves were collected at a rotation rate of 1600 r.p.m. The electrochemical active surface area (ECSA) was determined from cyclic voltammetry (CV) measurements performed in N_2 -saturated 0.1 M HClO_4 . The charge associated with hydrogen desorption/adsorption in the H-UPD region was integrated, and the ECSA was calculated by dividing this integrated charge by the specific charge density for Pt (210 $\mu\text{C}/\text{cm}^2$). To evaluate durability, accelerated stress tests were conducted by cycling the potential between 0.6 V and 1.0 V vs. RHE at a scan rate of 100 mV/s.

The electron transfer number (n) and kinetic current density (j_k) were calculated using the Koutecky-Levich (K-L) equation [1]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nF(D_o)^{2/3}\nu^{-1/6}C_o$$

where j refers to the current density measured during the electrochemical test. j_k , j_d , ω , F , C_o and ν are the kinetic current density, diffusion limit current density, electrode rotation rate (rpm), Faraday constant, oxygen solubility, and kinetic viscosity of the electrolyte, respectively. D_o is the diffusion coefficient of O_2 (0.2) in 0.1 mol/L HClO_4 [2,3].

1.4 Computational details

Theoretical calculations based on density functional theory (DFT) were conducted using the Vienna ab-initio simulation package (VASP) [4,5], with computational parameters consistent with those described in previous studies [6-10]. Gaussian smearing method

with a smearing width of 0.01 eV was adopted for the calculations [11]. The model of the commercial Pt/C catalyst was constructed as a five-layer Pt(111) slab with a (4×4) unit cell, denoted as Pt(111). PtNi alloy was modeled by substituting the surface Ni atoms with Pt atoms in a five-layer PtNi(111) slab with a (4×4) unit cell, denoted as PtNi. The NiO/PtNi, PtO/PtNi, NiO-PtO/PtNi interface models were modeled by loading a Ni₃O₃, Pt₃O₃ and Pt₃O₃-Ni₃O₃ cluster on the PtNi surface, respectively. The optimized most stable models are shown in Fig. S5-S8. A vacuum layer of 12 Å perpendicular to the slabs and 3×3×1 Gamma centered k-points were applied for the calculations on these models. The electrochemical reaction was analyzed using the computational hydrogen electrode (CHE) model [12,13].

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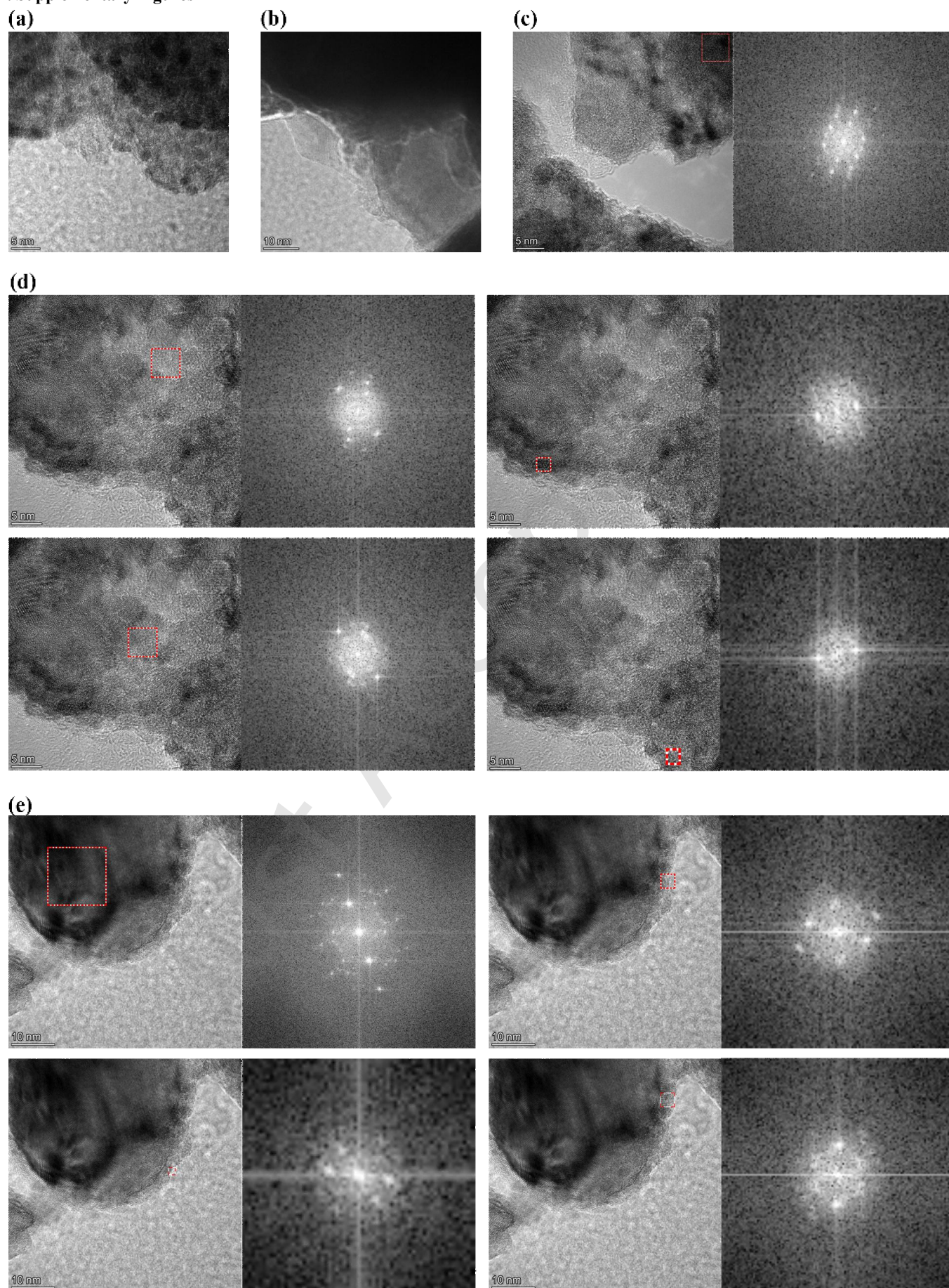
2. Supplementary Figures

Figure S1 HRTEM images of PtNi-MMH (a) and PtNi-700 (b). HRTEM images and the corresponding FFT patterns of PtNi-300 (c), PtNi-100 (d), and PtNi-500 (e).

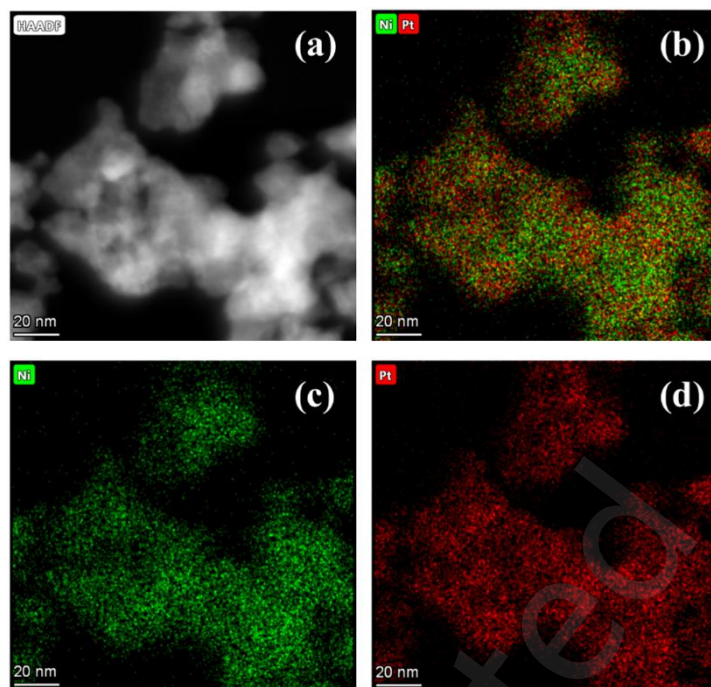


Figure S2 HAADF-STEM image and the corresponding EELS elemental mapping of PtNi-300.

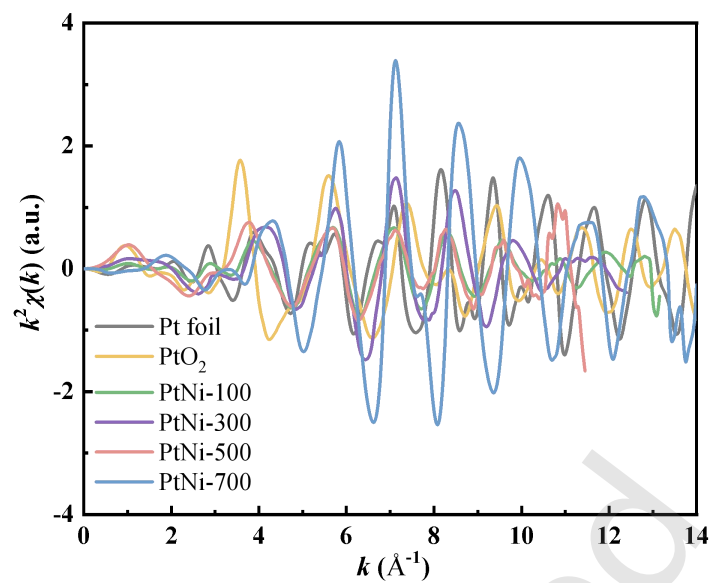


Figure S3 The K-space of Pt foil, PtO₂, and PtNi-r (r = 100, 300, 500, 700).

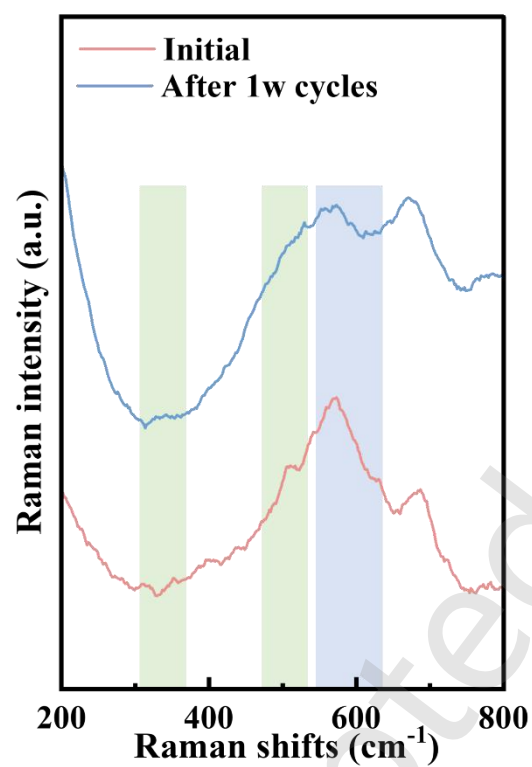


Figure S4 In situ Raman spectra of PtNi-500 during ORR before and after 10,000 cycles.

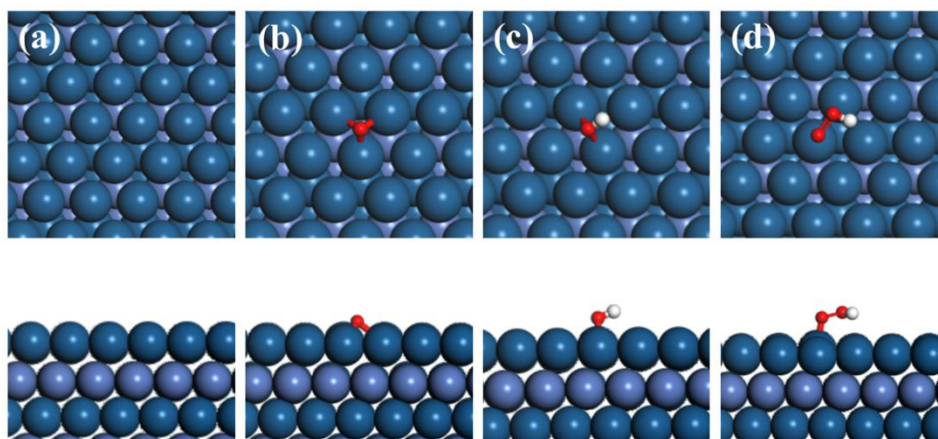


Figure S5 (a) Top view (up) and side view (down) of PtNi model with a Pt-skin layer. Top view (up) and side view (down) of surface O (b), OH (c) and OOH (d) configurations on PtNi.

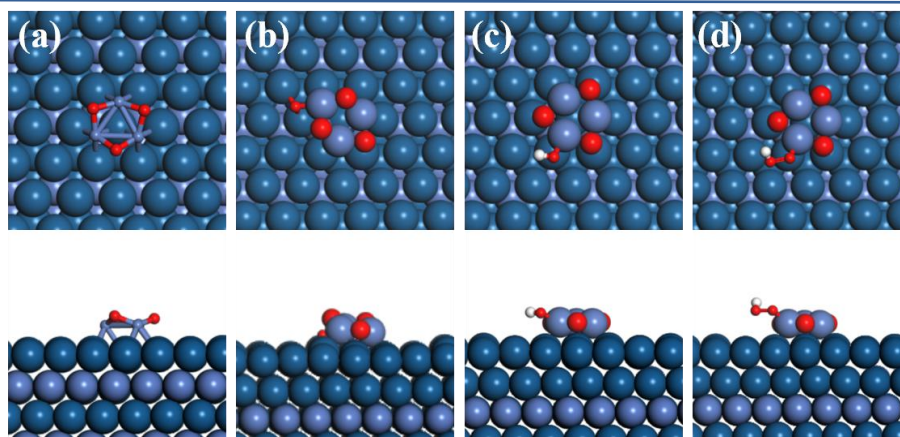


Figure S6 (a) Top view (up) and side view (down) of NiO/PtNi model. Top view (up) and side view (down) of surface O (b), OH (c) and OOH (d) configurations on NiO/PtNi.

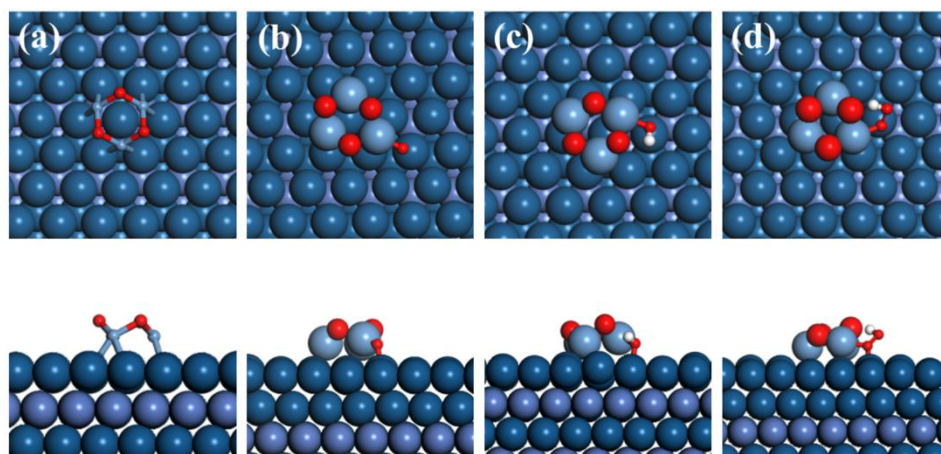


Figure S7 (a) Top view (up) and side view (down) of PtO/PtNi model. Top view (up) and side view (down) of surface O (b), OH (c) and OOH (d) configurations on PtO/PtNi.

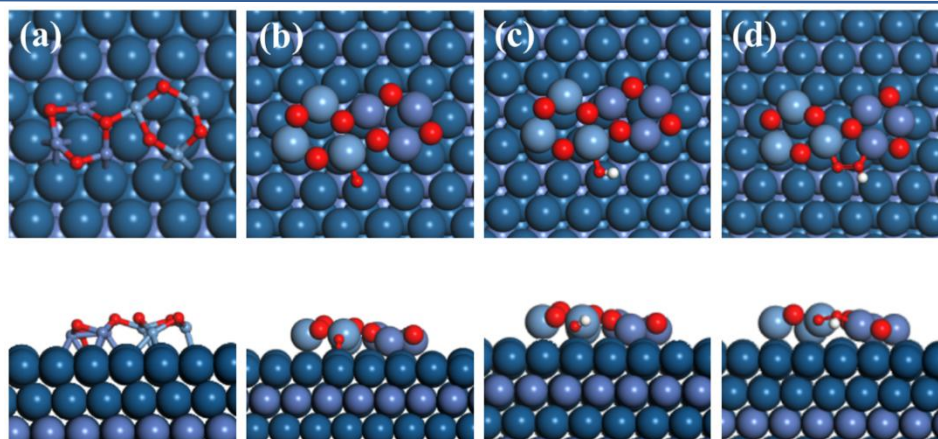


Figure S8 (a) Top view (up) and side view (down) of NiO-PtO/PtNi model. Top view (up) and side view (down) of surface O (b), OH (c) and OOH (d) configurations on NiO-PtO/PtNi.

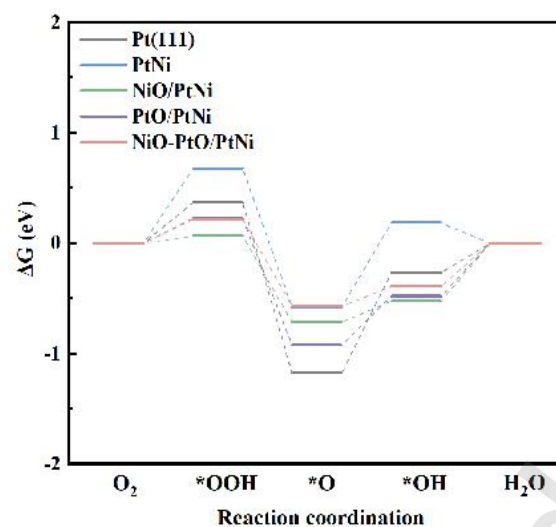


Figure S9 Free energy diagram for ORR on Pt(111), PtNi, NiO/PtNi, PtO/PtNi and NiO-PtO/PtNi at 1.23 V.

3. Supplementary Tables

Table S1. EXAFS data fitting results of Pt-r (r=100, 300, 500 and 700).

Sample	Path	N	R (Å)	σ^2 (10 ⁻³ Å ²)	ΔE_0 (eV)	R -factor
PtNi-100	Pt-O	0.7±0.2	1.98±0.02	3.4±0.6	6.6±1.2	0.002
	Pt-Ni ₁	1.5±0.3	2.58±0.02	6.0±1.4	3.8±1.2	
	Pt-Pt	5.6±0.8	2.71±0.02			
	Pt-Ni ₂	0.9±0.3	3.16±0.02			
PtNi-300	Pt-O	0.3±0.2	2.04±0.02	8.3±0.6	6.6±1.2	0.001
	Pt-Ni ₁	6.4±0.8	2.57±0.02	7.3±1.4	5.3±1.2	
	Pt-Pt	3.5±0.7	2.71±0.02			
	Pt-Ni ₂	1.1±0.3	3.28±0.02			
PtNi-500	Pt-O	1.6±0.3	1.98±0.02	4.0±0.6	6.6±1.2	0.009
	Pt-Ni	1.6±0.8	2.61±0.02	6.2±1.3	4.9±1.2	
	Pt-Pt ₁	4.1±0.7	2.71±0.02			
	Pt-Pt ₂	0.4±0.3	3.24±0.02			
PtNi-700	Pt-Ni	9.6±0.7	2.54±0.02	4.1±0.5	6.7±0.7	0.001
	Pt-Pt	0.8±0.3	2.64±0.02			

Table S2. Comparison of ORR performance of PtNi-based catalysts in 0.1M HClO₄ solution

Catalysts	E _{1/2} (V vs. RHE)	MA (A/mg _{Pt})	SA (mA/cm ²)	ADT		Ref.
PtNi-500	0.97	3.40	5.43	50 k	-3.6%	This work
TiAu@PtNi-400	0.93	2.72	5.26	20k	-<7%	[14]
PtNi@Ni-N-C	0.942	0.91	/	30k	-21.4%	[15]
PtNi/CNF-1200	0.92	~0.33	0.52	5k	-15%	[16]
PtNi ₃ @OMC-A	0.907	3.23	2.11	10k	-20.8%	[17]
PtNi-BNCs/C	0.93	5.16	3.52	50k	-1.3%	[18]
Pt _{1.4} Ni(100)	0.948	1.23	2.01	10k	0.942	[19]
PtNi/Pd	0.92	1.7	3.2	30k	-17.7%	[20]

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