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Article

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Tailoring Water Dissociation Energy by Platinum Single-Atom Catalyst Coupled with Transition Metal/metal Oxide Heterostructure for Accelerating Alkaline Hydrogen Evolution Reaction

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Abstract

High-activity catalysts in alkaline media are compelling for durable hydrogen evolution reaction (HER). Single-atom catalysts (SACs) provide an effective approach to reduce the amount of precious metals meanwhile maintain their catalytic activity. However, the sluggish activity of SACs for water dissociation in alkaline media has extremely hampered advances in highly efficient hydrogen production. Herein, we developed a platinum SAC immobilized NiO/Ni heterostructure (Pt_{SA}-NiO/Ni) as an alkaline HER catalyst. It was found that Pt SACs coupled with NiO/Ni heterostructure enable the tunable binding abilities of hydroxyl ions (OH^{*}) and hydrogen (H^{*}), which efficiently tailors the water dissociation energy for accelerating alkaline HER. In particular, the dual active sites consisting of metallic Ni sites and O vacancies modified NiO sites near the interfaces of NiO/Ni in Pt_{SA}-NiO/Ni have preferred adsorption affinity for H^{*} and OH^{*} groups, respectively, which efficiently lowers the energy barrier of water dissociation of Volmer step. Moreover, anchoring Pt single atoms at the interfaces of NiO/Ni heterostructure induces more free electrons on Pt sites due to the

elevated occupation of the Pt $5d$ orbital at the Fermi level and reaches a near-zero H binding energy (ΔG_{H^*} , 0.07 eV), which further promotes the H^* conversion and H_2 evolution. Further enhancement of alkaline HER performance was achieved by constructing Pt_{SA} -NiO/Ni nanosheets on the Ag nanowires to form a hierarchical three-dimensional (3D) morphology that provides abundant active sites and accessible channels for charge transfer and mass transport. Consequently, the fabricated Pt_{SA} -NiO/Ni catalyst displays extremely high alkaline HER performances with a quite high mass activity of 20.6 A mg^{-1} for Pt at the overpotential of 100 mV, which is 41 times greater than that of the commercial Pt/C catalyst, significantly outperforming the reported catalysts.

Keywords: single-atom catalysts (SACs), NiO/Ni heterostructure, water dissociation, alkaline media, hydrogen evolution reactions (HER)

Introduction.

Hydrogen (H_2) has been regarded as the most promising energy carrier alternative to fossil fuels due to the environmental friendliness nature and high gravimetric energy density.^{1,2} Electrocatalytic water splitting powered by wind energy or solar technologies for hydrogen generation is considered a sustainable strategy.³ For an optimal electrocatalyst, minimizing the energy barrier and increasing the active sites are desirable for boosting the hydrogen evolution reaction (HER).⁴⁻⁶ Despite the significant progress that has been presented in nonprecious catalysts, the HER performances are still second to platinum (Pt)-based materials due to its optimal binding ability with hydrogen.⁷⁻¹⁰ However, the high cost and scarcity of Pt extremely hamper its large-scale application in electrolyzers for H_2 production. Single-atom catalysts (SACs) provide an effective approach to reduce the amount of Pt meanwhile maintain its high intrinsic activity.¹¹⁻¹⁴ Recently, electrocatalytic HER in an alkaline condition has attracted more attention because catalyst systems are generally unstable in acidic media, resulting in safety and cost concerns in practice. Unfortunately, the alkaline HER activity of Pt-based catalysts is approximately two orders of magnitude lower than that in the acidic

condition caused by the high activation energy of the water dissociation step.¹⁵⁻¹⁸ Alkaline HER process involves two electrochemical reaction steps: (step (i)) electron-coupled H₂O dissociation to generate adsorbed hydrogen hydroxyl (OH*) and hydrogen (H*) (Volmer step), and (step (ii)) the concomitant interaction of dissociated H* into molecular H₂ (Heyrovsky or Tafel step).^{19,20} In particular, the additional energy in step (i) is required to overcome the barrier for splitting strong OH-H bond, leading to a hamper of Pt SACs for alkaline HER application. Therefore, reducing the water dissociation energy in Volmer step (step (i)) for Pt single-atom catalyst in alkaline media becomes vital for large-scale H₂ production of industrialization.

Some strategies have been developed to improve Pt SACs HER activity. For instance, employing the microenvironment engineering to immobilize single Pt atoms in MXene nanosheets (Mo₂TiC₂T_x) and onion-like carbon nanospheres supports could greatly reduce the H adsorption energy (ΔG_H) and, thus, facilitates the release of H₂ molecular.^{21,22} Besides, Pt single atoms anchored alloy catalysts (Pt/np-Co_{0.85}Se SAC) were constructed as an efficient HER electrocatalyst,²³ in which np-Co_{0.85}Se can largely optimize the adsorption/desorption energy of hydrogen on atomic Pt sites, thus improving the HER kinetics. Furthermore, by utilizing the electronic interaction between the Pt atoms and the supports, single-atom Pt anchored 2D MoS₂ (Pt_{SA}-MoS₂),²⁴ nitrogen-doped graphene nanosheets (Pt_{SA}-NGNs)²⁵ and porous carbon matrix (Pt@PCM)²⁶ show enhanced electrocatalytic HER efficiency due to the higher *d* band occupation near Fermi level, which can provide more free electrons for boosting the H* conversion. Despite significant progress in Pt SACs, these methods are difficult to decrease the energy barrier of water dissociation in the Volmer step (step (i)). Generally, the H₂O dissociation and H* conversion happen on different catalytic sites.²⁷ Especially, the HER activities of Pt-based catalysts in alkaline conditions are governed by the binding ability of hydroxyl species (OH*),²⁸⁻³⁰ and the alkaline HER kinetics could be optimized by independently regulating the binding energy of reactants (OH and H*) on dual active sites.³¹⁻³³ Inspired by these findings, the energy barrier of Pt SCAs for H₂O dissociation in Volmer step (step (i)) in alkaline media could be decreased by incorporating or creating the dual active sites in the catalyst to independently modulate

the binding energy of reactants (OH^* and H^*).

In this work, we developed a three-dimensional (3D) nanostructured electrocatalyst consisting of two-dimensional (2D) NiO/Ni heterostructure nanosheets supported single-atom Pt attached on one-dimensional (1D) Ag nanowires (Ag NWs) conductive network ($\text{Pt}_{\text{SA}}\text{-NiO/Ni}$). Density functional theory (DFT) calculations reveal that the dual active sites consisting of metallic Ni sites and O vacancies modified NiO sites near the interfaces of NiO/Ni heterostructure in $\text{Pt}_{\text{SA}}\text{-NiO/Ni}$ show the preferred adsorption affinity toward OH^* and H^* , respectively, which efficiently facilitates water adsorption and reaching a barrier-free water dissociation step with a lower energy barrier of 0.11 eV in Volmer step (step (i)) for $\text{Pt}_{\text{SA}}\text{-NiO/Ni}$ in the alkaline condition compared with that of $\text{Pt}_{\text{SA}}\text{-NiO}$ (0.34 eV) and $\text{Pt}_{\text{SA}}\text{-NiO}$ (1.27 eV) catalysts. Additionally, anchoring Pt single atoms at the interfaces of NiO/Ni heterostructure induces more free electrons on Pt sites due to the elevated occupation of the Pt 5d orbital at Fermi level and the more suitable H binding energy (ΔG_{H^*} , 0.07 eV) than that of Pt atoms at the NiO (ΔG_{H^*} , 0.93 eV) and Ni (ΔG_{H^*} , 0.26 eV), which efficiently promotes the H^* conversion and H_2 desorption, thus accelerating overall alkaline HER. (step (ii)). Furthermore, the Ag NWs supported 3D morphology provides abundant active sites and accessible channels for charge transfer and mass transport. As a result, the fabricated $\text{Pt}_{\text{SA}}\text{-NiO/Ni}$ catalyst exhibits outstanding HER activity with a quite lower overpotential of 26 mV at 10 mA cm^{-2} in 1 M KOH. The mass activity of $\text{Pt}_{\text{SA}}\text{-NiO/Ni}$ is $20.6 \text{ A mg}^{-1} \text{ Pt}$ at the overpotential of 100 mV, which is 41 times greater than that of the commercial Pt/C catalyst, significantly outperforming the reported catalysts. This work provides a new design principle toward single-atom catalyst systems for efficient alkaline HER.

Results

Synthesis and characterization of $\text{Pt}_{\text{SA}}\text{-NiO/Ni}$ catalyst. The fabrication process of $\text{Pt}_{\text{SA}}\text{-NiO/Ni}$ on Ag NWs is illustrated in Figure 1. In brief, the synthesized Ag NWs by a typical hydrothermal method³⁴ were first loaded on the flexible cloth to form a

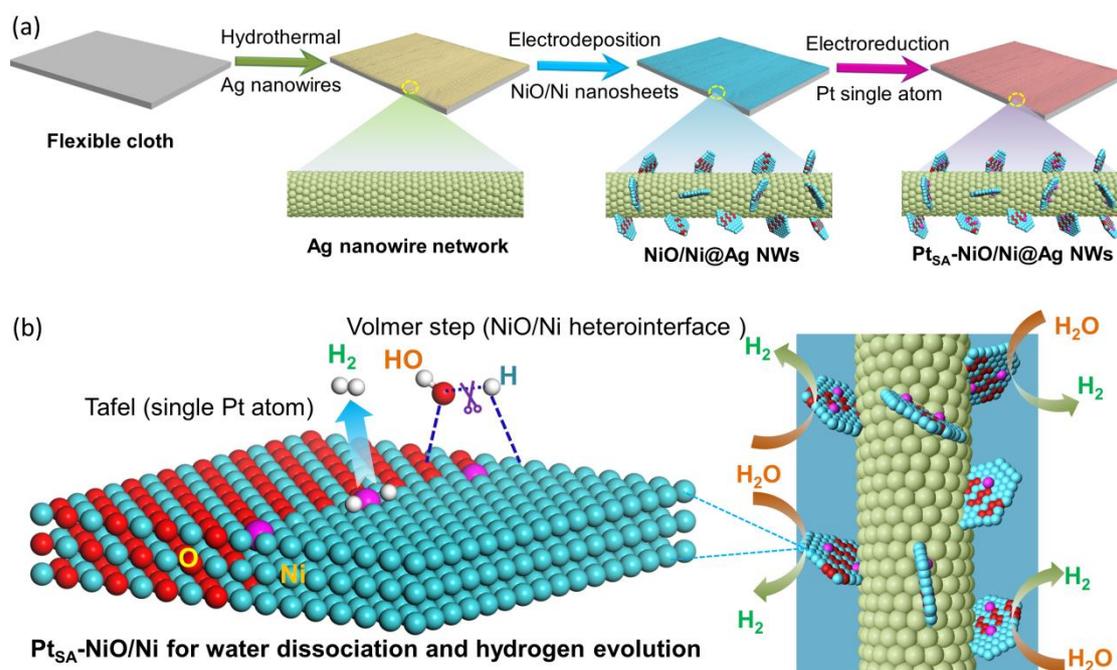


Figure 1. Schematic illustration of synthesis and water splitting mechanism of Pt_{SA}-NiO/Ni. (a) The synthesis process of Pt single atom anchored NiO/Ni heterostructure nanosheets on Ag nanowires network. (b) The mechanism of Pt_{SA}-NiO/Ni network as an efficient catalyst towards large-scale water electrolysis in alkaline media.

conductive network. Then Ni/NiO composite is attached to the Ag network by the facile electrodeposition process.³⁵ In detail, the Ag NWs network loaded cloth is immersed in nickel acetate aqueous solution followed by an electrochemical process with -3.0 V versus SCE (saturated calomel electrode) for 200 s (Figure S1), forming the uniformly distributed nanosheets on the Ag network (Figure S2). Transmission electron microscopy (TEM, Figure S3a-b) images, high-resolution TEM (HRTEM, Figure S3c) image, fast Fourier transform (FFT, Figure S3d), and elements mapping (Figure S4) images clearly show that the metallic Ni nanoparticles uniformly embed in amorphous NiO nanosheets. Besides, the X-ray diffraction (XRD, Figure S5) pattern shows that only metallic Ni signal without the peaks of NiO can be detected, and X-ray photoelectron spectroscopy (XPS, Figure S6) spectra suggest both metallic Ni and Ni oxide exists in Ni/NiO sample, further confirming the composition of metallic Ni on amorphous NiO. Interestingly, the deposited composition can be facilyly controlled by performing various voltage in the nickel acetate aqueous solution.³⁵ Specifically, as above discussion, a high voltage of -3 V versus SCE will generate the Ni/NiO

composite on Ag NWs (NiO/Ni), whereas a lower voltage of -1 V versus SCE could prepare the amorphous NiO on Ag NWs (NiO, Figure S7-9). Besides, the pure metallic Ni on Ag network (Ni, Figure S10-13) was fabricated by a traditional electrodeposition method with 1.2 V for 200 s in a mix solution containing 0.10 M NiCl₂ and 0.09 M H₃BO₃. Afterward, the single-atom Pt immobilized NiO/Ni (Pt_{SA}-NiO/Ni) is obtained by sequentially electroreduction process with cyclic voltammetry in 1 M KOH solution containing low-concentration Pt metallic salts. Abundant voids and O vacancy defects at the surface-exposed interfaces of NiO/Ni heterostructure induced by crystal-lattice dislocation and phase transition³⁶⁻³⁸ will provide efficient sites for trapping Pt single atom. The water dissociation of Volmer step in alkaline media is expected to be accelerated by O vacancies modified NiO near the interfaces interacted strongly with OH and metallic Ni interacted with H for H-OH bond destabilization (step (i)). A capture from the Volmer step, NiO/Ni heterostructure supported single-atom Pt sites could show more suitable H binding ability for the conversion and desorption of dissociated H (step (ii)), further accelerating overall HER kinetics of Pt_{SA}-NiO/Ni in an alkaline condition.

The phase evolution of samples is investigated by XRD pattern as shown in Figure 2a, in which no Pt characteristic peaks are detected, implying the absence of Pt cluster and particles in Pt_{SA}-NiO/Ni. The scanning electron microscopy (SEM, Figure 2b-c) images show the well-distributed and open 3D nanosheets morphology for Pt_{SA}-NiO/Ni. Compared with the original NiO/Ni (Figure S2), the exposed Pt_{SA}-NiO/Ni nanosheets morphology on Ag NWs should be attributed to the H₂-assisted delamination effect during Pt electro-reduction process in alkaline condition,^{21,34} which will provide more sites for Pt atoms immobilization and improve the HER performance. The scanning transmission electron microscopy (STEM, Figure S14) images suggest that the exfoliated nanosheets consist of few NiO/Ni layers for Pt_{SA}-NiO/Ni. The high-angle annular dark-field STEM (HAADF-STEM, Figure 2d) image displays bright spots along with the interfaces of NiO/Ni heterostructure, corresponding to heavy constituent atoms species, which efficiently confirms the immobilization of atomically dispersed Pt atoms in the NiO/Ni nanosheets. The magnified HAADF-STEM image (Figure 2e)

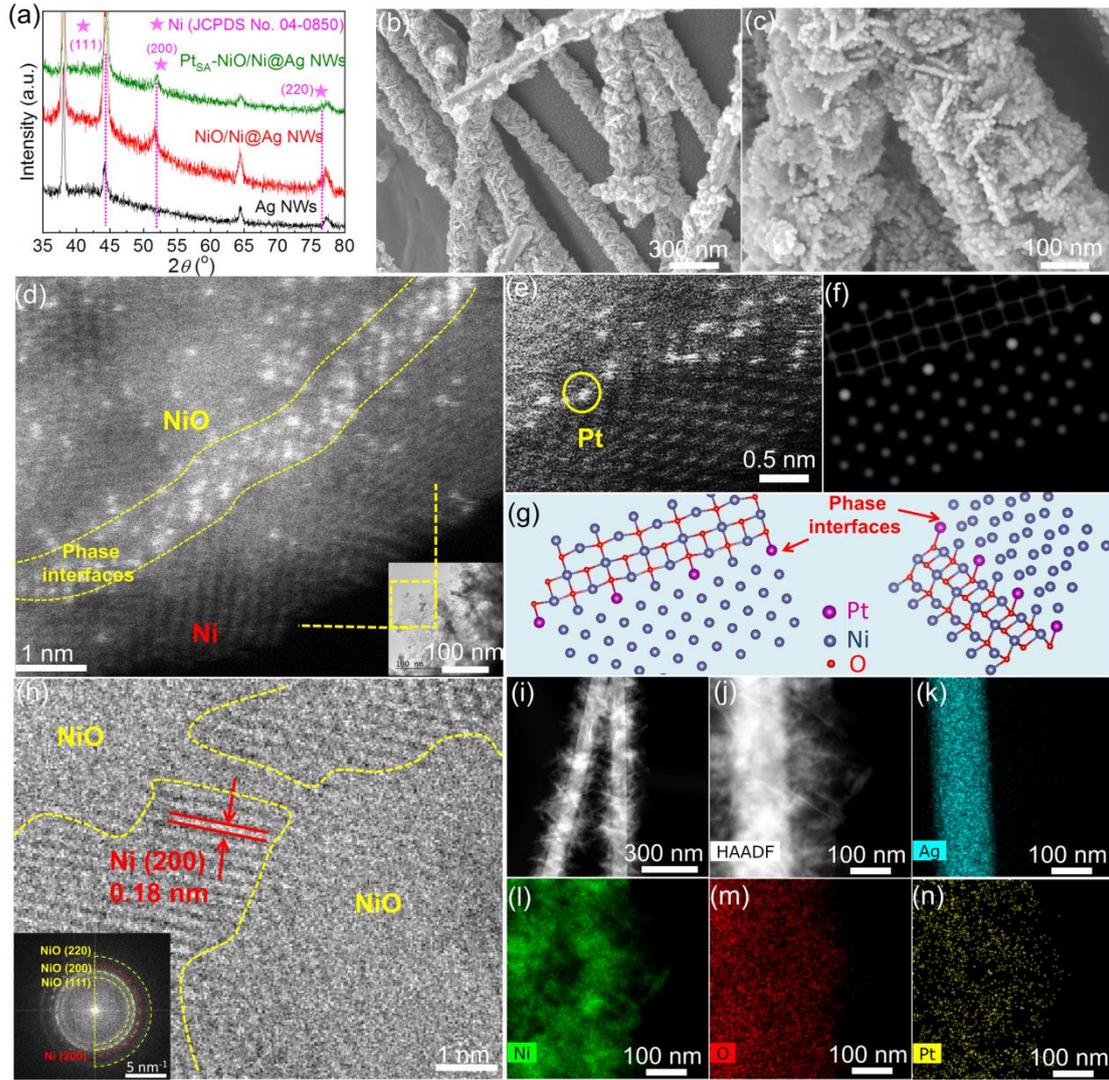


Figure 2. Structural characterization of the fabricated Pt_{SA}-NiO/Ni catalyst. (a) XRD patterns of Pt_{SA}-NiO/Ni, NiO/Ni, and Ag NWs. (b-c) SEM images of Pt_{SA}-NiO/Ni. (d) HAADF-STEM image of Pt_{SA}-NiO/Ni. (e-f) Magnified HAADF-STEM image of Pt_{SA}-NiO/Ni and (g) the corresponding DFT simulated image, showing the atomically dispersed Pt atoms at Ni position (circles in (e)). (h) HRTEM images of Pt_{SA}-NiO/Ni and the insert in (h) shows the related FFT image of Pt_{SA}-NiO/Ni. (i-j) Dark-field TEM images of Pt_{SA}-NiO/Ni with different magnifications and (k-n) the mapping of the corresponding elements.

suggests that the single Pt atoms are exactly immobilized at the interfaces of the NiO/Ni heterostructure. Based on these findings, a STEM simulation was performed to explore the atomic environment of Pt atom via the DFT-optimized structure (Figure 2f-g), and the simulated result suggests that the Pt atoms are fixed at the Ni positions by binding with O atom and Ni atoms near the interfaces of the NiO/Ni heterostructure. Further, the high-resolution TEM (HRTEM) shows one distinct lattice fringes of 0.18 nm, matching well with metallic (200) crystallographic planes (Figure 2h). The

selected-area electron diffraction pattern (inset in Figure 2h) shows four distinct rings: the red ring corresponds to the metallic Ni (200) plane,³⁹ and the yellow rings with a highly diffused halo are assigned to the amorphous NiO phase.^{35,40} These results further confirm the formation of single-atom Pt anchored NiO/Ni composition, and the interfacial coupling of Pt single atom with NiO/Ni does not change the phase structure of NiO/Ni. Moreover, the elemental mapping (Figure 2i-n and Figure S15) shows that Pt atoms are uniformly dispersed throughout NiO/Ni nanosheets. Besides, as a comparison, Pt_{SA}-NiO and Pt_{SA}-Ni were fabricated under the same conditions as Pt_{SA}-NiO/Ni but replacing NiO/Ni with NiO and Ni, respectively. The corresponding HAADF-STEM images (Figure S16) confirm the atomically dispersed Pt in the NiO and metallic Ni phase.

The electronic state evolution of the single Pt atoms in NiO/Ni, NiO, and Ni supports is explored by XPS as shown in Figure 3a. The Pt 4*f* spectrums of Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-Ni are close to Pt⁰ but show some positive shift with different extents compared with Pt foil, confirming the electrochemical reduction of PtCl₆²⁻ and the electronic interaction by charge transfer from Pt sites to the supports (NiO/Ni, NiO, and Ni).⁴¹ Specifically, the Pt_{SA}-NiO shows the largest positive shift in Pt 4*f* spectrum, suggesting the maximum electron loss of Pt species.^{42,43} Besides, the fitting curve of Pt XPS spectrums display Pt(IV) species in the samples, which derives from the adsorbed PtCl₆²⁻ ions on the surface of the sample.^{44,45} Further, the electronic state of Pt atoms in NiO/Ni, NiO, and Ni supports are further verified by performing X-ray absorption fine structure measurements. As shown in Figure 3b, the evolutions of Pt *L*₃-edge X-ray absorption near edge structure (XANES) spectra with different supports are distinguished, in which the intensity of white-line peaks corresponds to the transfer of the Pt 2*p*_{3/2} core-electron to 5*d* states, and thus is used as an indicator of Pt 5*d*-band occupancy.^{46,47} The overall white-line intensity gradually decreases as the change of support from NiO, NiO/Ni to metallic Ni, corresponding to the increase of 5*d* occupancy of Pt. Hence, higher 5*d* occupancy indicates the less charge loss of the single-atom Pt after coordinating with the supports, which is consistent with the results of XPS analysis in Figure 3a.

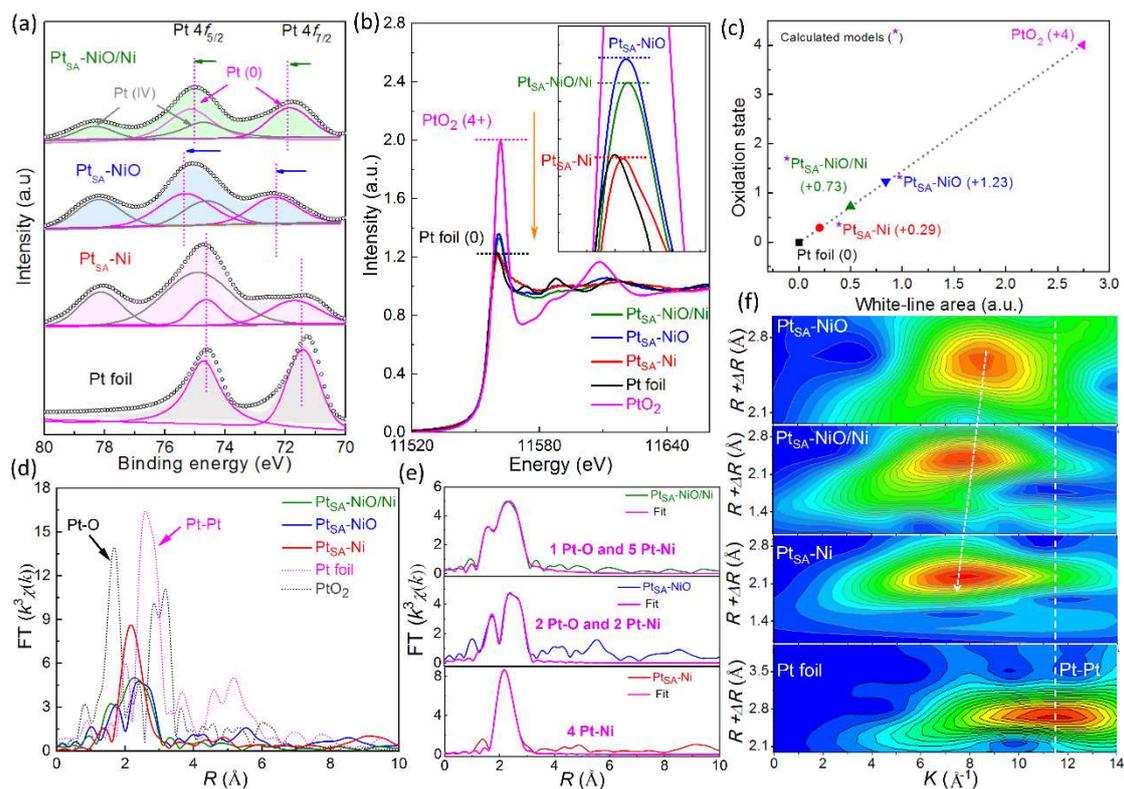


Figure 3. Electronic state and atomic structure characterization. (a) Pt $4f$ spectra, (b) XANES spectra, and (c) calculated Pt oxidation states derived from Δ XANES spectra of Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-Ni, and Pt foil is given as a reference. (d) Corresponding FT-EXAFS curves of Figure 3b. (e) EXAFS fitting curve of Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-Ni R -space. (f) EXAFS wavelet transform plots of Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, Pt_{SA}-Ni, and Pt foil.

To quantitate the electronic state structural information, the white-line peak evolution of Pt can be clearly described by the differential XANES spectra (Δ XANES, Figure S17) by subtracting the spectra from that of Pt foil. The valence state of Pt can be quantitatively examined by the integration of the white-line peak in Δ XANES spectra. As shown in Figure 3c, the average valence state of Pt increase from +0.29, +0.73, to +1.23 for the Pt_{SA}-Ni, Pt_{SA}-NiO/Ni, and Pt_{SA}-NiO catalysts, respectively. The evolution of the atomic coordination configuration of Pt was further revealed by extended X-ray absorption fine structure spectroscopy (EXAFS, Figure 3d), in which the typical Pt-Pt contribution peak of Pt foil at about 2.7 Å is absent for the fabricated Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-Ni catalysts, strongly confirming the single Pt atoms dispersion. Further, the first-shell EXAFS fitting of Pt_{SA}-NiO/Ni sample (Figure 3e and Table S1) gives a coordination number (CN) of 1.3 for Pt-O contribution and 5.8 for Pt-Ni contribution. For Pt_{SA}-NiO, the fitting results of EXAFS spectra suggested CN about

2.4 for Pt-O contributions and 2.1 for *CN* for Pt-Ni contributions. Whereas Pt-Ni contribution with 4.9 for *CN* and no Pt-O contributions are found in the fitting of Pt_{SA}-Ni EXAFS spectra. Combining the DFT-optimized structure (Figure S18), the Pt atoms are mainly immobilized at the interfacial Ni positions by coordinating with one O atom and 5 Ni atoms in Pt_{SA}-NiO/Ni, which is consistent with the conclusion of HAADF-STEM analysis (Figure 2d-g). To more precisely clarify the atomic dispersion and coordination conditions of Pt, the wavelet transform (WT) analysis was carried out due to its more efficient resolution ability in *K* spaces and radial distance,^{48,49} in which the atoms at similar coordination conditions and distances could be discriminated.^{50,51} As shown in Figure 3f, Pt_{SA}-NiO/Ni displays a different intensity maximum with Pt_{SA}-NiO and Pt_{SA}-Ni, and especially, the intensity maximum at 7.6 Å⁻¹ for Pt_{SA}-NiO/Ni is lower than that of Pt_{SA}-NiO (8.5 Å⁻¹), but high than that of Pt_{SA}-Ni (7.4 Å⁻¹), further confirming the interfacial coordination conditions for Pt atoms immobilized in NiO/Ni. Besides, the intensity maximum at 11.5 Å⁻¹ correspondings to Pt-Pt coordination is absent in the fabricated catalysts; further confirming the successful loading of single Pt atoms in Ni, NiO/Ni, and NiO supports.

Theoretical investigations. Based on the above structure analysis, theoretical investigations were performed to disclose the influences of the evolved coordinate configurations of the Pt atom on the electronic structure and catalytic activity of the catalysts. According to the HAADF-STEM and EXAFS measurements, the models for Pt_{SA}-NiO/Ni were shown in Figure 4a. Based on the calculated charge density distributions, an increased charge density area along the interface of NiO/Ni heterostructure was induced (Figure S19a-b). After coupling Pt single atom with NiO/Ni heterostructure, an electronic structure redistribution at the interfaces of the heterostructure is caused due to the different electronegativity of atoms (3.44 for O atom, 1.91 for Ni, and 2.28 for Pt). Especially, charge delocalizing from Pt to the bonded O atom and charge localizing from adjacent Ni atoms to Pt are displayed. Consequently, a locally enhanced electric field with a half-moon shape area around the Pt site was generated (Figure S19c-d), which is more intensive than that of Pt_{SA}-NiO

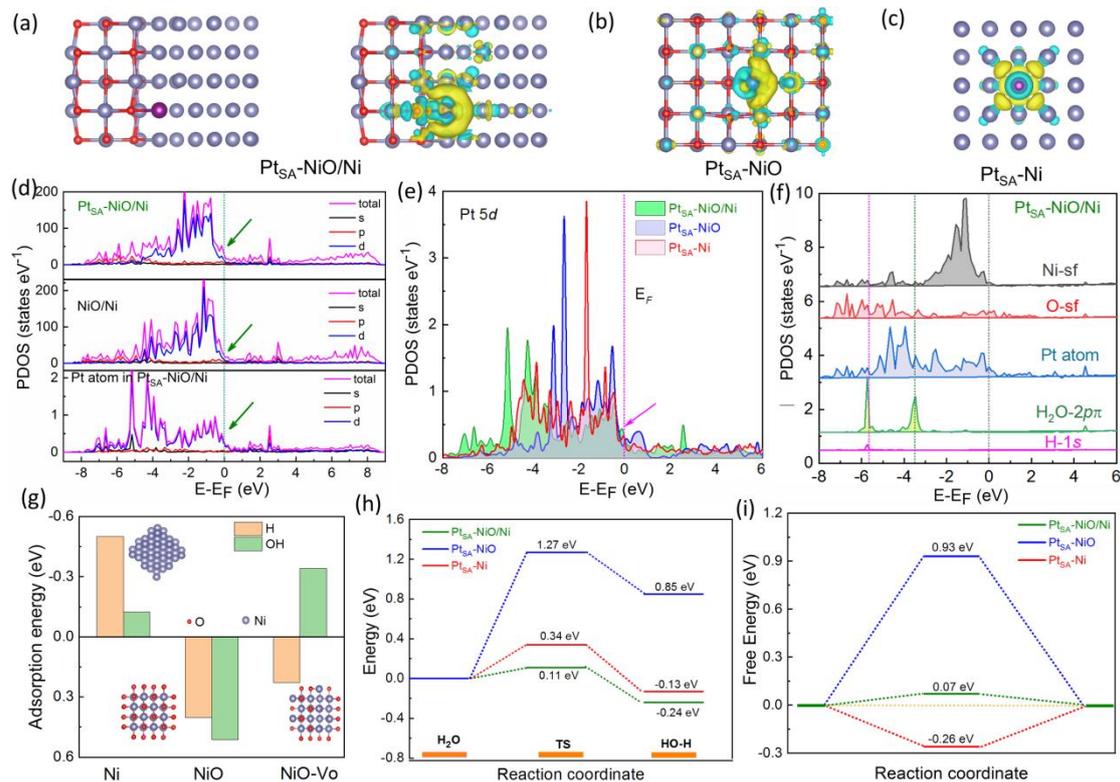


Figure 4. Theoretical investigations. Computational models and localized electric field distribution of (a) Pt_{SA}-NiO/Ni, (b) Pt_{SA}-NiO and (c) Pt_{SA}-Ni. (d) Calculated PDOS of NiO/Ni and Pt_{SA}-NiO/Ni, with aligned Fermi level. (e) Calculated Pt 5*d* band of Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-Ni. (f) The orbital alignment of the surficial sites for Pt_{SA}-NiO/Ni binding with H₂O molecule. (g) Calculated OH-binding energies (ΔE_{OH}) and H-binding energies (ΔE_H) for Ni, pure NiO, and O vacancies modified NiO surface. (h) Calculated energy barriers of water dissociation kinetic and (i) adsorption free energies of H* on the surface of the Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-Ni catalysts, respectively.

(Figure 4b) and Pt_{SA}-Ni (Figure 4c), suggesting Pt single atom coupled with NiO/Ni heterostructure could possess the more free electrons to promote the adsorbed H conversion and H₂ evolution.^{22,44} Moreover, the projected density of states (PDOS, Figure 4d, and Figure S20) of the single-atom Pt immobilized NiO/Ni heterostructure shows higher occupation than that of the pure NiO/Ni near the Fermi level, suggesting a promoted electron transfer and higher conductivity of Pt_{SA}-NiO/Ni. The contrast between the PDOS of NiO/Ni and Pt_{SA}-NiO/Ni reveals that the increased DOS of the Pt_{SA}-NiO/Ni near the Fermi level mainly derives from the contribution of Pt *d* orbitals (Figure 4d). These results suggest that the NiO/Ni heterostructure coupled single-atom Pt can effectively enhance the total *d*-electron domination of the catalyst near the Fermi level, which will benefit the activation of H₂O and lead to energetically catalytic activity.^{21,52} Moreover, the *d*-band features of the Pt atom in NiO/Ni, NiO and Ni

coordinated configurations are investigated. The wider $5d$ band and higher density near the Fermi level for NiO/Ni supported Pt atom than that of Pt_{SA}-NiO and Pt_{SA}-Ni ((Figure 4e and Figure S21) suggest that the NiO/Ni coupled Pt atom can induce more free electrons near Pt sites than Pt_{SA}-NiO and Pt_{SA}-Ni, which is more favorable for the H reactants adsorption and transfer. Besides, the Pt- $5d$ band of Pt_{SA}-NiO/Ni also shows a substantially broad range for overlapping with H- $1s$ and H₂O- $2p\pi$ orbitals (Figure 4f). Therefore, the Pt-site could play a protecting role for stabilizing the Ni valence state and a distributary role by binding OH and H species to low the deactivation of absorption sites in case of over-binding of intermediates on the active sites for NiO/Ni heterostructure coupled single-atom Pt.⁵³

Based on the above finding, we further explore the reaction barrier of the fabricated catalysts for H₂O splitting in alkaline conditions, consisting of the dissociation of H₂O molecule of Volmer step and the subsequent conversion of H to H₂, which mainly depends on how OH and H bond to the active sites on the surface of the catalysts.⁵⁴ We found that both H and OH bind weakly to the pure NiO surface. While metallic Ni surface shows a preference for stabilizing H, and O vacancies modified NiO facilitates the adsorption of OH species (Figure 4g and Figure S22). For NiO/Ni composition, the O vacancies on the interfaces of the NiO/Ni heterostructure (Figure S23) are induced by the crystal-lattice dislocation and phase transition.^{36,37,55} As an integration, NiO/Ni coupled single-atom Pt catalyst demonstrates the strongest H₂O adsorption ability (Figure S24) and largest energy release of -0.24 eV for water dissociation in Volmer step (Figure 4h). Moreover, Pt_{SA}-NiO/Ni hybrid catalyst only need the minimum energy barriers (0.11 eV) for the dissociation of H₂O into OH and H under the assistance of NiO/Ni interfaces (Figure S25), confirming the critical role of surface-exposed NiO/Ni interfaces for the H₂O dissociation of Volmer step in alkaline media. In the subsequent step, the NiO/Ni supported single-atom Pt sites at the NiO/Ni interfaces act as the proton-acceptor for the recombination of the dissociated proton (H*) and H₂ evolution due to its near-zero H binding energy (0.07 eV, Figure 4i and Figure S26) and strong electron supply capacity deriving from locally enhanced charge distribution (Figure 4a) and the higher occupation of Pt $5d$ band near Fermi lever

(Figure 4e). Consequently, the overall steps of Pt_{SA}-NiO/Ni hybrid catalyst for HER in alkaline media are significantly accelerated.

Electrocatalytic alkaline HER performances. Based on the structural characterizations and theoretical investigations, the Pt single-atom catalyst coupled with NiO/Ni heterostructure possesses the best intrinsic HER activity in alkaline media among the fabricated catalysts. Thus, the electrocatalytic activities of Pt_{SA}-NiO/Ni for alkaline HER was measured in 1 M KOH solution. As a comparison, the HER performance of Pt_{SA}-NiO, Pt_{SA}-Ni, NiO/Ni, and 20% Pt/C were also tested under the same conditions. As shown in Figure 5a, the Pt_{SA}-NiO/Ni shows the highest HER performance among all catalysts, and only needs a quite low overpotential of 26 and 85 mV to achieve the current density of 10 and 100 mA cm⁻², respectively, significantly superior to the Pt_{SA}-NiO, Pt_{SA}-Ni, NiO/Ni and the Pt/C catalyst (Figure 5b). Moreover, the mass activity of Pt_{SA}-NiO/Ni normalized to the loaded Pt mass (1.14 wt%, inductively coupled plasma-mass spectrometry) at an overpotential of 100 mV is 20.6 A mg⁻¹, which is 2.4, 2.3, and 41.2 times greater than that of Pt_{SA}-NiO (8.5 A mg⁻¹), Pt_{SA}-Ni (9.0 A mg⁻¹) and the commercial Pt/C catalyst (0.5 A mg⁻¹), respectively. These results suggest that single Pt atoms coupled with NiO/Ni can extremely maximize the alkaline HER activity of Pt-based catalysts, leading to a significant reduction in cost. Additionally, the Pt_{SA}-NiO/Ni exhibits a smaller Tafel slope of 27.07 mV dec⁻¹ than Pt_{SA}-NiO (37.54 mV dec⁻¹), Pt_{SA}-Ni (37.32 mV dec⁻¹), NiO/Ni (58.67 mV dec⁻¹), and Pt/C catalyst (41.69 mV dec⁻¹), which suggests a typical Volmer-Tafel mechanism for alkaline HER and implies that the rate-determining step of Pt_{SA}-NiO/Ni is the H₂ desorption (Tafel step) rather than the H₂O dissociation (Volmer step).^{56,57} Besides, Pt_{SA}-NiO/Ni catalyst exhibits a 2.0 and, 2.4-fold enhancement in the double-layer capacitance (*C*_{dl}) over Pt_{SA}-NiO and Pt_{SA}-Ni (Figure S27), respectively, suggesting the favorable nanostructure with more sites for Pt atoms immobilization and HER. Furthermore, the charge transfer resistance (*R*_{ct}) of Pt_{SA}-NiO/Ni (0.61 ohm, Figure 5e) is extremely low than that of Pt_{SA}-NiO, Pt_{SA}-Ni, and NiO/Ni catalysts, which mainly originates from the introduction of Ag NWs and enhanced electronic structure of single

Pt atoms coupled with NiO/Ni.

For real applications, HER catalyzing stability is another essential factor. As present in Figure 5f, the Pt_{SA}-NiO/Ni shows high durability in the alkaline electrolyte with negligible loss in HER performance for 5000 cycles or 30 hours. The characterizations of Pt_{SA}-NiO/Ni after the stability test, including HAADF-STEM image, elements mapping, and double-layer capacitance (Figure S28-30), suggest the negligible structure changes and single-atom dispersion for Pt_{SA}-NiO/Ni after long-term alkaline HER. Moreover, the turnover frequencies (TOFs) per Pt atom site are analyzed, and the TOFs of Pt_{SA}-NiO/Ni (5.71 H₂ s⁻¹) is 2.02, 1.99, and 38.06 times higher than that of Pt_{SA}-NiO, Pt_{SA}-Ni, and Pt/C catalyst, respectively (Figure 5g). To our knowledge, the electrocatalytic HER performances of our Pt_{SA}-NiO/Ni catalyst in the alkaline media are almost optimal among the reported SACs, and are comparable with the performances of catalysts in acid media (Figure 5h and Table S2), confirming the advance by the constructing single-Pt sites in NiO/Ni hybrid system.

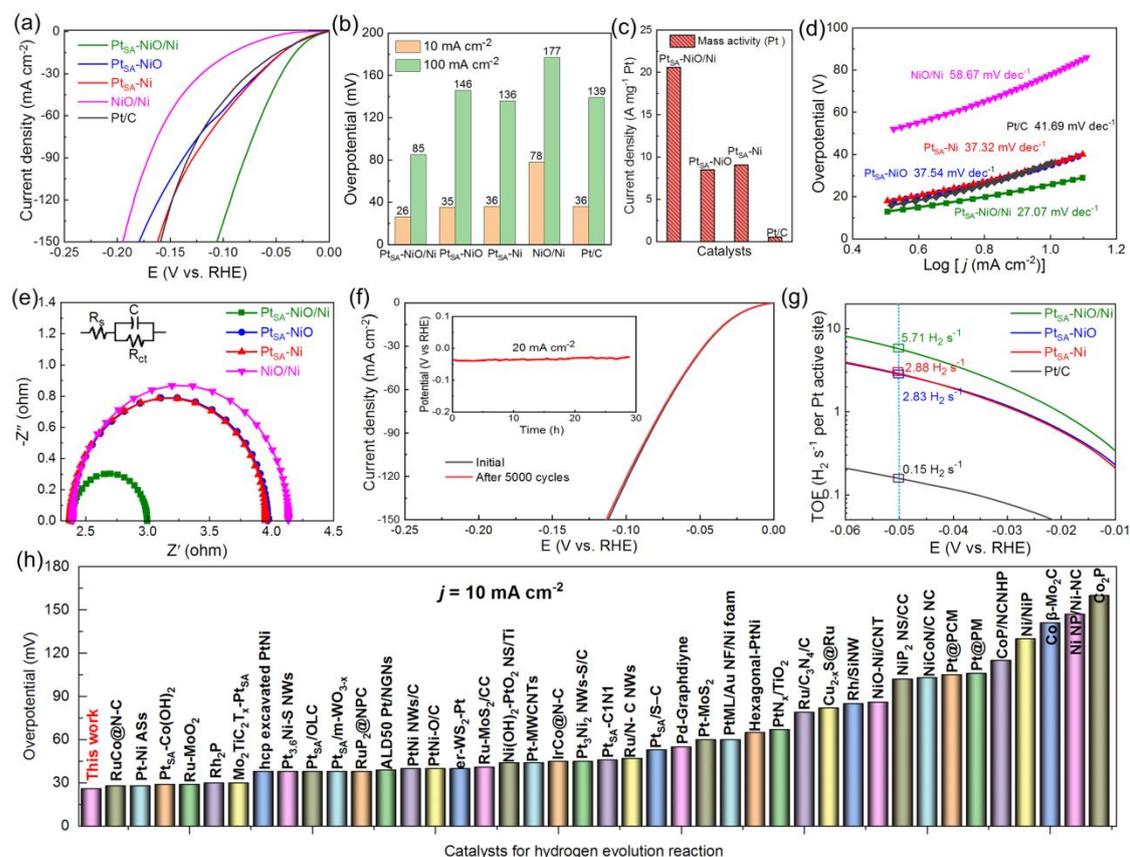


Figure 5. Electrochemical alkaline HER performances of the catalysts in 1 M KOH electrolyte. (a) HER polarization curves of Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, Pt_{SA}-Ni, NiO/Ni, and Pt/C. (b) The comparison

of overpotentials required to achieve 10 mA cm^{-2} for various catalysts. (c) The mass activity of the Pt-based catalysts. (d) Corresponding Tafel slope originated from LSV curves. (e) EIS (Electrochemical Impedance Spectroscopy) Nyquist plots of the catalysts. (f) Stability test of Pt_{SA}-NiO/Ni through cyclic potential scanning and chronoamperometry method (Inset in f). (g) TOFs plots of the Pt-based electrocatalysts. (h) Comparison of the HER activity for Pt_{SA}-NiO/Ni with reported catalysts, originating from Table S2.

Discussion

In summary, we reported a novel single-atom Pt (Pt_{SA}) immobilized NiO/Ni heterostructure nanosheets on Ag NWs network nanocomposite by the facile electrodeposition strategy, which serves as an efficient electrocatalyst for vigorous hydrogen production in alkaline media. Theoretical calculations revealed that the Pt SACs coupled with NiO/Ni heterostructure could efficiently tailoring water dissociation energy for accelerating alkaline HER. In particular, the dual active sites consisting of metallic Ni sites and O vacancies modified NiO sites near the interfaces of NiO/Ni have the preferred adsorption affinity toward both OH* and H*, which facilitates water adsorption and reaches a barrier-free water dissociation step with the lowest energy barrier of 0.11 eV in Volmer step (step (i)) for Pt_{SA}-NiO/Ni compared with that of Pt_{SA}-NiO (0.34 eV) and Pt_{SA}-NiO (1.27 eV) catalysts. Besides, fixing Pt atoms at the NiO/Ni interfaces induce a higher occupation of the Pt 5*d* band at the Fermi level and the more suitable H binding energy (ΔG_{H^*} , 0.07 eV) than that of Pt atoms at the NiO (ΔG_{H^*} , 0.93 eV) and Ni (ΔG_{H^*} , 0.26 eV), which efficiently promotes the H* conversion and H₂ desorption, thus accelerating overall alkaline HER. The further enhancement of alkaline HER performance was achieved by introducing Ag NWs network into 2D Pt_{SA}-NiO/Ni nanosheets to construct a seamlessly conductive 3D nanostructure. The unique nanostructural feature and highly conductive Ag NWs network provide abundant active sites and accessible channels for electron transfer and mass transport. Consequently, the 3D Pt_{SA}-NiO/Ni catalyst shows outstanding HER performances in alkaline conditions with a quite low overpotential of 26 mV at a current density of 10 mA cm^{-2} and extremely high mass activity of $20.6 \text{ A mg}^{-1} \text{ Pt}$ in 1 M KOH, significantly outperforming the reported catalysts. This study opens an efficient avenue for the advance of single-atom catalysts by introducing a water dissociation kinetic-

oriented material system.

Methods

Synthesis of Ag NWs. An oil bath method was used to synthesize Ag NWs according to our previous report.⁵⁸ Specifically, a mix solution consisting of ethylene glycol, FeCl₃ (7.19 mM), AgNO₃ (0.051 M), and polyvinylpyrrolidone (0.012 M) was heat and maintained under an oil bath pan with 110 °C for 12 hours. After that, the generated precipitate was washed with acetone and alcohol to get the pure Ag NWs. Subsequently, the Ag NWs were uniformly dispersed on a flexible cloth fabric by spray coating technology to fabricate a conductive network.

Synthesis of NiO/Ni on Ag NWs. Ni/NiO is grown on Ag NWs network by a facile electrodeposition process in the aqueous electrolyte of 20 mM C₄H₆NiO₄·4H₂O according to the recent report.³⁵ The electrodeposition process was performed by chronoamperometry method with -3 V vs SCE for 200 s under a standard three-electrode system, in which graphite sheet acted as a counter electrode, SCE acted as a reference electrode, and the fabricated Ag NWs network loaded on the cloth was directly used as working electrode. The obtained samples were washed with deionized water and then dried at room temperature.

Synthesis of NiO on Ag NWs. NiO is grown on Ag NWs network by the electrodeposition process with -1 V vs SCE for 600 s in an aqueous electrolyte of 20 mM C₄H₆NiO₄·4H₂O. The obtained samples were washed with deionized water and then dried at room temperature.

Synthesis of Ni on Ag NWs. Metallic Ni is grown on Ag NWs network by the electrodeposition process in an aqueous solution consisting of 0.10 M NiCl₂, 0.09 M H₃BO₃, and a solvent containing ethanol and deionized water with 2:5 in volume ratio. The electrodeposition process was performed by chronoamperometry with -1.2 V vs SCE for 200 s. The obtained samples were washed with deionized water and then dried at room temperature.

Synthesis of Pt_{SA}-NiO/Ni on Ag NWs. Pt_{SA}-NiO/Ni on Ag NWs was fabricated by the electrochemical reduction process in the three-electrode system, in which the fabricated NiO/Ni on Ag NWs was performed as the working electrode, graphite sheet acted as a counter electrode, saturated calomel electrode acted as a reference electrode. The corresponding electrochemical process was carried out by multi-cycle cathode polarization in 1 M KOH solution containing 50 μM H₂PtCl₆ with a scan rate of 50 mV s⁻¹ between 0 V and -0.50 V versus reversible hydrogen electrode (RHE) for 200 cycles.

Synthesis of Pt_{SA}-NiO on Ag NWs. Pt_{SA}-NiO on Ag NWs were fabricated by multi-cycle cathode polarization in 1 M KOH solution containing 50 μM H₂PtCl₆ with a scan rate of 50 mV s⁻¹ between 0 V and -0.50 V versus RHE for 200 cycles.

Synthesis of Pt_{SA}-Ni on Ag NWs. Pt_{SA}-Ni on Ag NWs were fabricated by multi-cycle cathode polarization in 1 M KOH solution containing 50 μM H₂PtCl₆ with a scan rate of 50 mV s⁻¹ between 0 V and -0.50 V versus RHE for 200 cycles.

Characterizations. The morphology measurement of the synthesized catalysts was performed by SEM (GeminiSEM 300). HRTEM images, HAADF-STEM images, and STEM-EDX mapping images were obtained by a TEM coupled with an energy spectrum analyzer (JEOL JEM2100). The Pt contents in the catalysts were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The XPS spectra of elements were tested by a surface analysis system (ESCALAB250Xi). The phase and crystal information were obtained by Cu K α radiation in an X-ray diffractometer (XRD, Bruker, D8 Advance Davinci). The EXAFS measurement of the Pt_{SA}-NiO/Ni, Pt_{SA}-NiO, and Pt_{SA}-NiO/Ni at the Pt L₃-edge was performed at 1W1B station at the Beijing Synchrotron Radiation Facility (BSRF). Data analysis and fitting were performed with Athena and Artemis in the Demeter package.

Electrochemical measurements. All electrochemical measurements were finished by an electrochemical workstation (CHI 660E) with a three-electrode configuration, in which fabricated catalysts were directly employed as the working electrode, graphite sheet acted as a counter electrode, saturated calomel electrode acted as a reference

electrode. All the presented potential in this work was transferred to RHE according to an experimental method.⁵⁹ LSV with 95% iR-corrections were tested under the potential range from 0.05 to -0.5 V and the scan rate of 5 mV s⁻¹. EIS was obtained by a frequency range from 100 k to 0.1 Hz with an overpotential of 230 mV vs RHE. For the preparation of 3D Pt/C@Ni foam, 5 mg 20 wt% Pt/C was dispersed in 0.9 mL alcohol containing 0.1 mL 5 wt% Nafion solution to form a homogeneous ink. Then, the obtained ink was coated on the Ni foam and dried in air to form a porous Pt/C@Ni foam electrode.

DFT theoretical calculations. All the structural optimizations, charge density difference analysis, Bader charge analysis, and energy calculations were carried out based on DFT as implemented in the Vienna Ab-initio Simulation Package (VASP).⁶⁰⁻⁶² The projector-augmented-wave (PAW) method was implemented to calculate the interaction between the ionic cores and valence electrons.^{63,64} The Perdew-Burke-Ernzerhof approach of spin-polarized generalized gradient approximation (GGA-PBE) was used to describe the exchange-correlation energy.⁶⁵ Calculations were performed with the cut-off plane-wave kinetic energy of 500 eV, and 8×4×1 *k*-mesh grids were employed for the integration of the Brillouin zone. Electronic relaxation was undertaken to utilize the conjugate-gradient (CG) method⁶⁶ with the total energy convergence criterion being 10⁻⁵ eV. Geometry optimization was employed by the quasi-Newton algorithm^{67,68} until all the residual forces on unconstrained atoms less than 0.01 eV/Å. Climbing image nudge elastic band (CI-NEB) calculations⁶⁹ were employed for finding transition barriers with the initial configuration of H₂O absorbed on the catalyst surface and final configuration of OH + H absorbed on the catalyst surface. To ensure the initial configuration correctly, an H₂O molecule was deposited on the catalyst surface and relaxed for calculating its local minimum total energy on different sites, and the last one is the initially stable configuration. The final configuration is also found by relaxing OH and H near the H₂O absorbed site of the initial configuration. Next, The equation for calculating adsorption enthalpy ΔE_{H^*} as the following:

$$\Delta E_{H^*} = E_{\text{slab+H}} - E_{\text{slab}} - \frac{1}{2} E_{\text{H}_2}$$

Where the $E_{\text{slab+H}}$ is the total enthalpy of H adsorbing on the catalysts, the enthalpy of the catalysts is E_{slab} , and the H_2 enthalpy is E_{H_2} .

The H and H_2O adsorbing on the slabs were investigated by comparing the formation energy of different sites. The equation for calculating adsorption enthalpy ΔE_{H^*} as the following:

$$\Delta E_{H^*} = E_{\text{slab+H}} - E_{\text{slab}} - \frac{1}{2} E_{\text{H}_2}$$

Where the $E_{\text{slab+H}}$ is the total enthalpy of H adsorbing on the catalysts, enthalpy of the catalysts is E_{slab} , the H_2 enthalpy is E_{H_2} . As similar, the equation for calculating the H_2O adsorption enthalpy $\Delta E_{\text{H}_2\text{O}^*}$ as the following:

$$\Delta E_{\text{H}_2\text{O}^*} = E_{\text{slab+H}_2\text{O}} - E_{\text{slab}} - E_{\text{H}_2\text{O}^*}$$

The free energy of adsorbed H and H_2O as follows:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{\text{ZPE}} - T\Delta S$$

$$\Delta G_{\text{H}_2\text{O}^*} = \Delta E_{\text{H}_2\text{O}^*} + \Delta E_{\text{ZPE}} - T\Delta S$$

where ΔE_{H^*} represent the H adsorption energy and $\Delta E_{\text{H}_2\text{O}^*}$ represent the H_2O adsorption energy, and ΔE_{ZPE} represents the difference related to the zero-point energy between the gas phase and the adsorbed state.

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Figures

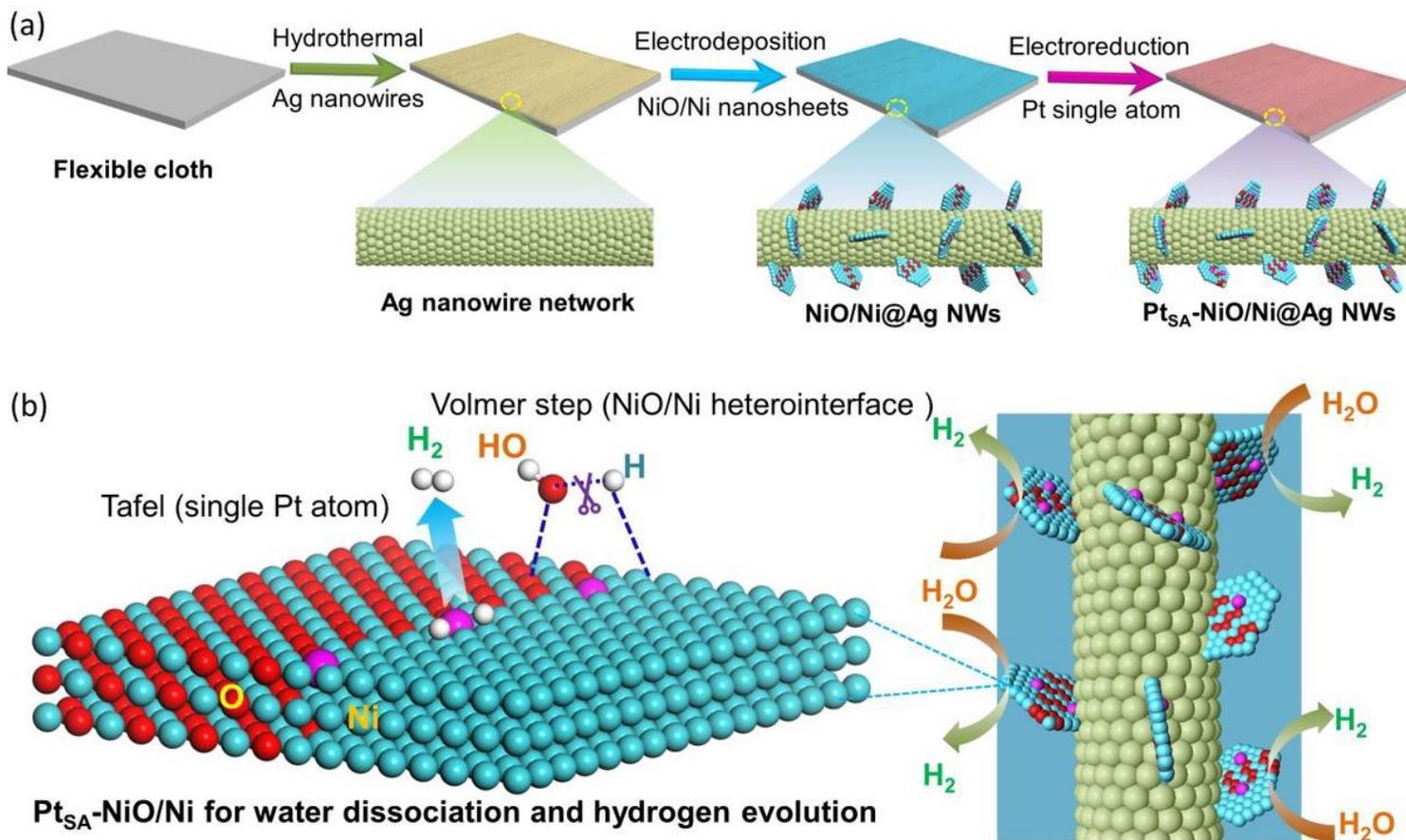


Figure 1

Schematic illustration of synthesis and water splitting mechanism of PtSA-NiO/Ni. (a) The synthesis process of Pt single atom anchored NiO/Ni heterostructure nanosheets on Ag nanowires network. (b) The mechanism of PtSA-NiO/Ni network as an efficient catalyst towards large-scale water electrolysis in alkaline media.

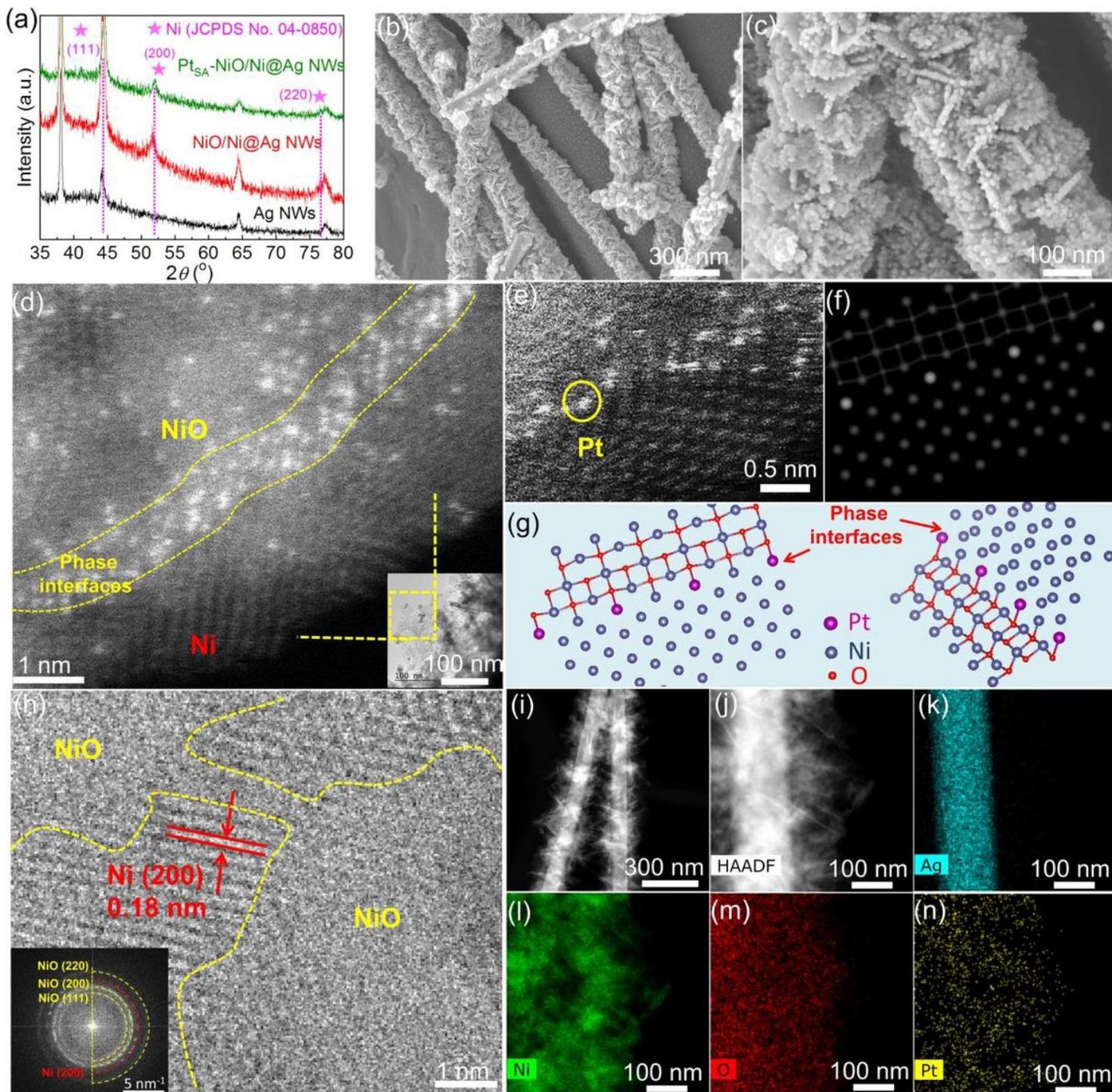


Figure 2

Structural characterization of the fabricated PtSA-NiO/Ni catalyst. (a) XRD patterns of PtSA-NiO/Ni, NiO/Ni, and Ag NWs. (b-c) SEM images of PtSA-NiO/Ni. (d) HAADF-STEM image of PtSA-NiO/Ni. (e-f) Magnified HAADF-STEM image of PtSA-NiO/Ni and (g) the corresponding DFT simulated image, showing the atomically dispersed Pt atoms at Ni position (circles in (e)). (h) HRTEM images of PtSA-NiO/Ni and the insert in (h) shows the related FFT image of PtSA-NiO/Ni. (i-j) Dark-field TEM images of PtSA-NiO/Ni with different magnifications and (k-n) the mapping of the corresponding elements.

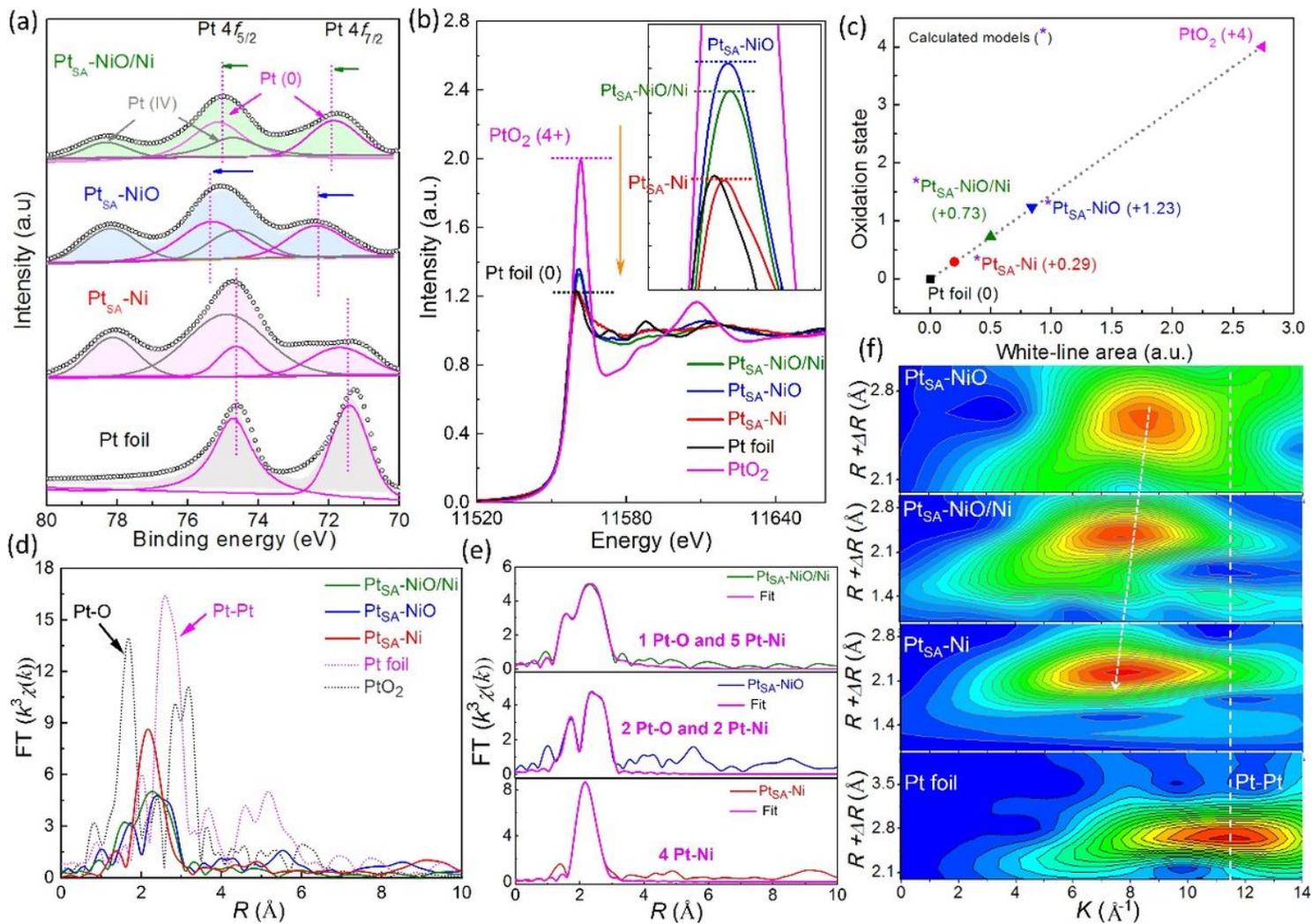


Figure 3

Electronic state and atomic structure characterization. (a) Pt 4f spectra, (b) XANES spectra, and (c) calculated Pt oxidation states derived from Δ XANES spectra of PtSA-NiO/Ni, PtSA-NiO, and PtSA-Ni, and Pt foil is given as a reference. (d) Corresponding FT-EXAFS curves of Figure 3b. (e) EXAFS fitting curve of PtSA-NiO/Ni, PtSA-NiO, and PtSA-Ni R-space. (f) EXAFS wavelet transform plots of PtSA-NiO/Ni, PtSA-NiO, PtSA-Ni, and Pt foil.

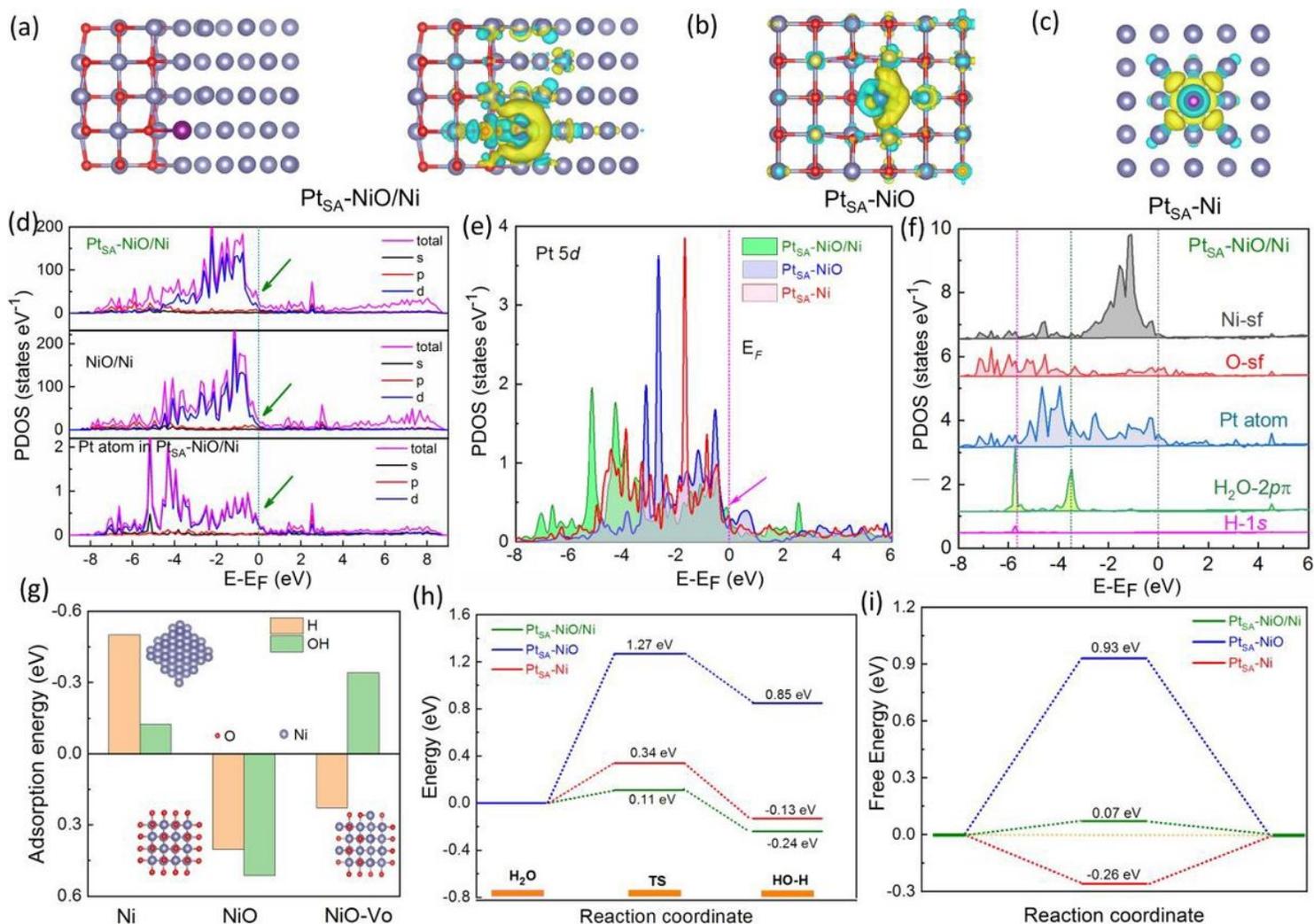


Figure 4

Theoretical investigations. Computational models and localized electric field distribution of (a) PtSA-NiO/Ni, (b) PtSA-NiO and (c) PtSA-Ni. (d) Calculated PDOS of NiO/Ni and PtSA-NiO/Ni, with aligned Fermi level. (e) Calculated Pt 5d band of PtSA-NiO/Ni, PtSA-NiO, and PtSA-Ni. (f) The orbital alignment of the surficial sites for PtSA-NiO/Ni binding with H₂O molecule. (g) Calculated OH-binding energies (ΔE_{OH}) and H-binding energies (ΔE_H) for Ni, pure NiO, and O vacancies modified NiO surface. (h) Calculated energy barriers of water dissociation kinetic and (i) adsorption free energies of H* on the surface of the PtSA-NiO/Ni, PtSA-NiO, and PtSA-Ni catalysts, respectively.

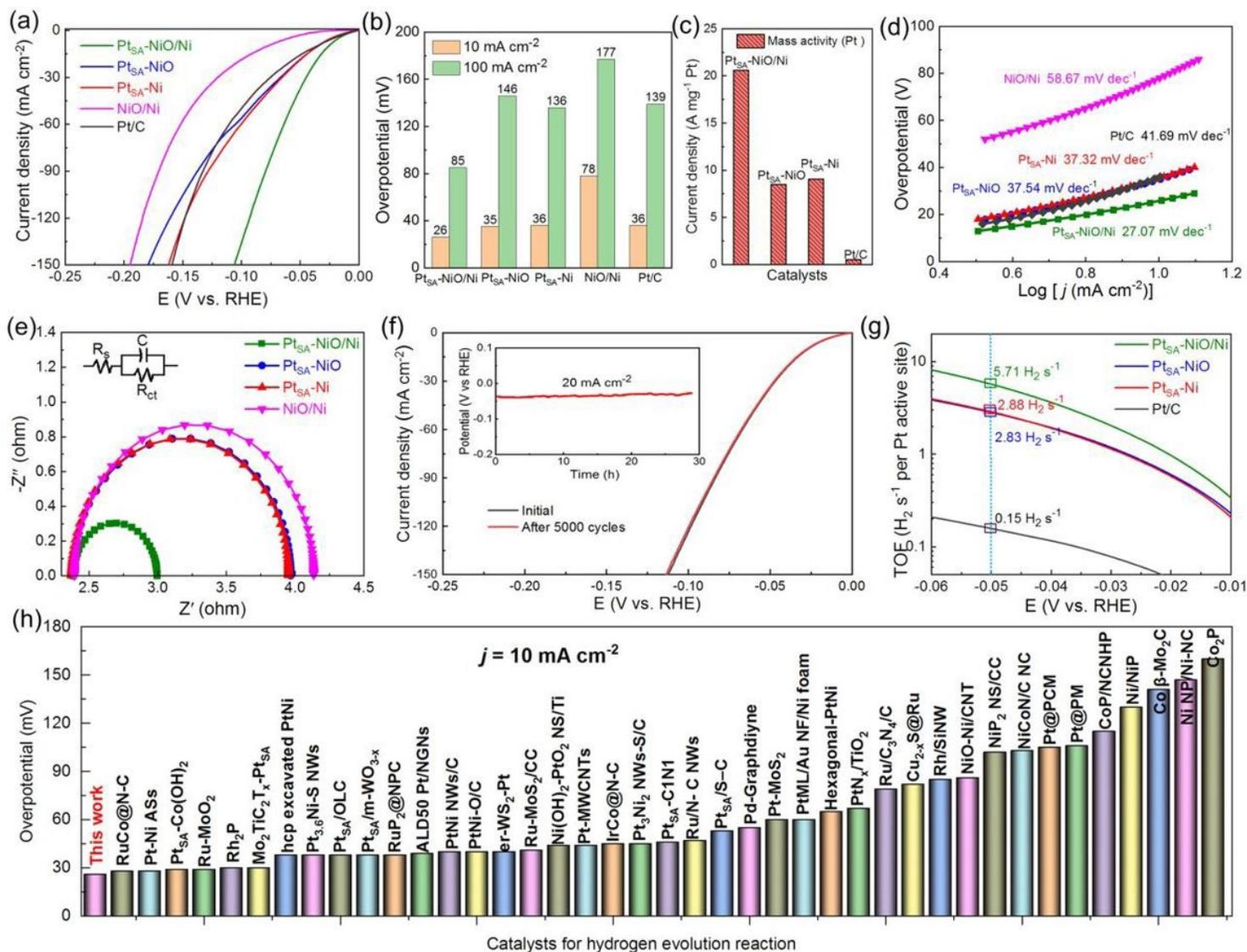


Figure 5

Electrocatalytic alkaline HER performances of the catalysts in 1 M KOH electrolyte. (a) HER polarization curves of PtSA-NiO/Ni, PtSA-NiO, PtSA-Ni, NiO/Ni, and Pt/C. (b) The comparison of overpotentials required to achieve 10 mA cm⁻² for various catalysts. (c) The mass activity of the Pt-based catalysts. (d) Corresponding Tafel slope originated from LSV curves. (e) EIS (Electrochemical Impedance Spectroscopy) Nyquist plots of the catalysts. (f) Stability test of PtSA-NiO/Ni through cyclic potential scanning and chronoamperometry method (Inset in f). (g) TOFs plots of the Pt-based electrocatalysts. (h) Comparison of the HER activity for PtSA-NiO/Ni with reported catalysts, originating from Table S2.

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