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N-modified NiO Surface for Superior Alkaline Hydrogen Evolution

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Abstract: Boosting the sluggish kinetics of hydrogen evolution reaction in alkaline environments is the key for large application of water-alkali and chlor-alkali electrolysis. Herein, for the first time, we use nitrogen atoms to precisely modulate electrochemical active sites on the surface of nickel oxide with low coordinated oxygen atoms, to achieve enhanced kinetics of alkaline hydrogen evolution. Theoretical and experimental results demonstrate that the surface charge redistribution after modulation simultaneously facilitates the initial water dissociation step, as well as the subsequent recombination of H_{ad} from low coordinated oxygen sites and desorption of OH_{ad}^- from nickel sites, thus accelerating the overall hydrogen evolution process. The N-modulated nickel oxide enriched in low coordinated oxygen atoms exhibits significantly enhanced activity with a small overpotential of -100 mV at the current density of -10 mA cm⁻² and a robust stability over 90 h for hydrogen evolution in 1.0 M KOH.

Hydrogen (H_2) has been considered as one of the ideal alternatives to the fossil fuels due to its outstanding energy density and environmental friendliness.^[1] Water-alkali or chlor-alkali electrolysis is a clean and efficient technology to the scalable and sustainable production of H_2 , especially when coupled with other renewable sources such as solar and wind.^[2] Unfortunately, the sluggish kinetics of hydrogen evolution reaction (HER) in alkaline environments causes high overpotentials.^[3] Thus, efficient HER electrocatalysts have been used to reduce the associated energy losses. Platinum (Pt)-based catalysts are the current benchmarking catalysts,^[4,5] but the high cost and scarcity limit their widespread uses.^[5] Therefore, the search for active, durable, and low-cost electrocatalysts is of paramount importance to accelerate the HER process in alkaline electrolysis.

The kinetics of HER in alkaline environments are governed by a subtle balance between the initial water dissociation (the Volmer step) and concomitant interaction of water dissociation products (H_{ad} and OH_{ad}^-) with adsorption sites on the surface of

electrocatalysts.^[6-9] The combination of 3d metal (e.g., Ni, Co, Fe) (hydro)oxides with Pt is a plausible way to accelerate the alkaline HER kinetics,^[6-14] although the use of precious Pt limits their practical application as mentioned above. These two-phase hybrid materials promote the dissociation of water ($H_2O + e^- \rightarrow H_{ad} + OH_{ad}^-$), which is then followed by the recombination of two H_{ad} atoms to form H_2 from the Pt surface, and by the desorption of OH_{ad}^- from the edges of metal (hydro)oxides to accommodate the adsorption of other H_2O molecules.^[6-8] Nevertheless, some uncertain properties of these interfaces, such as Schottky barrier,^[12] or unmatched lattice space,^[13] can undoubtedly hinder the electrons transfer and reaction intermediates transport between two phases, resulting in additional kinetic barriers. Moreover, the slow desorption of OH_{ad}^- impedes the re-adsorption of water molecules, reducing the rate of the subsequent water dissociation step. It is thus necessary to construct noble-metal-free electrocatalysts without phase interface to further enhance the kinetics of alkaline HER.

Since the 3d metal oxides have the capacity for promoting the water dissociation,^[7, 8, 15-19] further improving their activity for catalyzing the transformation of H_{ad} into H_2 is feasible to speed up the whole kinetics of HER in alkaline environments. Previous studies have reported that the electron densities of low coordinated oxygen (LCO) atoms on the surface of metal oxides are lower than those in regular sites in the bulk,^[20, 21] indicating the existence of active non-bonding states for the adsorption of H_{ad} . Inspired by these, here, for the first time, we put forward that the LCO atoms can replace Pt to act as the adsorption sites of H_{ad} on nickel oxide (NiO) to construct no-interface electrocatalysts. The nitrogen atoms can precisely modulate the electrochemical adsorption sites (both LCO sites and Ni sites) on the surface of NiO to further enhance HER kinetics in alkaline environments. The surface charge redistribution after modulation not only promotes the initial water dissociation but also facilitates H_{ad} recombination from LCO sites as well as OH_{ad}^- desorption from Ni sites, synergistically leading to the acceleration of the overall alkaline HER process. Accordingly, an ultrathin N-modulated NiO layer rich in LCO atoms on the surface of Ni foam (N-NiO/NF) was prepared via surface oxidizing and nitriding treatments. As expected, the N-NiO/NF electrode exhibits high activity with an extremely low overpotential of -100 mV at the current density of -10 mA cm⁻² and durable stability over 90 h for HER in 1.0 M KOH. Furthermore, the nitrogen-modulation strategy is demonstrated to effectively improve the alkaline HER activity of cobalt oxide (CoO_x). This atomic-level modulation strategy may open up a new avenue to exploit practical electrocatalysts based on 3d metal oxides for HER in alkaline environments.

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The density functional theory (DFT) calculations were first performed to determine whether the N doping influences the electronic structure of NiO and the surface adsorption energy of intermediate H_{ad} at LCO sites. The Gibbs free energy of hydrogen adsorption, ΔG_{H^+} , has been demonstrated to serve as a good descriptor for activities of electrocatalysts for HER independent to pH values.^[22] According to the Sabatier principle, the H binding should be neither too strong nor too weak, that is, ΔG_{H^+} should be close to 0.0 eV.^[22] We calculated the ΔG_{H^+} at the LCO site on the (100) surface of the correlative atomic models including NiO and N-doped NiO (N-NiO) with LCO atoms (Supporting Information, Figure S1). As shown in Figure 1a, the LCO site at NiO exhibits a very high ΔG_{H^+} value, while substituting O atoms with some N atoms can greatly decrease its ΔG_{H^+} (0.25 eV), which suggests that the N substitution can increase the activity of LCO atoms. The Bader charge analysis confirms that the charge of the LCO atom is reduced from -1.24 to -1.17 after N doping. Thus, some electrons are transferred from the LCO atom to the Ni atom and then to the N atom (Figure 1b), which leads to the fully occupied O 2p states to the partially occupied states with more active non-bonding states, as evidenced by the partial density of states (PDOS) of O 2p states (Figure 1c). Consequently, the activity of LCO atoms next to N atoms increases with the decreased ΔG_{H^+} . Taken together, these results indicate that the surface nitrogen modulation could favor the HER at the LCO sites.

Figure 1. (a) Calculated free energy diagram on the (100) surface of N-NiO and NiO. The LCO@N-NiO has the smallest ΔG_{H^+} , indicating that LCO sites are the dominating active sites for the generation of H_2 . (b) Electron transfer process among LCO, Ni, and N. (c) Calculated partial density of states of LCO in N-NiO and NiO, in which more non-bonding states are indicated within the yellow area after N-doping. (d) Schematic illustration of water adsorption, water dissociation, H_{ad} desorption to form H_2 from LCO sites and OH_{ad} desorption from Ni sites on the surface of N-NiO. Dark blue, yellow, red, green, and white spheres represent Ni, N, O, LCO, and H atoms, respectively.

In addition, the overall kinetics of HER in alkaline environments depend on a delicate balance between the rate of the water dissociation step, the rate of recombination of H_{ad} to form H_2 , which is optimized at LCO sites, and the rate of desorption of OH_{ad} to accommodate the adsorption of other H_2O

molecules on the same sites. Fast adsorption of H_2O implies fast dissociation of H_2O from the electrocatalysts surface. The strong interaction between 3d metal oxides and OH_{ad} will lead to an adverse effect, wherein the adsorption sites for reaction intermediates are blocked.^[7] Nenad M. Markovic et al. have proposed that the Ni^{5+} in Ni-(hydro)oxide have a relatively optimal interaction strength with OH_{ad} ,^[7] satisfying the Sabatier principle for electrocatalysts design. In the N-NiO system, the DFT calculation results indicate that the N doping causes the electron transfer from LCO atoms to Ni atoms. Such an increase of electron densities at Ni sites can weaken the electronic interaction between OH_{ad} and Ni sites, which is beneficial for the desorption of OH_{ad} . Thus, the nitrogen modulation could also optimize the adsorption/desorption of OH_{ad} , facilitating the re-adsorption of H_2O molecules.

Figure 2. (a) Digital image of N-NiO/NF. (b, c) SEM images, (d-g) elemental mapping images, and (h) cross-sectional TEM image of N-NiO/NF. (i, j) HRTEM images of N-NiO layer on Ni foam surface.

The surface charge redistribution after nitrogen modulation expedites both H_{ad} recombination from LCO sites and OH_{ad} desorption from Ni sites, which in turn accelerates the initial water adsorption step as well as the subsequent water dissociation step, eventually speeding up the overall HER kinetics. The detailed processes of HER can be described as follows (Figure 1d): when an H_2O molecule comes into the electric double layer, the H-OH bond will be weakened by the interaction of OH group with Ni atom and H atom with LCO atom, next the H_2O molecule dissociates into H_{ad} and OH_{ad} with the aid of a free electron. Finally, the H_{ad} desorbs from the LCO sites to form H_2 via either the Heyrovsky step ($H_2O + H_{ad} \cdot M + e^- \rightleftharpoons M + H_2 + OH^-$) or the Tafel recombination step ($2M \cdot H_{ad} \rightleftharpoons 2M + H_2$),^[8, 22] and OH_{ad} desorbs from the Ni site, followed by the adsorption of another H_2O molecule on the same sites.

Figure 3. (a) Ni 2p, (b) O 1s, and (c) N 1s XPS spectra of N-NiO/NF and NiO/NF. XPS analyses demonstrate the existence of LCO atoms and the different electronic structure between N-NiO/NF and NiO/NF.

Guided by these theoretical prediction, an ultrathin N-modulated NiO layer rich in LCO atoms was prepared on the surface of Ni foam (N-NiO/NF) by oxidizing Ni foam in air and then calcining it in NH_3 atmosphere (see details in Supporting Information). The optimized calcining time is 6 h (Supporting Information, Figure S2), so we have used the sample prepared for 6 h calcining time to obtain the corresponding experimental data. After these surface treatments, the color of the pristine Ni foam turns from gray to black (Figure 2a and Figure S3). The scanning electron microscopy (SEM) images reveal the nanostructured morphology of the N-NiO/NF surface (Figure 2b and 2c). This is in contrast to the relatively flat surface observed from surface-oxidized Ni foam (NiO/NF) (Supporting Information, Figure S4). The corresponding energy dispersive X-ray spectroscopy (EDS) mapping images for N-NiO/NF confirm that Ni, O, and N are homogeneously distributed over the Ni foam surface (Figure 2d-g). The microstructure of N-NiO/NF was then analyzed by transmission electron microscopy (TEM). To allow clear cross-sectional images, focused ion beam (FIB) was utilized for the preparation of the lamellar specimen. The porous N-NiO layer of ≈ 850 nm in thickness between metallic Ni substrate and Pt protection layer can be observed from the cross-sectional TEM image of N-NiO/NF (Figure 2h). High-resolution TEM (HRTEM) images of N-NiO/NF (Figure 2i and 2j) show distinct lattice fringes with an interplanar distance of 0.209 nm, which is consistent with the (200) lattice plane of NiO.^[23] The selected-area electron diffraction (SAED) pattern (Figure S5) indicates the polycrystalline nature of N-NiO layer. Additionally, the broad and diffused rings in SAED pattern could be attributed to the amorphous phase caused by FIB damages.^[24] However, X-ray diffraction (XRD) pattern with only diffraction peaks of Ni metal indicates that no peaks of oxides or nitrides can be detected (Supporting Information, Figure S6), mainly because of the strong signals of the Ni foam substrate.

X-ray photoelectron spectroscopy (XPS) was then carried out to confirm the existence of LCO atoms on the surface of N-NiO/NF and the redistribution of surface charges after modulation. The survey spectrum of N-NiO/NF primarily shows the presence of Ni, O, N, and C (Supporting Information, Figure S7). These element contents are 11.74%, 29.11%, 3.05%, and

56.10%, respectively. In detail, the Ni 2p spectra (Figure 3a) indicate that the element Ni mainly exists as NiO. The two peaks around 852.20 and 869.45 eV in N-NiO/NF spectrum are the characteristic peaks of the Ni-N bond.^[25, 26] More importantly, compared with that of NiO/NF, the Ni 2p_{3/2} peak in N-NiO/NF spectrum negatively shifts ~ 0.95 eV. Such a shift of binding energy is presumably caused by the acceptance of some extra electrons on the Ni atoms. In the O 1s spectrum, three peaks can be clearly identified (Figure 3b). The peaks at 530.00 and 532.73 eV are due to oxygen atoms in sites with a

normal coordination and hydroxyl species of the surface-adsorbed water molecule, respectively.^[27, 28] According to the previous reports, the peak located at 531.00–531.60 eV corresponds to the LCO atoms at special sites or domains on the surface of the samples.^[20, 21, 28] Formally, these LCO atoms could be described as O^- species, which have a lower electron density than the classical O^{2-} species because of a lower coordination number and higher covalence.^[20, 21] The peak area of LCO is the largest in these three peaks, which indicates that the element O mainly exists as the form of low coordination. Compared with that of NiO/NF, the LCO peak in N-NiO/NF spectrum positively shifts to ~ 0.58 eV. This shift of binding energy might be caused by the loss of some electrons from LCO atoms. Taken together, the peak shifts of Ni 2p and O 1s for N-NiO/NF could be attributed to the electron transfer from LCO atoms to Ni atoms, which coincides with above DFT calculations. In the N 1s spectrum (Figure 3c), the peak at 397.00 eV can be assigned to Ni-N bond,^[25, 29] the other peak around 399.48 eV can be associated with adsorbed N_2 .^[25] Therefore, all the above results clearly indicate the existence of LCO atoms on the surface of N-NiO/NF and the redistribution of surface charges after modulation.

To shed light on the role that the nitrogen modulation plays in the HER process, the obtained N-NiO/NF electrode was tested in the electrochemical HER in 1.0 M KOH solution (pH ≈ 13.6) using a typical three-electrode system (see details in Supporting Information). The activities of NiO/NF, Pt/C deposited Ni foam (Pt/C/NF) and pristine Ni foam were also measured for comparisons. As shown in Figure 4a, the N-NiO/NF only requires overpotential of ~ 100 mV to achieve geometric current density of -10 mA cm^{-2} , which is 125 mV smaller than that of NiO/NF. This performance is comparable to most recently reported nonprecious HER catalysts in alkaline conditions, including Ni-doped MoS_2 nanosheets (-98 mV at -10 mA cm^{-2}),^[30] mesoporous MoO_3-x (-138 mV at -10 mA cm^{-2}),^[31] cubic phase CoSe_2 (-190 mV at -10 mA cm^{-2}),^[32] and 3D porous NiMoN (-109 mV at -10 mA cm^{-2})^[33] (more details in Supporting Information, Table S2). The high HER activity of N-NiO/NF manifests that the nitrogen modulation could significantly accelerate the HER kinetics in alkaline environments.

Tafel slope is commonly used to discern the rate-determining step. If the Volmer step is the rate-determining step, the theoretical Tafel slope lies in the range of 100 to 130 mV dec⁻¹.^[8, 22] Besides, according to the Tafel equation ($\eta = a + b \log(j)$, where η is the overpotential, a is the Tafel constant, b is the Tafel slope, and j is the current density), the smaller the Tafel slope is, the faster the j increase with η will be. The calculated Tafel slopes of N-NiO/NF and NiO/NF locate in the theoretical range (Figure 4b), implying the critical role of the Volmer step for HER in 1.0 M KOH. More importantly, the Tafel slope of N-NiO/NF (112.58 mV dec⁻¹) is smaller than that of NiO/NF (121.07 mV dec⁻¹), suggesting the favorable kinetics of the Volmer step.

Figure 4. (a) IR-compensated polarization curves after normalizing the currents to the geometric area and (b) corresponding Tafel slopes of N-NiO/NF and NiO/NF, along with Pt/C/NF and blank Ni foam for comparison. (c) Specific current densities of N-NiO/NF and NiO/NF after normalizing the geometric current densities to the corresponding ECSA. (d) Nyquist plots of N-NiO/NF and NiO/NF at the overpotential of -100 mV. The inset is the corresponding Randles equivalent circuit. (e) Polarization curves of N-NiO/NF before and after 2000 cycles. (f) Galvanostatic measurement of N-NiO/NF at the geometric current density of -10 mA cm⁻² for 90 h. All the measurements were performed in 1.0 M KOH at room temperature.

An electrocatalyst with large electrochemically active surface area (ECSA) can expose more active sites.^[34] To exclude the contribution of the increased ECSA to the enhanced electrocatalytic activity of N-NiO/NF for HER, the specific current densities were calculated by normalizing the geometric current

densities in Figure 4a to the corresponding ECSA (Figure 4c). The ECSA was estimated from the electrochemical double-layer capacitance (C_{dl}) according to the method established previously (Supporting Information, Figure S8).^[35] The N-NiO/NF has a larger ECSA than that of NiO/NF (Supporting Information, Figure S8), which indicates that the partial activity of N-NiO/NF comes from the larger ECSA. When normalized to the ECSA, the N-NiO/NF displays much higher specific current density than that of NiO/NF in the whole potential region (Figure 4c), demonstrating N-NiO/NF is intrinsically more active than NiO/NF. The improved performance would be mainly attributed to the increased HER kinetics due to the nitrogen modulation toward active sites on NiO surface.

The kinetics of the HER processes on the samples were examined by electrochemical impedance spectroscopy (EIS) to further clarify the effect of nitrogen modulation (see details in Supporting Information). The Nyquist plots were obtained by carrying out the EIS experiments at -100 mV overpotential and then fitted by a simplified Randles equivalent circuit (Figure 4d). In the Randles circuit, R_s is related to the series resistance arising from the electrolyte and all contacts, CPE is the constant phase angle element, which models the behavior of the double layer capacitance of solid electrode in the real situation, and R_{ct} stands for the charge transfer resistance.^[36] It should be noticed that a small R_{ct} gives rise to fast charge transfer kinetics. The fitted R_{ct} of N-NiO/NF (12.8 Ω) exhibits a significant decrease in comparison with that of NiO/NF (43.79 Ω) (Supporting Information, Table S1), which highlights that the charge transfer kinetics during the HER process is effectively facilitated after modulation.

The stability is another key factor of catalysts for practical use. The stability of the N-NiO/NF was assessed by long-term cycling and then continuous HER at a constant current density (see details in Supporting Information). The cyclic voltammetry (CV) was performed between -0.20 and +0.06 V vs RHE at 50 mV s⁻¹. After 2000 cycles, the HER activity has negligible change compared to initial one (Figure 4e). Figure 4f shows galvanostatic curve at a constant geometric current density of -10 mA cm⁻² for 90 h. The overpotential fluctuates around -128 mV and no noticeable increase is observed, showing excellent stability. As compared in Table S2, this stability locates in the top positions of recently reported HER catalysts in alkaline solutions. Furthermore, the morphology and surface element valence states of N-NiO/NF are well retained after 10 h HER test at -10 mA cm⁻² (Supporting Information, Figure S9 and S10), substantiating the excellent stability. In addition, the electrode will work at high current densities for practical application, so the stability of N-NiO/NF at a higher current density and corresponding Faradaic efficient of evolved H₂ were also measured. The sample exhibits extraordinary stability at the current density of -100 mA cm⁻² and a nearly 100% Faradaic efficiency can be obtained during the electrolysis process (Supporting Information, Figure S11).

The nitrogen-modulation strategy towards LCO sites and metal sites could also be useful for improving the HER activity of CoO_x. The CoO_x (CoO_x/Co foil) and N-modified CoO_x (N-CoO_x/Co foil) were prepared on the surface of Co foil by the similar surface treatment. As depicted in Figure S12, the XPS analyses confirm the existence of LCO atoms. The polarization

curves demonstrate that the overpotential of N-CoO_x/Co foil decreases by more than -125 mV at the geometric current density of -10 mA cm⁻² compared with that of CoO_x/Co foil in 1.0 M KOH, proving that the nitrogen modulation could be extended to improve the HER activity of other 3d metal oxides in alkaline environments.

In summary, we have engineered the electrochemical active sites on the surface of nickel oxide at the atomic level to improve the alkaline HER kinetics. The combination of theoretical predictions and experimental results reveal that the surface charge redistribution after nitrogen modulation is beneficial to the initial water dissociation as well as following H_{ad} recombination from LCO sites and OH_{ad} desorption from Ni sites. The modulated NiO rich in LCO atoms exhibits significantly enhanced activity with a small overpotential of -100 mV to achieve the current density of -10 mA cm⁻² and durable stability over 90 h for HER in 1.0 M KOH. We believe that this facile modulation strategy may be applied to other transition metal oxides to prepare practical electrocatalysts for alkaline electrolysis.

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The surface charge redistribution after nitrogen modulation simultaneously facilitates the formation of H_2 from low coordinated oxygen (LCO) sites and the desorption of OH^-_{ad} from nickel sites, which in turn promotes the initial water adsorption step as well as followed water dissociation step. The modulated NiO rich in LCO atoms exhibits significantly enhanced activity and robust stability for hydrogen evolution reaction in alkaline environments.

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