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Supporting Information

Seamless Separation of OH_{ad} and H_{ad} on a Ni-O Catalyst

Toward Exceptional Alkaline Hydrogen Evolution

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EXPERIMENTAL

Synthesis of Electrocatalyst NiOS Nanostructure

The electrocatalyst NiOS nanostructure was synthesized via a hydrothermal protocol. The precursor solution was prepared by dissolving 5.05 g of sodium *n*-dodecyl sulfate (SDS) and 3.73 g of thiourea in 87.5 mL of deionized (DI) water. Nickel foam was cleaned in ethanol, diluted acid and water under sonication in turn. Pre-cleaned Ni foam ($3.5 \text{ cm} \times 3 \text{ cm}$) was then placed in the Teflon-lined autoclave with the precursor solution. The autoclave was sealed and heated at 180°C for 20 hours. After it cooled down to the room temperature, the obtained black sample was thoroughly rinsed with water and ethanol, and then dried under vacuum at 60°C.

Fabrication of annealed NiO sample

Annealed NiO film was fabricated by annealing pre-cleaned Ni foam at 400°C under ambient condition for 2 hours.

Characterizations

Scanning electronic microscopy (SEM, Zeiss Auriga 60 Field Emission Scanning Microscope) was used to observe the surface morphology. X-ray diffraction (XRD, Rigaku Flex600) was acquired to identify the crystallinity and the microstructure. Transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) images were obtained with a high-resolution JEOL 2100 FE instrument equipped with an EDAX X-ray detector and a high angle annular dark field (HAADF) detector. X-ray photoelectron spectroscopy (XPS) measurements were performed on a ULVAC-PHI Versa Probe III with monochromatic Al Kα source energy of 1486.6 eV. The high-resolution and survey scans were shifted to align the adventitious C1s peak at 284.8 eV. The Raman spectroscopy was conducted on a RENISHAW inVia Raman Microscope with 532 nm laser illumination.

Electrochemical performance evaluations

Electrochemical performances for hydrogen evolution reaction were carried out on a Gamry Reference 3000 Potentiostat with a three-electrode electrochemical configuration, where the prepared electrocatalyst NiOS nanostructures work as the working electrode, the Pt wire as the counter electrode, and the Ag/AgCl electrode as the reference electrode. The activation of NiOS electrocatalyst was performed *in-situ* while processing hydrogen evolution in 1M NaOH aqueous solution by fixing an applied potential negative than

-0.3V vs RHE for a time period. More negative the applied potential is, the shorter time period the activation process. The activation process ends with a symptom of steady current density. The polarization curves were acquired in 1M NaOH aqueous solution with a scan rate of 20 mV/s, and a negative-direction scanning from negative potential moving positively. All potentials were converted to reversible hydrogen electrode (RHE) based on the Nernst equation $E_{\rm RHE}=E_{\rm Ag/AgCl}+0.059 \text{pH}+E_{Ag/AgCl}$, in which $E_{Ag/AgCl}=0.197$ V at 25°C. The polarization curves are corrected against the ohmic potential drop. The value of uncompensated solution resistance (R_s) was obtained based on the potentiostatic electrochemical impedance spectroscopy (EIS). The EIS were acquired within a frequency range of 10⁴ Hz ~ 0.1 Hz at the potential -0.3V vs RHE. For the collection of the temperature-dependent polarization curves, the electrochemical cell was placed in an oil bath that was used to control the electrolyte temperature. The linear sweep voltammetry scanning was performed after the temperature was stabilized.

To acquire the apparent electrochemical activation energy E_a , the temperature-dependent polarization curves were acquired within the range from room temperature to 70°C. According to the Arrhenius equation

$$\frac{\partial log^{[n]}(j_0)}{\partial \frac{1}{T}} = -\frac{E_a}{2.302R}$$

Where E_a is the apparent electrochemical activation energy (kJ mol⁻¹), j_0 is the exchange current density, T is the temperature (K), and R is the gas constant. Arrhenius plots could be obtained by plotting the logarithm of the exchange current density $\log(j_0)$ versus reciprocal of temperature (1/T), of which the slope ggives rise to the apparent electrochemical activation energy E_a .

Fabrication of Pt/C electrode

The 40% Pt/C particle was dispersed in propanol and water with a volume ratio 1:4, and 5% Nafion was added. The ink was sonicated for 30 min, then dropped onto the cleaned carbon paper and dried in air overnight.



Figure S1. The fabrication was achieved by the sulfur hybridization into NiO to form a NiOS structure first, which then underwent a self-activation by a desulfurization during the hydrogen evolution process. In crystal structures, green, red, blue, light gray, yellow and dark gray represent Ni, O, low coordinated O, vacancy, S and H, respectively.



Figure S2. Microstructures of the as-prepared NiOS nanostructure on Ni foam fabricated by a hydrothermal methodology. (a-c) SEM images for the as-prepared cone-like NiOS nanostructure with different magnifications; (d) TEM and (e) HRTEM images; (f) the element distribution mapping on a single NiOS cone. (g) XRD patterns for Ni foam and as-prepared NiOS nanostructures. (h) schematic illustration for the proposed hybridization of NiO and NiS₂ to form NiOS structure. Green, red and yellow represent Ni, O and S, respectively.

Such a NiOS structure was fabricated under a hydrothermal condition with Ni foam as the nickel resource and thiourea as the sulfur precursor. As shown in Figures S2 a-c, cone-like nanostructures with a length of ~3 μ m and a diameter of ~1 μ m uniformly formed on the surface of 3D Ni foam skeleton. TEM image in Figure S2d further confirms the cone-like structure. Well-identified lattice fringes were detected in HRTEM observation (Figure S2e) with an average lattice distance d = 0.254 nm (inset in Figure S2e), which is very close to, but a bit larger than, that of (111) crystal plane in NiO (d = 0.241 nm). The chemical composition was also analyzed *via* high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) combined with EDX elemental mapping (Figure S2f). It revealed that Ni, S and O were synchronously dispersed across the entire cone.

X-ray diffraction spectroscopy was performed on Ni foam, NiO and NiOS nanostructures for the comparison of the crystal structure. It is well known that Ni foam is apt to be oxidized and covered with a NiO layer. As shown in XRD pattern for Ni foam in this study (dotted line in Figure S2g), feature diffraction patterns for both NiO (JCPDS# 47-1049) and metallic Ni (JCPDS# 04-0850) could be distinguished. We found that there does exist a NiO film even immediately after cleaning in the acid and ethanol solution. That indicates it is almost inevitable to avoid the presence of NiO on Ni foam. In the diffraction pattern of the as-prepared NiOS structure, all peaks could be apparently assigned to cubic NiO phase, and no other peaks belonging to regular nickel sulfides appear. Additionally, the diffraction patterns for metallic nickel disappear completely in NiOS nanostructures, suggesting that metallic nickel was fully consumed to form this NiOS structure during the hydrothermal process. Two possibilities are responsible for this fact. (i) The majority of nickel sulfide compounds exist in amorphous form or present very poor long-range order. However, this could be ruled out due to the direct evidence from HRTEM image showing clear long-range lattice fringe. (ii) Sulfur atoms were successfully inserted into, while not destroying, the original cubic NiO crystal structure. This could happen as sulfur has the very similar electronegativity and size with oxygen, which does not generate intensive distortion on the crystal structure. [S1] From the XRD pattern, NiO in this study crystalizes in the cubic Fm-3m space group with a unit cell parameter a=b=c=4.1771 Å (JCPDS 47-1049). Meanwhile, fluorited NiS₂ shows the similar cubic Fm-3m space crystal structure with unit cell parameter a=b=c=4.026 Å (Materialsproject ID: mp-849053, please see Figure S3 and more details in Supporting Information). Additionally, comparison of their XRD patterns displays considerable overlap between NiO and calculated fluorited NiS₂, as shown in Figure S5. It is therefore plausible that the partial substitution of sulfur is feasible maintaining the major crystal feature of the pristine cubic NiO (Figure S2h). A concept mechanism was proposed that the reaction started from surface NiO to form NiOS with the insertion of sulfur atoms into the lattice, which initiated an *in-situ* epitaxy growth by etching the nickel skeleton with the presence of sulfur ions under basic condition. Accordingly, results above suggest that a highly crystalline NiOS nanostructure was in situ formed with such one-step hydrothermal process.

Fluorite NiS₂ (mp-849053)

https://materialsproject.org/materials/mp-849053/ Space Group Fm-3m [225], Cubic Lattice Parameters a=4.026 Å; b=4.026 Å; c=4.026 Å $\alpha=60.000^\circ$; $\beta=60.000^\circ$; $\gamma=60.000^\circ$



Figure S3. Crystal structure (left, cited from Materials Project.) of the fluorite NiS₂, and comparison of XRD patterns (right) between calculated fluorite NiS₂ and NiO. NiS₂ is Fluorite structured and crystallizes in the cubic Fm-3m space group. The structure is three-dimensional. Ni⁴⁺ is bonded in a body-centered cubic geometry to eight equivalent S²⁻ atoms. All Ni-S bond lengths are 2.47 Å. S²⁻ is bonded to four equivalent Ni⁴⁺ atoms to form a mixture of edge and corner-sharing SNi₄ tetrahedra.



Figure S4. SEM images with different magnifications for NiO by annealing nickel foam at 400°C under ambient conditions. The insets represent the digital photo of the annealed NiO sample.



Figure S5. XRD patterns for Ni foams, annealed NiO and NiOS nanostructure.



Figure S6. XPS (a) Ni 2p3/2, (b) O 1s spectra for the annealed NiO sample.

The annealed NiO was detected as the reference sample as shown in Figures S6*a* and *b*. The unique multiplet splitting Ni 2p3/2 spectrum (Figure S6*a*) reveals the typical feature for NiO with three peaks located at 853.9 eV, 855.8 eV, and 861.2 eV, respectively. [S2] The peak at 853.9 eV is attributed to Ni²⁺, whereas the peak at 855.8 eV is due to the presence of Ni^{δ +} (NiO_x, δ >2) with a Ni^{δ +}/Ni²⁺ ratio of 1.68. [S3,S4]. The wide bump wave centered at around 861.2 eV is attributed to the satellite peak for Ni 2p3/2. It is noted that the metallic Ni⁰ peak, regularly located at 852.7±0.4 eV [S5], was not detected, suggesting Ni foam was fully covered with a thick NiO film over the entire surface. O1s in the annealed NiO exhibits the typical characteristics for oxygen in metal oxides with three deconvoluted peaks at 529.5 eV, 531.0 eV and 532.1 eV, respectively (Figure S6*b*). The peak at 529.5 eV corresponds to the lattice oxygen (Ni-O), and the high binding energy peak at 532.1 eV represents the adsorbed water molecules or oxygen species. The peak at 531.0 eV was commonly assigned to either the defected oxygen in the lattice or hydroxyl (OH) on the surface. [S2-S5] The possibility of being OH could be precluded since NiO sample was obtained by annealing at 400°C. Accordingly, this peak here originates from the unfully coordinated oxygen in NiO lattice.

Explanation for XPS of NiOS structure

In the as-prepared NiOS structure, the surface chemistry is quite different from that of the annealed NiO (Figure S6). The apparent S 2p signal in Figure 2a is immediately evident of S present in the obtained NiOS structure. The remarkable peak located at 169 eV indicates the formation of abundant S-O bonds, consistent with EDX mapping (Figure S2f). Two sets of S 2p3/2 and S 2p1/2 doublets could be identified at 162.81 eV/163.99 eV, and 163.59 eV/164.76 eV with a separate distance of around 1.18 eV. The first doublet is attributed to S^{2-} in regular sulfides; whereas the second is assigned to S_{2}^{2-} , which takes up to 38.8% of total S. This means that large amounts of inserted sulfurs exist in the form of bridging/edging S_2^{2-} , which has been considered as HER active centers on the edge in some sulfide electrocatalysts. In term of Ni 2p3/2 spectrum as shown in Figure 2b, the major band is composed of two deconvoluted peaks at 854.5 eV and 856.5 eV, respectively, which correspond to Ni²⁺ and Ni³⁺ oxidation status with a Ni³⁺/Ni²⁺ ratio of 7.05. [S2-S5] Such a huge increment, compared to that of the annealed NiO (Figure S6a), in Ni oxidation status is a result from the presence of both S in the lattice and OH groups on the surface. For Ols spectrum (Figure 2c), a major wave band centered at around 532 eV emerges, which can be deconvoluted into three peaks located at 533.3 eV, 531.9 eV and 530.9 eV, respectively. Relative to the regular NiO (Figure S6b), the lattice oxygen peak at 529.5 eV disappears, indicating the completely different local chemical environment in the as-prepared NiOS, and further consolidating that the obtained NiOS structure is not simply a mixture of oxides and sulfides. The peak at 530.9 eV is attributed to the unfully coordinated oxygen in NiOS structure, please see Figure S6. Whereas the peak at 531.9 eV is ascribed to the surface hydroxyl given that this electrocatalyst was synthesized in alkaline aqueous solution. The peak at 533.3 eV is due to the adsorbed water or oxygen species as regularly. Along with TEM characterization (Figure S2), it is concluded that the insertion of S significantly alters the local chemical environments although the as-prepared NiOS nanostructure preserves the major cubic crystal structure of NiO.



Figure S7. Schematic illustration of deprotonation for oxy/hydroxide Ni during the activation process.



Figure S8. Exchange current density j_0 corresponding to the samples in Figure 3a and b. According to the Tafel equation $\eta = a + b \log j$, where *b* is the Tafel slope, *j* is the current density. The exchange current density j_0 , therefore, could be obtained from the Tafel slope intersection with the abscissa, as shown in the supporting information Table S2.



Figure S9. Cyclic voltammetry spectra for the Ni-O catalyst layer (a,b) and the annealed NiO (c,d) measured in 1 M NaOH electrolyte with a scanning rate of 50 mV/s but different potential windows.

To confirm these peaks are related to the H_{ad} desorption, we performed CV curves with different potential windows (Figure S9). For both electrodes, the anodic peaks appear only when the starting potential is negative than 0 V vs RHE; while no peaks when the starting potential ≥ 0 V vs RHE. These peaks indeed originate from the H_{ad} desorption off the surface with different adsorption types, instead of from the other oxidation reactions.[S6, S7]

Alkaline HER on the resultant Ni-O catalyst

A mechanism was proposed based on the results. When a water molecule comes close and gets adsorption on the Ni atoms (process i in Figure S10) through the interaction with OH group, the H-OH bond will be weakened. As shown as the process ii in Figure S10, the H₂O molecule then dissociates into H_{ad} and OH_{ad} with the aid of a free electron. As a consequence, the OH_{ad} remains adsorbed on Ni atom; meanwhile, the generated H_{ad} will be seamlessly captured by the negatively charged oxygen (low coordinated oxygen, process iv in Figure S10). Finally, the adsorbed OH_{ad} will release to refresh the surface (process iii in Figure S10), and the adsorbed H_{ad} release from active oxygen sites to generate H₂ via either Heyrovsky step or the Tafel recombination step (process v in Figure S10). In this study, H₂ generation most performs through Heyrovsky step due to that the Tafel slope of 60.8 mV/dec is larger than 30 mV/dec. In the regular NiO catalyst (Figure S10a), H_{ad} can only get adsorbed after the release of OH_{ad} from Ni atom. The strong interaction between OH_{ad} and Ni, however, hinders the release of OH_{ad} and, thus, blocks the adsorption of H_{ad}. In Ni-O catalyst layer, this issue was solved by separating OH_{ad} and H_{ad} adsorption onto different active centers (Figure S10b). In such an action, the resultant Ni-O catalyst not only promotes the initial water dissociation but also facilitates H_{ad} recombination from O⁻ sites as well as OH_{ad} desorption from Ni sites, leading to the accelerated alkaline HER.



Figure S10. The proposed alkaline HER mechanism on (a) regular NiO, and (b) the resultant Ni-O catalyst in this study. (i) water adsorption, (ii) water dissociation, (iii) desorption of OH_{ad} , (iv) H_{ad} adsorption, and (v) H_2 generation.

Annealed NiO	Ni	853.9	855.8	861.2
	0	529.5	531.0	532.1
As-prepared	Ni	854.5	856.5	862.1
NiOS	Ο	530.9	531.9	533.3
	S	162.82/164.0	163.59/164.76	169.1
Activated Ni-O	Ni	855.4	856.6	862.3
	0	530.9	531.9	533.2
	S	No	No	No
Note: The unit for bir	nding energy is	eV.		

Table S1. Binding energy for Ni, O, and S in annealed NiO, As-prepared NiOS nanostructure andActivated Ni-O nanostructures, respectively, from XPS spectra.

Parameters	Activated Ni-O	As-Prepared NiOS	Pt/C	Annealed NiO	Ni Foam
$\eta @10 \text{ mA/cm}^2$	90 mV	162 mV	66 mV	223 mV	229 mV
$\eta @ 100 \text{ mA/cm}^2$	163 mV	296 mV	186 mV	302 mV	390 mV
Tafel Slope	60.8 mV/dec	124.4 mV/dec	40.8 mV/dec	108.5 mV/dec	138.4 mV/dec
\dot{J}_0	0.394	0.285	0.571	6.3×10 ⁻²	0.145
R _{ct}	2.67Ω	13.71 Ω	1.78 Ω	17.02 Ω	-

Table S2. Summary of the HER performances for samples in Figure 3.

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