# Supporting Information

## Nanosheets Assembled Nickel Sulfide Nanosphere with Enriched $Ni^{3+}$ Sites for Efficient Water Splitting and Zinc-Air Batteries

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## EXPERIMENTAL SECTION

**Reagents and Materials.** Nickel(Ⅱ) chloride anhydrous ($NiCl_2$, 98%) and Potassium hydroxide (KOH, 90%) are acquired from Tianjin Kermel company. Ethanol ($C_2H_6O$, 99.7%), Carbon disulfide ($CS_2$, 99%) and Carbon paper (CP) are purchased from Tianjin Guangfu Fine Chemical Research Institute. High purity nitrogen gas (99.99%) and deionized water (18.2 MΩ cm) are presented from Tianjin University.

**Materials Synthesis.** In this work, $NiS_x$ nanospheres are synthesized by a hydrothermal method. The specific steps are as follows: 0.26 g $NiCl_2$ is weigh and dissolves in 35 ml deionized water, followed by magnetic stirring until forming a homogeneous solution. After this, 800 μl ethylenediamine is slowly added and continuous stirrers for 30 minutes. Then, 250 μl colloidal $CS_2$ is added into the solution after stirring for 30 minutes to form a uniform mixture, and the autoclave is placed in oven at 180℃ for 8h, after nature cooling in fuming cupboard, the samples are separated by centrifugation, washed using deionized water and ethanol two times. Finally, the NiS product is collected after lyophilizing. As for the synthesis of $Ni_3S_4$ and $NiS_2$ samples, the adding amount of $CS_2$ just is changed to 450 μl and 550 μl, respectively.

**Materials Characterization.** The synthesized compounds are characterized by X-ray diffraction (XRD) which are produced by Bruker/D8 Advanced with Cu Kα radiation source (λ=0.15418 nm) and X-ray photoelectron spectroscope (XPS) which are collected by a Escalab 250Xi. The morphologies and elemental analysis of samples are studied by scanning electron microscopy (SEM, Hitachi s4800, 30KV) and transmission electron microscopy (TEM, JEOL JEM-2100F, 200KV). Brunauer Emmett Teller (BET) is measured by an AutosorbiQ instrument (Quantachrome U.S.).

**Electrocatalytic Measurements.** The electrochemical measurement is tested using the Iviumstat electrochemical workstation. The OER, ORR and HER performances are measured in a three electrode system in a 1.0 M KOH electrolyte, platinum electrode and saturated calomel electrode (SCE) are used as counter electrode and reference electrode, respectively and prepared samples are designed as working electrode.

Overall water splitting is tested in a two electrode system. For making the working electrode for HER and OER, first to dispose the CP and mix 10 mg $NiS_x$ samples into 400 µl deionized water, then add 500 µl ethanol and 100 µl Nafion to form a homogeneous solution. For ORR electrode, 3 mg Vulcan carbon and 7 mg $NiS_x$ mixed powder was used to prepare the catalyst ink. The working electrode is a CP (1 cm*1 cm) covered with 150 µl prepared solution. Cyclic voltammograms (CV) are conducted firstly to reach a steady state. The linear sweep voltammetry (LSV) curves of HER are obtained at - 0.8 V ~ - 1.6 V, OER LSV curves are at 0.9 V ~ 0 V, ORR LSV curves are at 0.1 ~ - 0.8 V and the scanning speed is 5 mV $s^{-1}$. The collected data is calculated according to the *iR*-compensation, the equation is $E_{corr} = E_{mea} - iR_s$. And all data is transformed to reversible hydrogen electrode (RHE) following the equation $E_{vs\cdot RHE} = E_{vs.SCE} + 0.059 * pH + 0.241$. Electrochemical impedance spectroscopy (EIS) is measured with the frequencies from 10 kHz to 0.01 Hz. A series of CV curves are tested at 50, 70, 90, 110, 130 mV $s^{-1}$ scanning rates to obtain the electrochemical capacitance ($C_{dl}$) dataset. The aim to testify the stability of samples, ChronoPotentiometry data at 10 mA $cm^{-2}$ current density is collected. Using water drainage method, the amount of $O_2$ and $H_2$ are gathered to prove the faradaic efficiency of catalysts by comparing the amount of $O_2$ and $H_2$ theoretical calculation. The Zinc-air battery is assembled by Zn plate (1*2 cm) as anode and $NiS_2$ electrode as the cathode. The electrolyte is 6.0 M KOH and 0.2 M $ZnCl_2$, which is saturated with $O_2$ before test. The open-circuit, discharge curve and the charge-discharge performance are measured using LAND-CT2001A testing devices.

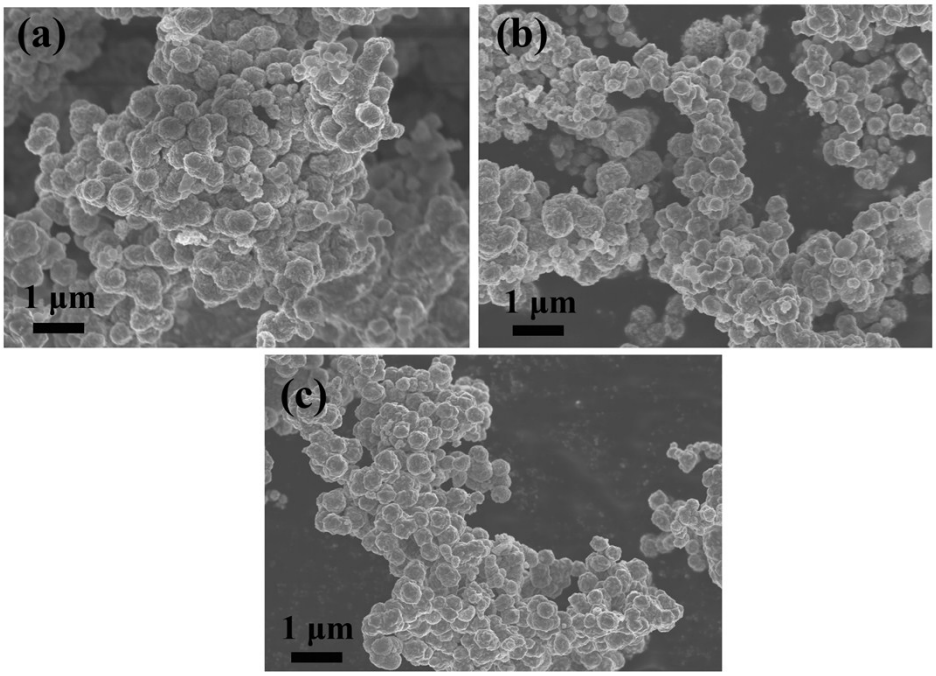


**Fig. S1** SEM images of (a) NiS, (b) $Ni_3S_4$, and (c) $NiS_2$.

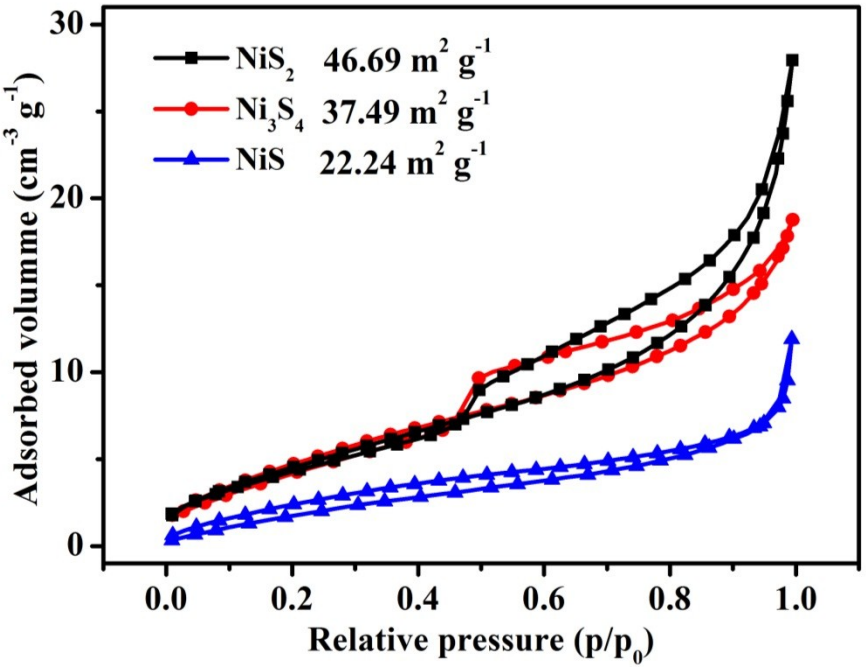


**Fig. S2** $N_2$ adsorption-desorption isotherms of NiS, $Ni_3S_4$, and $NiS_2$.

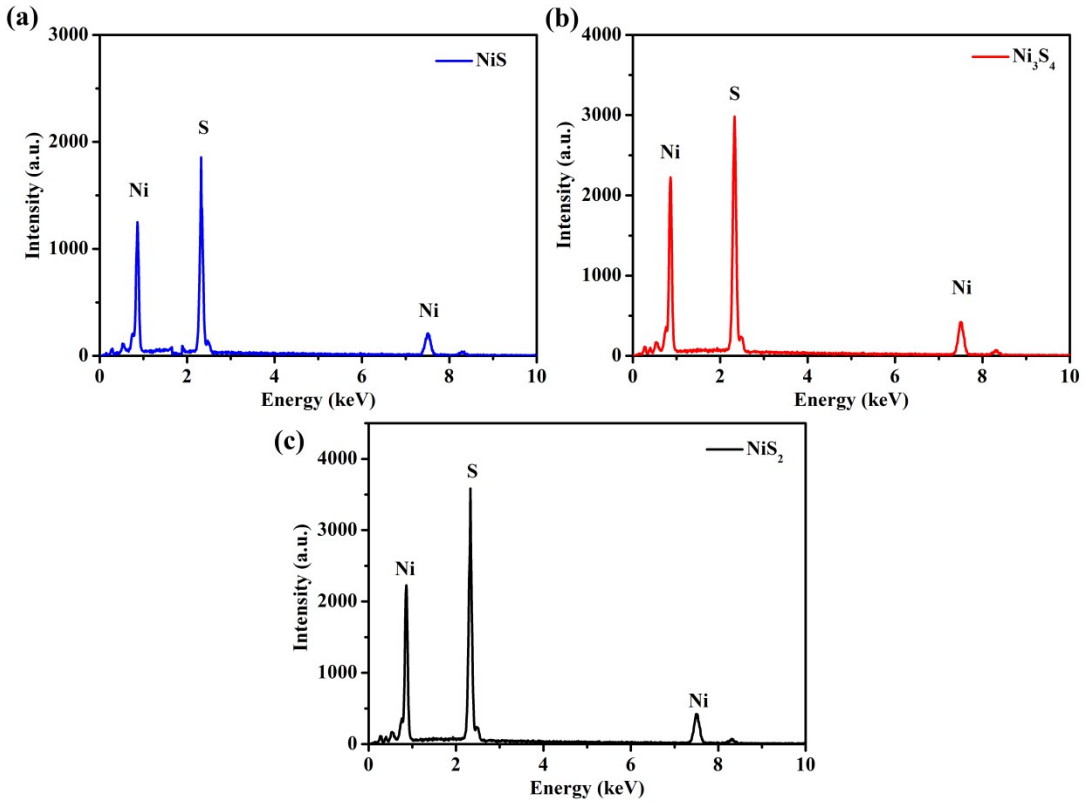


**Fig. S3** EDS spectra of NiS, $Ni_3S_4$ and $NiS_2$.

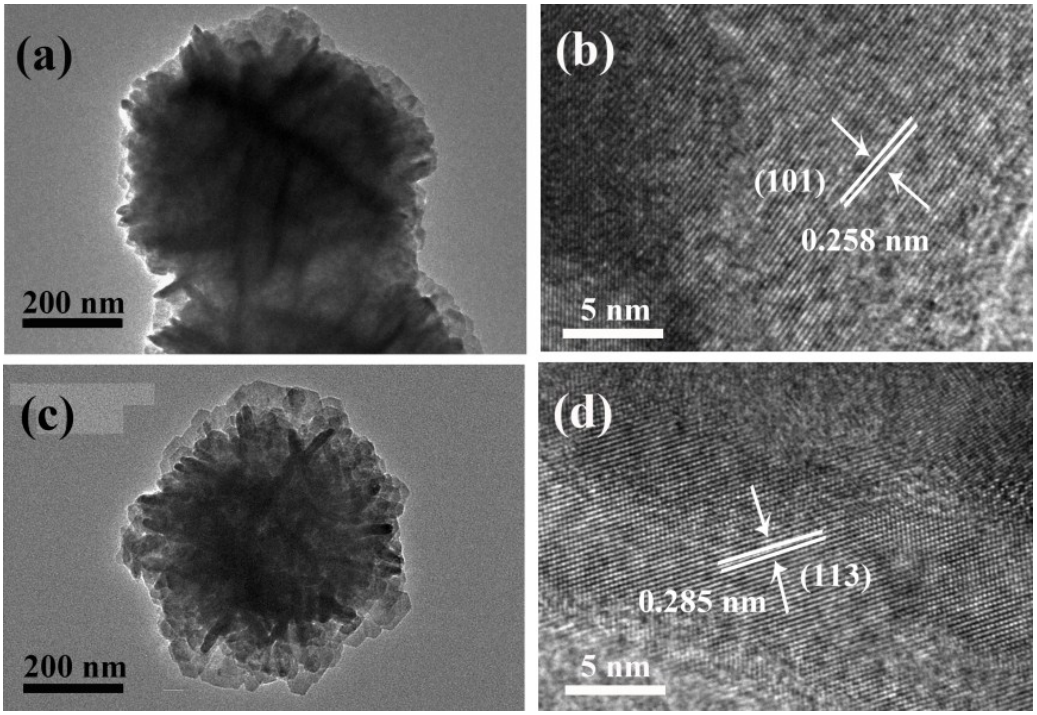


**Fig. S4** TEM and HRTEM images of (a, b) NiS and (c, d) $Ni_3S_4$. The measured distance of 0.26 and 0.28 nm is assigned to the (101) and (113) planes of NiS and $Ni_3S_4$.

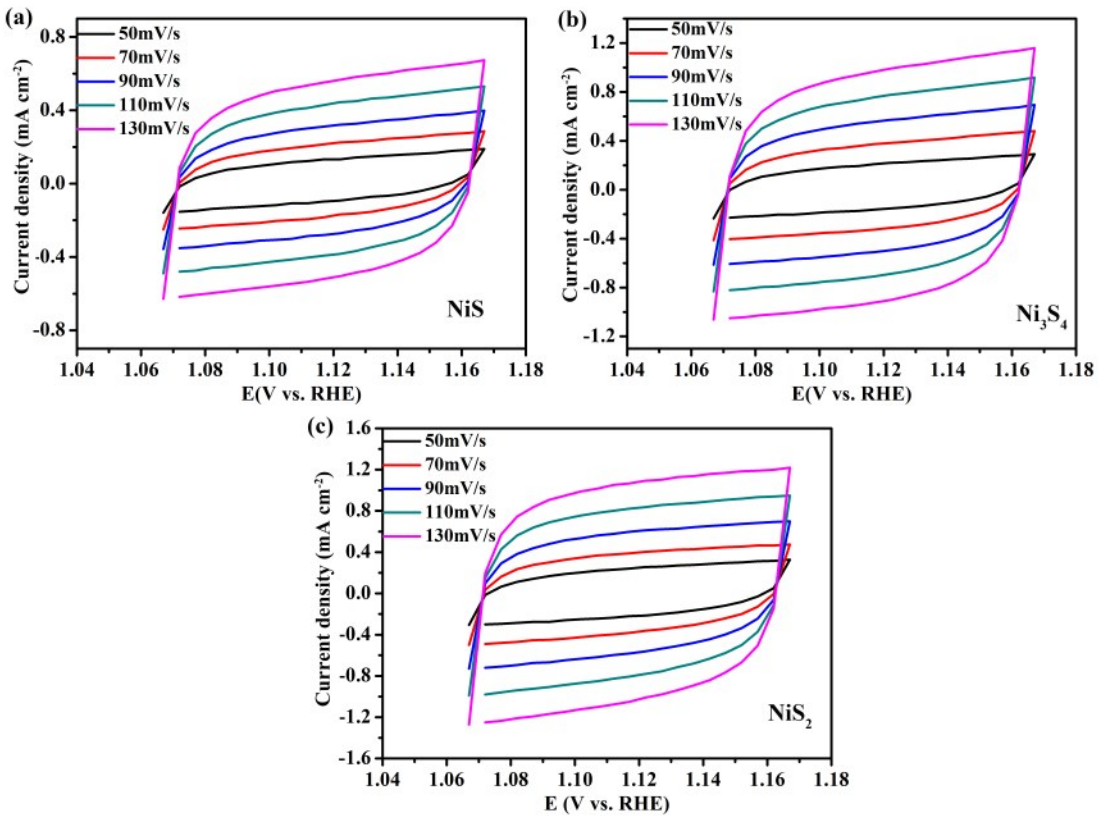


**Fig. S5** Cycle voltammograms of (a) NiS, (b) $Ni_3S_4$ and (c) $NiS_2$ from 1.067 to 1.167 V in 1.0 M KOH at different scan rates.

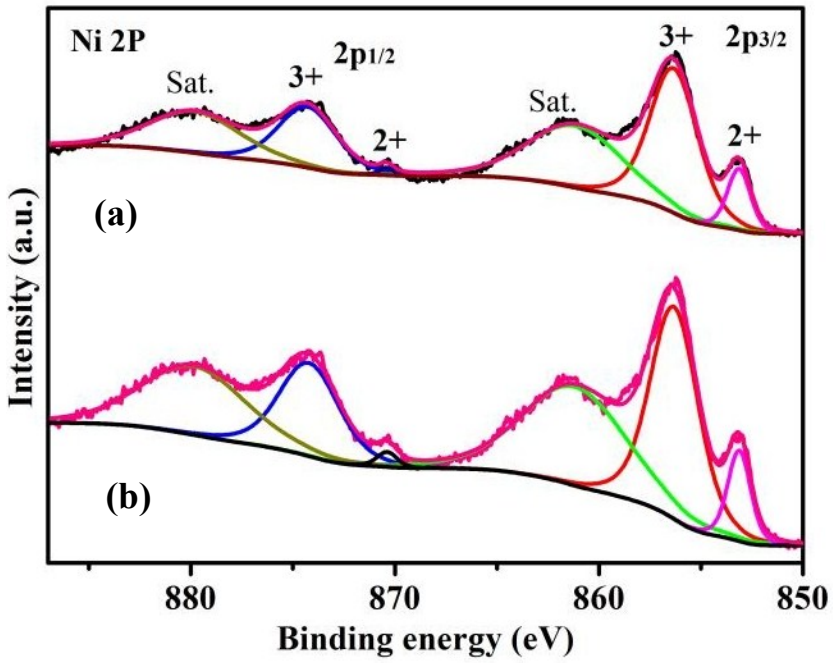


**Fig. S6** Ni 2P XPS spectrum of $NiS_2$ (a) and (b) after 1000 OER cycles.

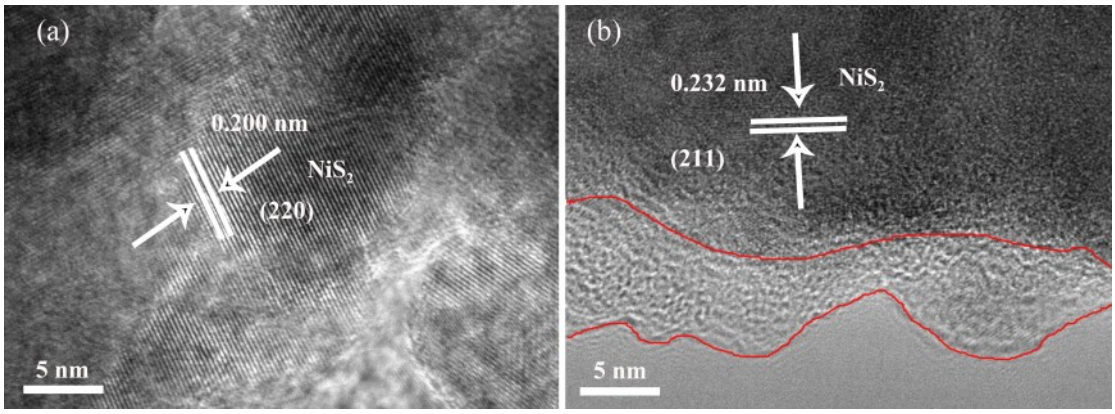


**Fig. S7** HRTEM images of $NiS_2$ (a) before and (b) after 1000 OER cycles. After 1000 cycles, the $NiS_2$ catalyst reveals the formation of amorphous NiO/NiOOH. In XPS spectra, the area of $Ni^{3+}$ gets larger than original $NiS_2$ (Fig. S5), which indicates the generation of higher valence state of $Ni^{3+}$ after OER test.

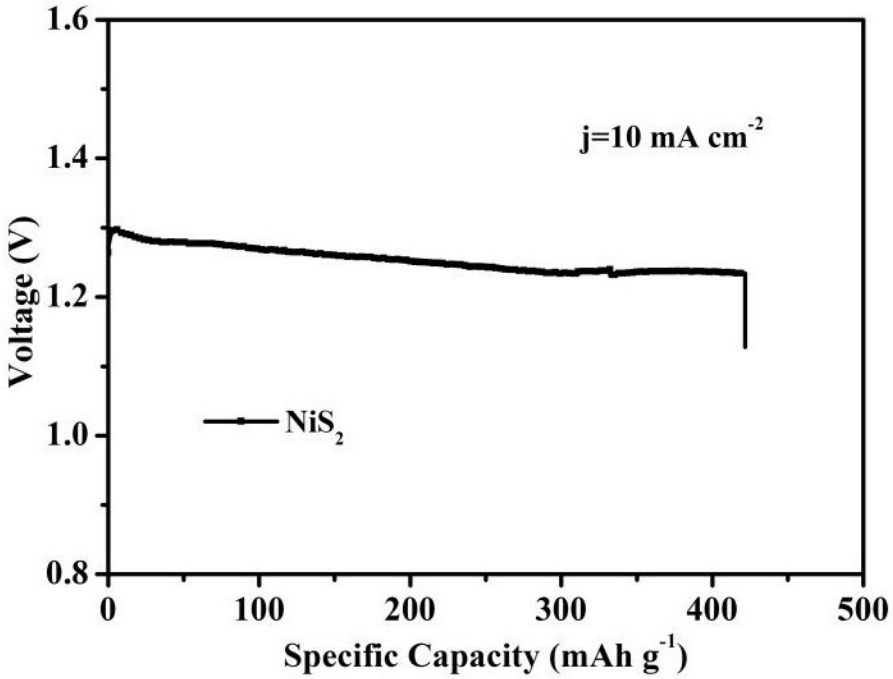


**Fig. S8** Discharge curve of the Zn-air battery of $NiS_2$ electrode at 10 mA $cm^{-2}$

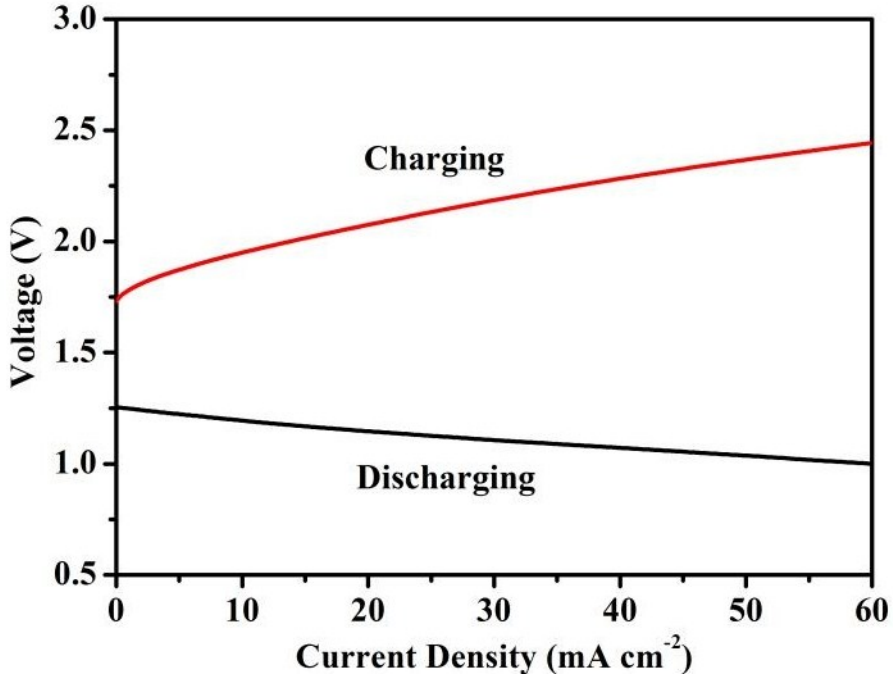


**Fig. S9** Charge/discharge polarization curves at 10 mA $cm^{-2}$ in Zn-air battery for $NiS_2$ electrode.

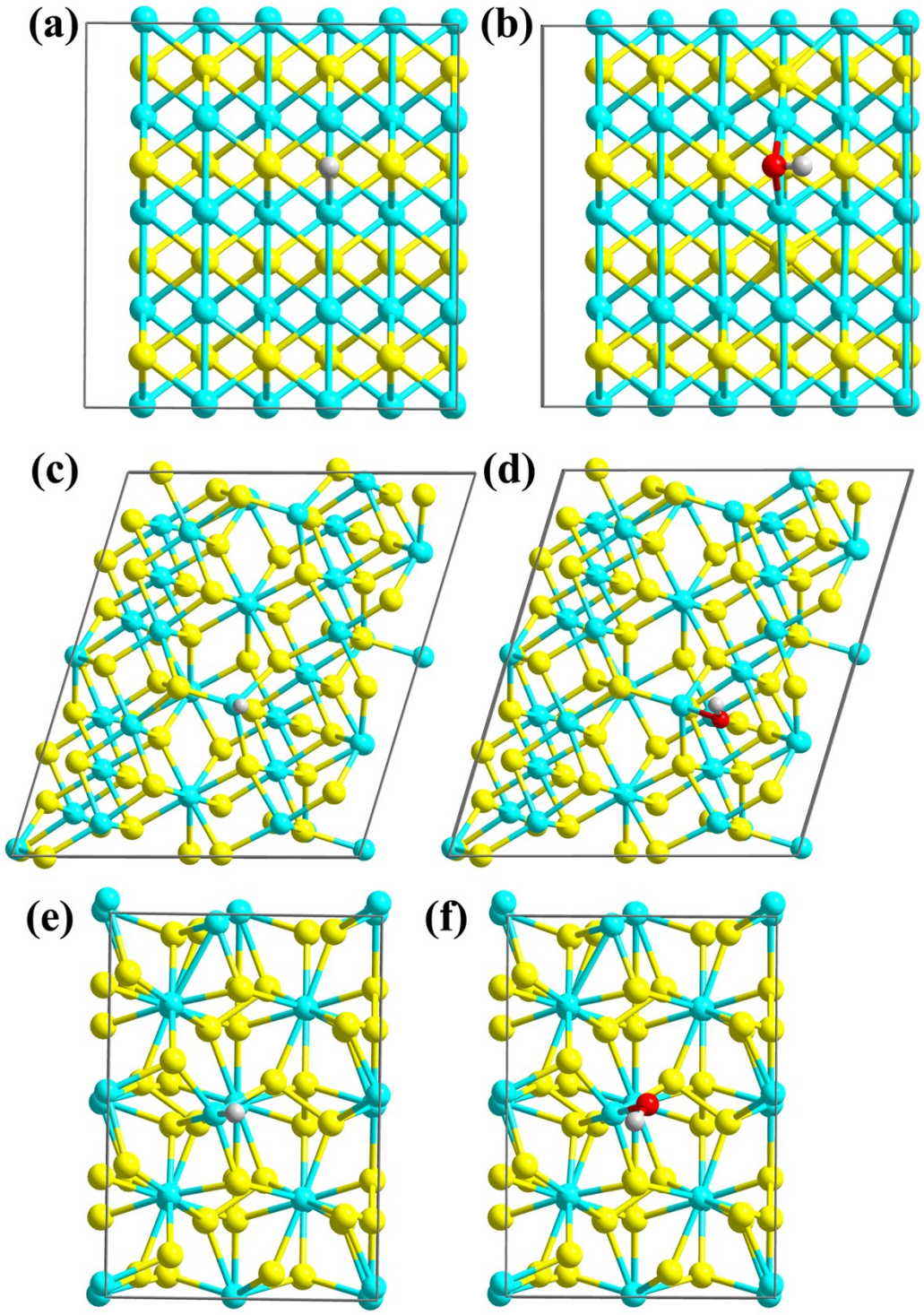


**Fig. S10** Top view of the adsorption models of H* and OH* intermediates on the surface of (a, b) NiS, (c, d) $Ni_3S_4$ and (e, f) $NiS_2$. Cyan=Ni, yellow=S, white=H, red=O.

**Table S1.** EDS and XPS results of Ni and S atomic percentage in NiS, $Ni_3S_4$, and $NiS_2$.

| Catalysts | EDS | | XPS | |
|---|---|---|---|---|
| | Ni (%) | S (%) | Ni (%) | S (%) |
| NiS | 48.75 | 51.25 | 50.12 | 49.88 |
| $Ni_3S_4$ | 41.17 | 58.83 | 43.62 | 56.38 |
| $NiS_2$ | 32.90 | 67.10 | 34.44 | 65.56 |

**Table S2.** Comparison of performance parameters of NiS, $Ni_3S_4$, and $NiS_2$ in this work.

| Catalysts | Reaction | Overpotential At 10mA $cm^{-2}$ (mv)/Half-wave potential (V) | Tafel slope (mV $dec^{-1}$) | $R_{ct}$ (Ω) | $C_{dl}$ (mF $cm^{-2}$) | BET areas ($m^2$ $g^{-1}$) |
|---|---|---|---|---|---|---|
| $NiS_2$ | OER<br>HER<br>ORR | 241<br>147<br>0.80 | 60<br>105<br>82 | 1.89<br>2.09 | 11.3 | 40.69 |
| $Ni_3S_4$ | OER<br>HER<br>ORR | 270<br>187<br>0.77 | 71<br>124<br>92 | 3.01<br>3.15 | 9.8 | 37.49 |
| NiS | OER<br>HER<br>ORR | 322<br>220<br>0.74 | 105<br>145<br>97 | 4.32<br>4.54 | 6.07 | 22.24 |
| Pt/C | HER | 29 | 68 | | | |
| $RuO_2$ | OER | 310 | 61 | | | |

**Table S3.** Comparison of OER performance parameters in this work with the results in references.

| Catalyst | Electrode | Electrolyte | Current density (mA cm-2) | Overpotential (mV) | Reference |
|---|---|---|---|---|---|
| $NiS_2$ nanosphere | Carbon paper | 1.0 M KOH | 10 | 241 | This work |
| Co-P film | Copper foil | 1.0 M KOH | 10 | 345 | 1 |
| N-doped $Ni_3S_2$ | Nickel foam | 1.0 M KOH | 100 | 330 | 2 |
| $Ni_{0.85}Se$ films | Glassy carbon | 1.0 M NaOH | 10 | 320 | 3 |
| $MoS_2$/NiS nanowire | Nickel foam | 1.0 M KOH | 15 | 271 | 4 |
| Nanocrystalline NiS particles | Carbon paper | 1.0 M KOH | 10 | 345 | 5 |
| $NiCo_2S_4$ nanowires | Ni foam | 1.0 M KOH | 15 | 320 | 6 |
| NiS sheres | Ni foam | 1.0 M KOH | 50 | 335 | 7 |

**Table S4** Comparison of HER performance parameters in this work with the results in references.

| Catalyst | Electrode | Electrolyte | Current density (mA cm-2) | Overpotential (mV) | Reference |
|---|---|---|---|---|---|
| $NiS_2$ nanosphere | Carbon paper | 1.0 M KOH | -10 | 147 | This work |
| $CoO_x$@CN | GCE | 1.0 M KOH | -10 | 232 | 8 |
| $NiSe_2$ | Nickel foam | 0.5M $H_2SO_4$ | -10 | 190 | 9 |
| $CoS_2$ HNSs | Carbon | 1.0 M KOH | -10 | 193 | 10 |

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| $MoS_2$/NiS nanowire | Nickel foam | 0.5 M $H_2SO_4$ | -10 | 89 | 4 |

**Table S5** Comparison of HER performance parameters in this work with the results in references.

| Compounds | $\triangle G_{H^*}$ (eV) | $\triangle G_{OH^*}$ (eV) | $d_{H\text{-}Ni}/d_{O\text{-}Ni}/d_{O\text{-}H}$(Å) |
|---|---|---|---|
| NiS | -1.9741 | -0.5460 | 1.852/1.996/0.978 |
| $Ni_3S_4$ | 0.1738 | 0.0850 | 1.458/1.857/0.983 |
| $NiS_2$ | -0.0058 | 1.0109 | 1.466/1.890/0.981 |

# References


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