Electronic Supplementary Information

Phase-pure Pentlandite Ni_{4.3}Co_{4.7}S₈ Binary Sulfide as Efficient Bifunctional Electrocatalyst for Oxygen Evolution and Hydrogen Evolution

Yongfu Tang^{1, 2, 3, *}, Hongbin Yang¹, Jiaojiao Sun¹, Meirong Xia^{1, *}, Wenfeng Guo^{1, 3}, Like Yu¹,

Jitong Yan¹, Jia Zheng¹, Limin Chang^{2, *}, Faming Gao¹

¹Hebei Key Laboratory of Applied Chemistry, College of Environmental and Chemical

Engineering, Yanshan University, Qinhuangdao, 066004, China.

²Key Laboratory of Preparation and Application of Environmental Friendly Materials (Jilin

Normal University), Ministry of Education, Changchun, 130103, China

³State Key Laboratory of Metastable Materials Science and Technology, Yanshan University,

Qinhuangdao, 066004, China

*Correspondence to: tangyongfu@ysu.edu.cn; xmr0125@126.com; changlimin2139@163.com

1. Description of the Movies

Supplemental Movie S1 Electrochemical water splitting via dynamic potential scanning model. As shown, when the voltage between the cathode and anode was higher 1.23 V, gas bubbles evolution was clearly observed, indicating the water splitting. The amount of gas was increasing with the increment of voltage.

Supplementary Movie S2 Electrochemical water splitting via galvanostatic electrolysis model. As shown, gas bubbles evolution was also observed in different current density.

2. Experimental section

2.1 Synthesis of the nickel cobalt sulfide samples

2.1.1 Synthesis of the pentlandite Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples

Synthesis of the Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples were performed as follow: 10 mL 0.1 mol L⁻¹ Co(NO₃)₂·6H₂O solution was diluted to 30 mL with deionized water. 1 mL ethanediamine was added dropwise with stirring for 30 minutes to obtain the mixed solution. Then, 10 mL 0.1 mol L⁻¹ thiourea solution was added dropwise to the mixed solution with stirring for 30 minutes. Four pieces of Ni foam and 0.115 g ultra-fine Ni powder were added as metallic Ni sources for the synthesis of the Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples, respectively. The obtained mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and was heated at 180 °C for 12 h. The final Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples were obtained after centrifugalization, washing and drying.

2.1.2 Synthesis of the hexagonal CoS, Ni_{0.1}Co_{0.9}S and other metal sulfide samples

The synthesis of the hexagonal CoS and Ni_{0.1}Co_{0.9}S samples was similar to the synthesis of the pentlandite Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples just without Ni sources (CoS) and using the Ni(NO₃)₂·6H₂O solution as ionic Ni source to investigate the effect of the metallic Ni sources on the formation of pentlandite nickel cobalt binary sulfides. For comparison, another two metal sulfide samples were synthesized to illustrate the roles of the ethylenediamine as chelating agent and the ionic cobalt source in the formation of pentlandite nickel cobalt binary sulfides as follow. (1) a similar process to the synthesis of pentlandite Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples

just without the cobalt source, and then the Ni₃S₂ phase combining metallic Ni phase were obtained, which was called as Ni₃S₂ sample. (2) a similar process to the synthesis of pentlandite Ni_{4.3}Co_{4.7}S₈ and Ni_{1.4}Co_{7.6}S₈ samples without the ethylenediamine as chelating agent, and then the mixed phases not being ascribed to any phase-pure metal sulfide were obtained, which was called as mixed phase Ni_xCo_yS sample.

2.2 Physiochemical Characterizations

The real Ni/Co ratios in the sheet-assembled hollow nickel cobalt sulfides spheres were measured using a AA-6800F/G atomic absorption spectrophotometer (AAS, Shimadzu Corp., Japan). The phase structure and of the samples were analyzed using X-ray diffraction (XRD) patterns (Bruker AXS D8 diffractometer with Cu K α radiation) with the detected diffraction angle (2 θ) ranging from 10° to 90° with a step size of 0.06°. The morphology of these samples was characterized by transmission electron microscopy (TEM, HT7700, 100 kV), high resolution TEM (JEOL 2010, JEOL Ltd. Corp., Japan, 200 kV) and scanning electron microscopy (SEM, KYKY-2800B, 15 kV) with an energy dispersive X-ray spectroscopy (EDS) detector. X-ray photoelectron spectra (XPS) was performed on a PHI QUANTERA II X-ray photoelectron spectrometer with Al K α radiation at 0.6 eV.

2.3 Preparation and electrochemical measurements of the electrodes

Cycle voltammetry (CV) and linear sweep voltammetry (LSV) were tested by a CHI 604E workstation to characterize the electrochemical performance of the nickel cobalt sulfide electrodes. All the working electrodes were prepared as follows. Nickel cobalt sulfide, acetylene black, and polytetrafluoroethylene (PTFE, 5 wt %) were mixed with mass ratio of 80:15:5 in ultrasonic bath to obtain a uniform slurry. The slurry was coated on a nickel foam (1 × 1 cm²) and dried in a vacuum oven at 70 °C for 12 h. After being pressured at 10 MPa for 10 s, the working electrodes were prepared. To decrease the test deviation during the electrochemical measurements, the mass loading of all the prepared electrodes was approximately 4.0 mg cm⁻². CV measurements of the working electrode with scan rate of 50 mV s⁻¹ were performed for 6 cycles in a three-electrode system to remove the adsorbed impurity in the electrode. The LSV measurements were conducted in the 1.0 M KOH electrolyte with scan rate of 5 mV s⁻¹ to evaluate the HER and OER performance of the electrodes. The Hg/HgO electrode and the Pt foil are used as reference electrode and counter electrode, respectively. The Tafel slope was calculated according to Tafel equation $\eta = a + blg(j)$, where η , a, b and j are the over-potential, Tafel constant, Tafel slope, kinetic current density.

To evaluate the practical application of the obtained nickel cobalt sulfide electrodes, the prototype electrolysis device for water splitting were assembled with these electrodes with the 1.0 M KOH electrolyte. The performance was evaluated via the dynamic potential scanning and galvanostatic electrolysis models. The potential scanning rate was 5 mV s⁻¹ and the different current densities were used in the galvanostatic electrolysis measurement.

2.4 Density functional theory calculation via VASP

All calculations were carried out using Vienna ab initio simulation package

(VASP).¹⁻⁴ This method uses a plane-wave basis and projector augmented wave (PAW) to describe the electron-ion interactions.⁵ Exchange and correlation energies are approximated using functionals proposed by generalized gradient approximations (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE).⁶ The Brillouin zone integrations are performed with Monkhorst-Pack grids⁷ and a generalized Gaussian smearing ($\sigma = 0.1 \text{ eV}$) for the integrations in reciprocal space.⁸ A plane-wave energy cutoff is 400 eV because this cutoff was satisfactory for this type of calculation in prior work from this group.⁹ Meshes of (3 x 3 x 3) k points are used for all of the calculations.

2.5 References for experimental section

- 1 G. Kresse and J. Furthmuller, Phys. Rev. B, 1996, 54, 11169.
- 2 G. Kresse and J. Hafner, Phys. Rev. B, 1993, 47, 558.
- 3 G. Kresse and J. Hafner, Phys. Rev. B, 1994, 49, 14251.
- 4 G. Kresse and J. Furthmuller, Comput. Mater. Sci., 1996, 6, 15.
- 5 P. E. Blöchl, Phys. Rev. B, 1996, 50, 17953
- 6 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865
- 7 H. J. Monkhorst and J. D. Pack, Phys. Rev. B, 1976, 13, 5188.
- 8 L. Li, X. Feng, Y. Nie, S. Chen, F. Shi, K. Xiong, W. Ding, X. Qi, J. Hu, Z. Wei, L.
- J. Wan and M. Xia, ACS Catal., 2015, 5, 4825-4832
- 9 R. A. Sidik and A. B. Anderson, J. Phys. Chem. B, 2006, 110, 936-941.

3. Supplementary Tables

Sample	Co Species	Relative intensity (%)	Ni Species	Relative intensity (%)	S Species	Relative intensity (%)
CoS	Co ²⁺	69.1			$Sp_{1/2}$	49.0
	Co ³⁺	30.9			Sp _{3/2}	51.0
Ni _{0.1} Co _{0.9} S	Co ²⁺	58.2			$Sp_{1/2}$	49.0
	Co ³⁺	41.8			Sp _{3/2}	51.0
Ni _{1.4} Co _{7.6} S ₈	Co ²⁺	78.2	$Sp_{1/2}$	32.5	$Sp_{1/2}$	56.1
	Co ³⁺	21.8	Sp _{3/2}	67.5	Sp _{3/2}	43.9
Ni _{4.3} Co _{4.7} S ₈	Co ²⁺	74.1	$Sp_{1/2}$	39.5	$Sp_{1/2}$	47.8
	Co ³⁺	25.9	$Sp_{3/2}$	60.5	Sp _{3/2}	52.2

Table S1. Relative intensities of surface species in the CoS, $Ni_{0.1}Co_{0.9}S$, $Ni_{1.4}Co_{7.6}S_8$ and $Ni_{4.3}Co_{4.7}S_8$ catalysts from XPS data.

Table S2. The BJH desorption surface area of the CoS, $Ni_{0.1}Co_{0.9}S$, $Ni_{1.4}Co_{7.6}S_8$ and $Ni_{4.3}Co_{4.7}S_8$ samples.

	BJH Surface Area (m ² /g)			
CoS	19.74			
Ni _{0.1} Co _{0.9} S	23.5			
$Ni_{1.4}Co_{7.6}S_8$	19.23			
Ni _{4.3} Co _{4.7} S ₈	26.43			

electrocatalysts						
	φ(OER)	η(OER)	OER Tafel slope	φ(HER)	η(HER)	HER Tafel
	/V $_{\rm vs.\ RHE}$	/mV	$/mV dec^{-1}$	/V $_{vs.\;RHE}$	/mV	slope/mV dec ⁻¹
Ni _{4.3} Co _{4.7} S ₈	1.36	133.8	194.2	-0.148	148.0	90.0
Ni _{1.4} Co _{7.6} S ₈	1.42	189.4	303.1	-0.176	196.6	156.9
Ni _{0.1} Co _{0.9} S	1.47	243.2	153.5	-0.174	174.2	157.7
CoS	1.43	200.1	139.9	-0.174	174.2	157.7
Ni_3S_2	1.57	338.3	148.3	-0.210	209.8	135.5
RuO ₂	1.49	262.8	145.8			
Pt/C				-0.356	35.6	49.0
Bare NF	1.66	434	105.5	-0.238	238.0	175.0

Table S3 The comparison of electrochemical parameters for the OER and HER of the as-prepared metal sulfide electrocatalysts in this work, the commercial Pt/C and RuO_2

 $\varphi(OER)$: The potential for the OER at the current density of 20 mA cm⁻²,

 $\eta(\text{OER})$: The over-potential for the OER at the current density of 20 mA cm^2,

 ϕ (HER): The potential for the HER at the current density of 10 mA cm⁻²,

 η (HER): The over-potential for the HER at the current density of 10 mA cm⁻²,

Crystal Cell	Groups	a /Å	b/Å	c/Å	α/degree	β/degree	γ/degree
Co ₉ S ₈	Fm-3m	9.799	9.799	9.799	90	90	90
Ni _{4.5} Co _{4.5} S ₈	Fm-3m	10.216	9.905	9.871	90.24	89.67	90.09

Table S4 Crystal lattice parameters of the geometry optimizated pentlandite Co_9S_8 and $Ni_{4.5}Co_{4.5}S_8$ cells

Supplementary Figures



Figure S1 XRD patterns of (a) the CoS and Ni_{0.1}Co_{0.9}S, (b) Mixed phase Ni_xCo_yS sample obtained via the similar hydrothermal process to the synthesis of Ni_{4.3}Co_{4.7}S₈ sample only without the chelating agent ethylenediamine, (c) Ni₃S₂ sample obtained with only metallic Ni source without Co sources. The detailed information for the synthesis of these samples were given in the experimental section.



Figure S2 SEM images of the as-prepared metal sulfide electrocatalysts. (**a-b**) $Ni_{1.4}Co_{7.6}S_8$ electrocatalyst, showing sphere morphology with wrinkle surface, the micron-level size (~ 5 µm) of which is markedly larger than that of the $Ni_{4.3}Co_{4.7}S_8$ electrocatalyst (~ 400 nm), (**c-d**) CoS and (**e-f**) $Ni_{0.1}Co_{0.9}S$ electrocatalyst, both of which showing the hollow sphere structure with external diameter of about 600 nm and shell thickness of about 200 and 150 nm, respectively.



Figure S3 Nitrogen adsorption-desorption isotherms and pore size distributions (insets) of (a) CoS, (b) $Ni_{0.1}Co_{0.9}S$, (c) $Ni_{1.4}Co_{7.6}S_8$ and (d) $Ni_{4.3}Co_{4.7}S_8$. The BHJ surface area of these two metal sulfide samples was given in **Table S2**. The highest surface area of $Ni_{4.3}Co_{4.7}S_8$ should be ascribed to its mesoporous structure (**Fig. S3d**) and the smaller sphere size and shrink surface (**Fig. 2a-2b**).



Fig. S4 CV curves of the $Ni_{4.3}Co_{4.7}S_8$, $Ni_{1.4}Co_{7.6}S_8$, $Ni_{0.1}Co_{0.9}S$, CoS and Ni_3S_2 electrodes. The $Ni_{4.3}Co_{4.7}S_8$ electrode exhibits the highest integral area, corresponding to the highest electrochemical surface area.



Fig. S5 Chronoamperometry curves of the Ni_{4.3}Co_{4.7}S₈ electrocatalyst for (a) HER with overpotential of 200 mV, (b) OER with overpotential of 100 mV and (c) water splitting with overpotential of 150 mV.



Figure S6 Top view of the (001), (100), (101), (102), (110), (103), (201) and (202) surfaces of CoS-type hexagonal metal sulfide, including all the surfaces except the other equal surface (eg. (010) equal to (100)) shown in the XRD patterns. Yellow and blue balls represent the sulfur and metal (Co or Ni) atoms, respectively. Only metal-sulfide bonds were observed in the hexagonal metal sulfide.



Figure S7 (a) top view for the (022) surface of the pentlandite $Ni_{4.5}Co_{4.5}S_8$ (blue balls represent for Ni or Co atoms and yellow balls for S atoms), (b) Active site of the [FeNi]-hydrogenase (PDB: 4U9H). As shown, Ni- and Co- centers bridged sulfurs structure (dash red circle) similar to the active site of the [FeNi]-hydrogenase (PDB: 4U9H) with near metal atoms distances (0.248 nm and 0.257 nm).



Figure S8 Band structure of the (a) Co_9S_8 and $Ni_{4.5}Co_{4.5}S_8$ crystal cells. The red line represents the energy of Fermi level. As shown, the $Ni_{4.5}Co_{4.5}S_8$ exhibits markedly higher band density near to the Fermi level than the Co_9S_8 , corresponding to higher density of state (DOS) of $Ni_{4.5}Co_{4.5}S_8$ than that of Co_9S_8 (**Fig. 5e**) as well as the higher d-band center (-1.52 eV) of $Ni_{4.5}Co_{4.5}S_8$ than that of Co_9S_8 (-2.84 eV).



Fig. S9 EIS spectra of the $Ni_{4.3}Co_{4.7}S_8$, $Ni_{1.4}Co_{7.6}S_8$, $Ni_{0.1}Co_{0.9}S$, CoS and Ni_3S_2 electrodes.