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Supporting Information

Engineering Co₉S₈/WS₂ array films as bifunctional electrocatalysts for efficient water splitting

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Experimental section:

All the chemicals were of analytical grade and used as purchased without further purification. Synthesis of cobalt precursors: The Titanium foil substrates were firstly ultrasonically rinsed for 30min in acetone, isopropyl alcohol and ethanol absolution, respectively. In a typical procedure for synthesizing Co-precursor nanobelt array/Ti, the washed Ti foil was placed vertically into a 50 mL Teflon-lined stainless steel autoclaves, which had been fed with 1.5g of Co(CH₃COO)₂, 0.36g of urea and 40 mL distilled water and stirred for 30 min. After that, the autoclave was sealed, maintained at 200 °C for 12 h, and cooled naturally to room temperature. Finally, a layer of pink film was deposited on the Ti substrate. The preparation of Co-precursors with nanoneedle and nanorhombus arrayson Ti foil is quite similar to that described above but with a few modifications, and the reaction conditions are listed in Table S3.

Synthesis of Co_9S_8 : The obtained Co-precursor film was transferred into 50 mL Teflon-lined stainless steel autoclave with 30 mL of 0.5 M Na₂S water solution and maintained at 140 °C for 5 h to convert the Co-precursors to Co_9S_8 films. The Co_9S_8 film was thoroughly washed with water and ethanol, and dried at 60 °C for 12 h under vacuum. The sulfurization process of Co_9S_8 nanoneedle and nanorhombus arrays is similar to the Co_9S_8 nanobelt film.

Synthesis of Co₉S₈/WS₂: In briefly, 10 mg (NH₄)₂WS₄ wasfirst dispersed in 30 ml DMF with addition of N₂H₄ \star H₂O (0.5 mL), and stirred for 15 min.Then the mixed solution was transferred into a 50 ml Teflon-lined autoclave with a piece of Co₉S₈/Ti, which was sealed and heated in an oven at 200 °C for 10 h and then cooled to room temperature naturally. The resulting Co₉S₈/WS₂/Ti was washed by water and ethanol several times, and dried at 60 °C for 12 h under vacuum.Finally, the films were treated at 300 °C in an atmosphere of H₂ (5%) mixed with N₂ (95%) for2 h, and the hybrid Co₉S₈/WS₂/Ti was obtained. The loading amount of the Co₉S₈/WS₂ nanobelt, nanoneedle and nanorhombus arrayson Ti foil is about 2.2, 6.2, and 4.5 mg cm⁻², respectively. The ICP analysis shows that the molar content of WS₂ in the Co₉S₈/WS₂ nanobelt, nanoneedle and nanorhombus composites is about 17%, 15 and 18%, respectively.

Material Characterization:

Crystal structures of products was examined by X-ray diffraction (Shimadzu XRD-6000, Cu KR radiation, $\lambda = 1.5418$ Å). The morphology of products were characterized using field-

emission scanning electron microscope (FESEM; JEOL JSM-7600F), transmission electron microscope (TEM; JEOL JEM-2100F). The composition of the products was analyzed using energy-dispersive X-ray spectroscope (EDS) attached to the TEM instrument. Elemental ratios of Co, W and S were performed by inductively coupled plasma atomic emission spectroscopy

(ICP-AES, Thermo Elemental IRIS 1000). X-ray photoelectron spectroscopy (XPS) was conducted by KratosAxis Ultra DLD electron spectrometer at an accelerating voltage of 13 kV and a pass energy of 35.75 eV (PHI, PHI5300 system).

Electrochemical Measurements:

All electrochemical studies were performed using an Autolab electrochemical work station (Autolab Instrument) in a standard three-electrode setup with the Co_9S_8/WS_2 film as working electrode, a Ag/AgCl (1M KCl) electrode as the reference, and carbon rod as a counter electrode in 1.0 M KOH solutions. The solutions were purged with nitrogen for 10 min prior to the experiments in order to remove oxygen. All the electrocatalytic activity of $Co_9S_8@WS_2$ films with an active area of 0.5 cm² towards the HER or OER was examined by polarization curves using linear sweep voltammetry at a scan rate of 2 mV s⁻¹ in 1.0 M KOH at room temperature from -0.8 to -1.6 V vs. Ag/AgCl and from 0.2 to 1.0 V vs. Ag/AgCl, respectively. Furthermore, bare Co_9S_8 and Pt electrodes were used as working electrodes for comparison. The 3D Co_9S_8/WS_2 film catalysts as anode and cathode. Polarization curves were obtained using LSV with a scan rate of 5 mV s⁻¹. The long-term durability test was performed using constant current electrolysis (a current density of 10 mA cm⁻²). All the potentials were referred to the reversible hydrogen electrode (RHE) without specification.

DFT calculations:

DFT calculations were performed using the Vienna Ab initio Simulation package (VASP),^[1,2] to study the structures and energies of H adsorption on Co_9S_8 (111) surface, zigzag WS₂ with 50% S termination as well as Co_9S_8/WS_2 hybrid structure. The electron-ion interaction was modelled using the projector augmented wave (PAW) method.^[3,4] The spin-polarized GGA (generalized-gradient approximation) scheme with the Perdew–Burke–Ernzerh of (PBE) form was used for the exchange and correlation functional.^[5] The plane-wave cutoff energy was set to 400 eV.

 Co_9S_8 (111) surface was simulated based on a slab supercell approach. The Co-terminated surface is made up of five Co layers and two O layers, where the bottom one Co and one O layer are frozen, and other layers are allowed to be relaxed.

To simulate Co₉S₈@WS₂ hybrid structure, a (2x1) Co₉S₈ (111) supercell was built to avoid interactions between WS₂ and its images in x direction. The zigzag WS₂ was cut from 2D WS₂ layer and some edge S atoms were removed to create 50% S termination. The WS₂ was bonded with Co₉S₈ (111) surface through S-Co bonds in range of 2.17Å-2.35Å. Periodic boundary conditions were employed along y directions for WS₂ and along x and y directions for Co₉S₈ (111) surface. A vacuum region of 10 Å was used, which is large enough to avoid the interactions between the adsorbate and its image in z direction. As shown in Figure 1, possible H adsorption sites were considered on the three substrates, respectively. The adsorption energy is defined as $E_{ads} = E_{A+substrate}-E_{substrate} - E_A$, where the $E_{A+substrate}$ is the total energy of the adsorbed system, $E_{substrate}$ could be the energy of the Co₉S₈ (111) surface or the WS₂ or the Co₉S₈@WS₂ hybrid structure, and E_A is the energy of isolated H atom or OH group. By definition, a negative value corresponds to exothermic adsorption.



Figure S1. XRD patterns of Co_9S_8 with a) nanobelt, b) nanoneedle and c) nanorhombus arrays.



Figure S2. XRD patterns of Co_9S_8/WS_2 with a) nanobelt, b) nanoneedle and c) nanorhombus arrays. The XRD peak at ~ 35° in nanoneedle and nanorhombus arrays is attributed to the (101) plane of $Co_{1-x}S$ (JCPDS No: 42-826). The formation of $Co_{1-x}S$ may be attributed to the different reactants, structures and morphologies of Co-precursors and further hybridization with WS₂. Although there is a little $Co_{1-x}S$ in the samples, it can not influence the investigation of the electrocatalytic activity for the Co_9S_8/WS_2 . Furthermore, we performed the ICP measurement and the ratio of Co to S in all the three samples is about 9 : 8.



Figure S3. EDS images of Co_9S_8/WS_2 with a) nanobelt, b) nanoneedle, and c) nanorhombus arrays.



FigureS4. XPS spectrum of Co_9S_8/WS_2 nanobelt array: (a) survey XPSspectrum and (b–d) high-resolution Co 2p, W 4f, and S2p spectrum. As a comparison, Co 2p of bare Co_9S_8 nanobelt is shown in Figure S4b. It is found that the binding energy of Co 2p3/2 in Co_9S_8/WS_2 composite shift positive. This result indicates the existence of strong electronic interactions between Co_9S_8 and WS_2 , which implies the establishment of coupling interfaces.

Table S1 The ICP analysis of content of Co, W, S for bare Co_9S_8 and Co_9S_8/WS_2 nanoneedle, nanorhombus, and nanobelt arrays.

Sample	Atomic% (Co)	Atomic% (W)	Atomic% (S)
Co ₉ S ₈ nanoneedle array	52.3	0	47.7
Co_9S_8 nanorhombus array	52.1	0	47.9
Co ₉ S ₈ nanobelt array	52.5	0	47.5
Co ₉ S ₈ /WS ₂ nanoneedle array	44.2	6.7	49.1
Co ₉ S ₈ /WS ₂ nanorhombus array	42.0	7.7	50.3
Co ₉ S ₈ /WS ₂ nanobelt array	43.5	7.5	49.0



Figure S5. SEM images of Co_9S_8 with a-c) nanoneedle, d-f) nanorhombus, and g-i) nanobelt arrays. The insets of Figure S5a, d and g are their cross-sectional SEM images. The insets of Figure S5c, f and i are their HRTEM images.



Figure S6 N2 gas adsorption-desorptionisotherms and pore-size distribution insets of a) bare Co_9S_8 and b) Co_9S_8/WS_2 nanobelt, nanoneedle and nanorhombus arrays, resepctively. N_2 adsorption-desorption isotherms and pore size distributions (inset) of bare Co₉S₈ and the composites are shown in Figure S6 to confirm the porous structure of these samples. And the detailed parameters of all the samples are shown in Table S2. N₂ sorption isotherms of the Co₉S₈/WS₂ can be identified as type-IV isotherms.In addition, the pore size analysis also illustrates that the Co₉S₈/WS₂ composite is consist of both micro- and mesopores with two pore sizes of 1.8 and 3.6 nm.The measured Brunauer-Emmett-Teller surface area of Co_9S_8/WS_2 nanobelt array is 78.9 m² g⁻¹, which is the highest among the Co_9S_8/WS_2 composites. This trend is the same as observed for the ECSA, as shown in Figure 3d. Compared to the bare Co₉S₈ nanobelt, the increased specific area of Co₉S₈/WS₂ nanobelt array is attributed to the considerable nanocrystal boundaries and some new quasi pores or micropores after coupling with WS2, which may favor to increase the amount of exposed active catalytic sites. The high exposed active catalytic sites are also verified by the ECSA measurement. The high physical high surface area and large electrochemical surface area arejointly beneficial for effective mass transport and expose more accessible active sites for electrochemical reactions, thus, the Co₉S₈/WS₂ nanobelt array shows the best HER and OER activity.

Table S2 BET specific surface area, and total pore volume of bare Co_9S_8 and Co_9S_8/WS_2 composites with different structures.

Samples	Co_9S_8 nanonee dle array	Co_9S_8 nanorhom bus array	Co ₉ S ₈ nano belt	Co ₉ S ₈ /WS ₂ nanone edle array	Co ₉ S ₈ /WS ₂ nanorho mbus array	Co ₉ S ₈ /WS ₂ nano belt array
			array			
BET specific surfacear ea (m ² g ⁻	17.2	12.1	24.9	26.9	38.6	78.9
Pore volume (cm ³ g ⁻¹)	0.045	0.030	0.053	0.071	0.087	0.198



Figure S7 SEM images of Co-precursors a-c) nanoneedle, d-f) nanorhombus, and g-i) nanobeltarrays.

Table	S3.	Reaction	parameters	and	morphologies	of	products	under	different	reaction
conditi	ions.									

Samples	$Co(Ac)_2$	$CO(NH_2)_2$	NH ₄ F	Reaction temperature and time	Morphologies
Ι	1.5 g	0.36 g	0	200 °C, 12 h	nanobelts
II	1.5 g	0.36 g	0.37g	120 °C, 12 h	nanoneedles
III	0.5 g	0.12 g	0.37g	120 °C, 12 h	nanorhombuses
IV	0.5 g	0.12 g	0	120 °C, 12 h	a small amount of nanobelts
V	1.5 g	0.36 g	0	120 °C, 12 h	random nanoneedles
VI	0.5 g	0.12 g	0	200 °C, 12 h	a small amount of sample
VII	0.5 g	0.12 g	0.37g	200 °C, 12 h	nanorhombuses
VIII	1.5 g	0.36 g	0.37g	200 °C, 12 h	narrow nanorhombuses



Figure S8. SEM images of Sample IV (a), V (b), VI (c), VII (d), and VIII (e).



Figure S9. XRD patterns of Co-precursors with nanoneedle, nanobelt and nanorhombus arrays.



Figure S10.Polarization curves of Co_9S_8/WS_2 nanobelt, nanoneedle and nanorhombus arrays under 1 M KOH.



Figure S11. HER a) and OER b) activities of Co_9S_8/WS_2 nanobelt, nanoneedle and nanorhombus arrays based on the potential with the same current per mass at 4.55 mA mg⁻¹, respectively. The 4.55 mA mg⁻¹ as a reference is obtained from the loading amount of 2.2 mg cm⁻² for Co_9S_8/WS_2 nanobelt at 10 mA cm⁻².



Figure S12.Polarization curve of WS₂under 1 M KOH.



Figure S13.a) Polarization curves of Pt/C and IrO₂ electrodes under 1 M KOH.



Figure S14. SEM image of Co_9S_8/WS_2 nanobelt electrode in water splitting test after 60 min.



Figure S15. Polarization curves of Co_9S_8/WS_2 nanobelt, nanoneedle and nanorhombus under 1 M KOH.



Figure S16. CV curves of Co_9S_8/WS_2 nanobelt, nanoneedle and nanorhombus arrays under 1.0 M KOH.



Figure S17. a) CV curves of Co_9S_8 nanobelts under 1.0 M KOH and b) corresponding scan rate dependence of the current densities.



Figure S18. Electrochemical impedance spectroscopy (EIS) Nyquist plots of the samples under 1.0 M KOH solution.



Figure S19. Polarization curves of Co_9S_8/WS_2 nanoneedle and nanorhombus, and Pt-IrO₂ for overall water splitting in a two-electrode configuration.

Sample	Loading	Tafel slope (mV dec ⁻¹)	Current density $(mA \ cm^{-2})$	Potential (mV)	Reference
NiSe/Nickel foam	2.8 mg cm ⁻²	120	10 (50)	96 (182)	Angew. Chem. Int. Ed. 2015, 54, 9351-9355
a-CoSe/Ti	3.8 mg cm ⁻²	84	10 (50)	121 (~180)	Chem. Commun., 2015, 51, 16683- 16686
Ni ₃ Se ₂ /Cu foam	3.0 mg cm ⁻²	80	10	100	Catal. Sci. Technol., 2015, 5, 4954- 4958
Co _{0.85} Se/NiFe- LDH/graphene foil	4.0 mg cm ⁻²	160	10	280	Energy Environ. Sci., 2016, 9 , 478- 483
Ni ₃ S ₂ /Nickel foam	1.6 mg cm ⁻²	N. A.	10	223	J. Am. Chem. Soc. 2015, 137, 14023-14026
Ni/NiS/Nickel foam	11 mg cm ⁻²	123.3	10 (50)	230	Adv. Func. Mater. 2016, 26, 3314- 3323
Cubic CoSe ₂ /carbon cloth	-	85	10 (50)	190 (400)	Adv. Mater. 2016, 28, 7527-7532
Ni ₂ Se ₃ /Nickel foam	8.87 mg cm ⁻²	79	10	203	Nano Energy 2016, 24, 103-110
Co/Co ₉ S ₈ @S,N- doped graphene	0.305 mg cm ⁻²	96	10	290	Nano Energy 2016, 30, 93-102
Ni-MoS ₂ /carbon cloth	0.89 mg cm ⁻²	60	10 (50)	98 (150)	Energy Environ. Sci., 2016, 9, 2789-2793
CoS _x	0.05 mg cm ⁻²	N. A.	5	~100	Nat. Mater. 2016, 15,197-203
Co-S/carbon Tubes/carbon paper	$\sim 0.32 \text{ mg cm}^{-2}$	131	10	190	ACS Nano, 2016, 10, 2342-2348
$NiS_x/nickel foam$	142.2 mg cm ⁻²	99	10 (50)	60 (140)	Adv. Energy Mater. 2016, 6, 1502333
CoS@C	0.28 mg cm ⁻²	N. A.	10	250	ACS Appl. Mater. Interfaces 2015, 7, 980-988
MoS ₂ /Ni ₃ S ₂ /nickel foam	9.7 mg cm ⁻²	81	10 (50)	110 (150)	Angew. Chem. Int. Ed. 2016, 55, 6702 –6707
NiMo ₃ S ₄ /glassy carbon	0.3 mg cm ⁻²	98	10	257	Angew. Chem. Int. Ed. 2016, 5, 15240–15245
Co ₉ S ₈ /WS ₂ /Ti	2.2 mg cm ⁻²	80.2	10 (50)	138 (168)	This work

Table S4. Comparison of HER activity measured for Co_9S_8/WS_2 nanobelt array with other reported HER chalcogenide-based catalysts in 1.0 M KOH aqueous solution.

Table S5. Comparison of overall water splitting performance in 1.0 M KOH for Co_9S_8/WS_2 nanobelt array with other chalcogenide-based electrocatalysts.

Sample	Loading amount	Current density (mA cm ⁻²)	Potential (V)	Reference
NiSe/Nickel foam	2.8 mg cm ⁻²	10	1.63	Angew. Chem. Int. Ed. 2015, 54, 9351 -9355
a-CoSe/Ti	3.8 mg cm ⁻²	10	1.65	Chem. Commun., 2015, 51, 16683-16686
Ni ₃ Se ₂ /Cu foam	3.0 mg cm ⁻²	10	1.65	Catal. Sci. Technol., 2015, 5, 4954-4958
Co _{0.85} Se/NiFe- LDH/graphene foil	4.0 mg cm ⁻²	10	1.67	Energy Environ. Sci., 2016, 9, 478-483
Ni ₃ S ₂ /Nickel foam	1.6 mg cm ⁻²	13	1.76	J. Am. Chem. Soc. 2015, 137, 14023-14026
Ni/NiS/Nickel foam	11 mg cm ⁻²	1.7	1.61	Adv. Func. Mater. 2016, 26, 3314-3323
(Ni,Co) _{0.85} Se/NiCo	6 mg cm ⁻²	10	1.446	Adv. Mater. 2016, 28, 77-85
LDH/carbon cloth				
Cubic CoSe ₂ /Carbon cloth	N.A.	10	1.63	Adv. Mater. 2016, 28, 7527-7532
Ni ₃ Se ₂ /Nickel foam	8.87 mg cm ⁻²	10	1.612	Nano Energy 2016, 24,103-110
Co/Co ₉ S ₈ @S,N- doped graphene	1.0 mg cm ⁻²	20	1.58	Nano Energy 2016, 30, 93–102
Co-S/carbon	~0.32 mg cm ⁻²	10	1.743	ACS Nano, 2016, 10, 2342-2348
Tubes/carbon paper				
NiS _x /nickel foam	142.2 mg cm ⁻²	10	1.43	Adv. Energy Mater. 2016, 6, 1502333
MoS ₂ /Ni ₃ S ₂ /nickel	9.7 mg cm ⁻²	10	1.56	Angew. Chem. Int. Ed. 2016, 55, 1-7
foam				
Co ₉ S ₈ /WS ₂ /Ti	2.2 mg cm ⁻²	10	1.65	This work

It should be noted that all the electrolyte is 1.0 M KOH aqueous solution, except the systems in References (Nat. Mater. 2016, 15,197-203; Nano Energy 2016, 30, 93–102) uses 0.1 M

KOH aqueous solution.



Figure S20. (a) Co_9S_8 (111) surface (top view); (b) Co_9S_8 (111) surface (side view); (c) WS_2 with 50% S termination (top view); and (d) WS_2/Co_9S_8 hybrid structure (side view). All considered adsorption sites are marked accordingly.



Figure S21. Optimized configurations of H adsorbed at (a) $Co_9S_8_S$; (b) $Co_9S_8_Co_{top}$; (c) $WS_2_S_8_{edge}$; (d) $WS_2/Co_9S_8_S1_8_{edge}$; (e) $WS_2/Co_9S_8_S2_8_{edge}$.



Figure S22. Optimized configurations of OH adsorbed at (a) Co₉S₈_Co_{top}; (b) WS₂_S_S_{edge}; (c) WS₂/Co₉S₈_S2_S_{edge}.

Table S6. H adsorption energies on Co₉S₈ (111), WS₂ and Co₉S₈/WS₂ hybrid structure.

Adsorption site	E _{ads} (eV)	$d_{H-S}/d_{H-Co}(\text{\AA})$
Co ₉ S ₈ S	-1.47	1.390
$Co_9S_8_Co_{top}$	-2.26	1.494
$Co_9S_8Co_{bri}$	-2.48	1.703/1.704
WS ₂ _S_top	-1.76	1.368
$WS_2S_W_{edge}$	-2.57	1.360
$WS_2/Co_9S_8_S1_S_{edge}$	-1.62	1.368
WS_2/Co_9S_8 $S2_S_{edge}$	-1.99	1.368
$WS_2/Co_9S_8 S_W_{edge}$	-2.21	1.399

Adsorption site	E _{ads} (eV)	$d_{O-S}/d_{O-Co}/d_{O-W}(\text{\AA})$
Co_9S_8 Co_{top}	-3.06	1.816
Co ₉ S ₈ _Co _{bri}	-3.33	1.996/1.994
$WS_2 S_{edge}$	-1.96	1.709
$WS_2W_S_{edge}$	-4.43	2.137/2.139
WS_2/Co_9S_8 $S2_S_{edge}$	-1.98	1.744
$WS_2/Co_9S_8 W_S_{edge}$	-4.29	2.125/2.125

Table S7. OH adsorption energies on Co_9S_8 (111), WS_2 nanoribbon and Co_9S_8/WS_2 hybrid structure.

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