## **Electronic Supplementary Information**

## PEGylated deep eutectic solvent for controllable solvothermal synthesis of porous NiCo<sub>2</sub>S<sub>4</sub> for efficient oxygen evolution reaction

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Table S1 Related solvent, different ratio of Ni source and Co source of the as-prepared samples.

Table S2 Brunauer-Emmett-Teller (BET) surface areas and mean pore diameters obtained by  $N_2$  absorption-desorption curves;  $R_s$ ,  $R_{ct}$  and  $C_{dl}$  values obtained from electrochemical impedance spectroscopy (EIS) analysis of the synthesized samples.

## Synthetic procedures

**Synthesis of the NiCo<sub>2</sub>O<sub>4</sub>.** The NiCo<sub>2</sub>O<sub>4</sub> was obtained by the similar procedure described as NiCo<sub>2</sub>S<sub>4</sub> except using PEG 200 instead of PEGylated DES as solvent media.

**Synthesis of the NiS**<sub>2</sub>. The NiS<sub>2</sub> was obtained by the similar procedure described as NiCo<sub>2</sub>S<sub>4</sub> except only adding 10 mmol Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  without Co(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ .

**Synthesis of the CoS**<sub>2</sub>. The CoS<sub>2</sub> was obtained by the similar procedure described as NiCo<sub>2</sub>S<sub>4</sub> except only adding 10 mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O without Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

**Synthesis of the CoS<sub>2</sub> + Ni<sub>2</sub>CoS<sub>4</sub>**. The CoS<sub>2</sub> + Ni<sub>2</sub>CoS<sub>4</sub> were obtained by the similar procedure described as NiCo<sub>2</sub>S<sub>4</sub> except using 10 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10 mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

**Synthesis of the Ni<sub>2</sub>CoS<sub>4</sub>.** The Ni<sub>2</sub>CoS<sub>4</sub> was obtained by the similar procedure described as NiCo<sub>2</sub>S<sub>4</sub> except using 20 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10 mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.



**Fig. S1** IR spectra (a), <sup>1</sup>H NMR spectra (b), and differential scanning calorimetry spectra (c) of thiourea (black), PEG 200 (red), and the obtained deep eutectic solvent (green).



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**Fig. S3** Scanning electron microscopy (SEM) images of the  $NiCo_2O_4$  at low magnification a) and high magnification b); c) High-resolution transmission electron microscopy (HRTRM) image of hierarchically structured  $NiCo_2O_4$  with numerous pores; and d) HRTRM image and the corresponding lattice fringes of  $NiCo_2O_4$ .



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**Fig. S10** Nitrogen adsorption and desorption isotherms and inserted corresponding pore size distribution of the  $CoS_2$  nanoparticles. And the result showed that  $CoS_2$  had multi pore size distribution.



**Fig. S11** Nitrogen adsorption and desorption isotherms and inserted corresponding pore size distribution of the mixture of  $CoS_2$  and  $Ni_2CoS_4$ . And the result showed that the mixture  $CoS_2$  and  $Ni_2CoS_4$  had nearly single pore size distribution.



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**Fig. S13** Polarization curve of the bare glassy carbon electrode in 1 M KOH at 5 mV·s<sup>-1</sup> by utilizing Ag/AgCl (3 M KCl) electrode and Pt wire as reference and counter electrode, respectively.



**Fig. S14** Equivalent circuit used to model the AC-impedance of the working electrode/electrolyte.  $R_s$  stands for the uncompensated series resistance;  $R_{ct}$  stands for low-frequency response can be assigned to charge-transfer process of oxygen evolution at the catalyst interface;  $C_{dl}$  represents the accompanying capacitance of  $R_{ct}$ ; and CPE epresents a constant-phase element.



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**Fig. S17** Experimental (red dots, from GC analysis) and theoretical (black line, from transferred charge) amounts of  $O_2$  evolved during controlled potential electrolysis at 1.6 V (vs. RHE) with the NiCo<sub>2</sub>S<sub>4</sub> modified GC electrode.



**Fig. S18** Chronopotentiometry test (a) of OER by NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> modified GC in 1 M KOH at a current density of 10 mA·cm<sup>-2</sup>; Chronoamperometry test (b) of NiCo<sub>2</sub>O<sub>4</sub>, NiS<sub>2</sub>, CoS<sub>2</sub>, Ni<sub>2</sub>CoS<sub>4</sub> + CoS<sub>2</sub>, and Ni<sub>2</sub>CoS<sub>4</sub> modified GC in 1 M KOH at 1.6 V (*vs.* RHE) without iR compensation.

**Table S1** Related solvent, different ratio of Ni source and Co source of the as-preparedsamples.

Sample	Solvents	Ni source	Co source	Ratio
NiCo <sub>2</sub> S <sub>4</sub>	DES	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	Co(NO <sub>3</sub> )₂·6H₂0	1:2
NiCo <sub>2</sub> O <sub>4</sub>	PEG 200	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	$Co(NO_3)_2 \cdot 6H_20$	1:2
NiS <sub>2</sub>	DES	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	a_	a_
CoS <sub>2</sub>	DES	a_	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	a_
$Ni_2CoS_4 + CoS_2$	DES	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	1:1
Ni <sub>2</sub> CoS <sub>4</sub>	DES	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> 0	$Co(NO_3)_2 \cdot 6H_20$	2:1

<sup>a</sup>Indicates no data.

**Table S2** Brunauer-Emmett-Teller (BET) surface areas and mean pore diameters obtained by  $N_2$  absorption-desorption curves;  $R_s$ ,  $R_{ct}$  and  $C_{dl}$  values obtained from electrochemical impedance spectroscopy (EIS) analysis of the synthesized samples.

Sample	BET area	mean pore diameter	R <sub>s</sub>	R <sub>ct</sub>	C <sub>dl</sub> (μF⋅cm⁻²)
	(m²⋅g⁻¹)	(nm)	(′Ω·cm⁻²)	(′Ω·cm⁻²)	
NiCo <sub>2</sub> S <sub>4</sub>	33.10	8.931	0.04739	7.046	9.950
NiCo <sub>2</sub> O <sub>4</sub>	112.6	15.77	0.04842	10.37	8.699
NiS <sub>2</sub>	11.33	17.35	0.04834	17.70	9.637
CoS <sub>2</sub>	6.511	12.15	0.05007	32.68	9.090
$Ni_2CoS_4 + CoS_2$	6.346	5.995	0.04791	65.98	9.264
Ni <sub>2</sub> CoS <sub>4</sub>	8.265	5.632	0.04956	63.06	9.008