Supporting Information

Structural, Electronic and Electrocatalytic Evaluation of Spinel Transition Metal Sulfide Supported Reduced Graphene Oxide

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Synthesis of Co layered double hydroxide (LDH)@rGO

20 mg of graphene oxide (GO), 3 mmol cobalt nitrate, and 4 mmol urea, were added to 20 mL of deionized (DI) water, and the mixture was sonicated for 15 min. After that, 2 mmol of ammonium fluoride was added slowly with constant stirring. Then, sufficient amount of DI water was added in the 60 mL of autoclave, and the mixture was transferred into hydrothermal reaction vessel and kept at 150 °C for 5 h. The system was permitted to cool to ambient temperature, and the product was collected, washed with DI water and ethanol for several times, and dried at 60 °C overnight.^{1, 2}

Synthesis of CS@rGO catalysts

To obtain a homogeneous solution, 5 mL of N_2H_4 was added dropwise to 6 mmol of $Na_2S.9H_2O$ with constant stirring. In a hydrothermal vessel, 20 mg of Co LDH@rGO was dispersed in 20 mL of DI water and a homogeneous mixture of N_2H_4 and $Na_2S.9H_2O$ was added drop by drop. Furthermore, sufficient amount of DI water was added into 60 mL of autoclave and hydrothermally treated for 4 h at 180 °C. The obtained product was collected and washed several times with DI water and ethanol. The final product was dried at 60 °C overnight.^{3, 4}

Computational method

To examine the crystal structure of the $ZnCo_2S_4$ we used Vienna ab initio simulation package (VASP), as density functional theory (DFT) method.⁵ Generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof exchange-correlation functional was applied through this theoretical study.⁶ Additionally, to avoid the interactions between adjacent layers, the vacuum slabs were taken over 16 Å.⁷ The energy cutoff of 600 eV was applied for the plane wave basis. The projector augmented wave (PAW) method was utilized to describe the electron-ion interactions.⁸ The dispersion forces were corrected through Grimme's DFT-D3

functional by a semi-empirical GGA-type theory.⁹ The relaxation of the structures was lower than 0.05 eV according to the Hellman-Feynman forces. The Γ -point-centered k-point meshes applied for the Brillouin zone integrations were 6×6×6 in density of states (DOS) calculation. Formation energy (E_F) is defined as in equation below:

$$E_F = E^* - \sum_i n_i E_i,$$

where E^* , n_i , E_i denote the energy of each crystal structure, the number of the elements in the crystal, the energy of each constituting element, respectively. Calculation of the free energy for H* adsorption (ΔG_H) was based on the formula, which is proposed by Norskov et al.¹⁰

$$\Delta G_{\rm H} = E_{\rm H^*/surf} - E_{\rm surf} - (E_{\rm H2})/2 + \Delta E_{\rm ZPE} - T\Delta S$$

where $E_{H^*/surf}$, E_{surf} , E_{H2} , ΔE_{ZPE} , and ΔS are total energies of the slab with H*, the clean surface, the isolated hydrogen molecule, the zero-point energy change, and the entropy change, respectively.

Measurements of capacitance and ECSA

Cyclic voltammetry was carried out to probe the electrochemical double layer capacitance (C_{dl}) of various samples at non-Faradaic potentials between 0.05 and 0.25 V (vs RHE in 1.0 M KOH) with sweep rates of 20, 40, 60, 80, and 100 mV s⁻¹. By plotting the difference of current density between the anodic and cathodic sweeps at 0.15 V vs RHE in 1.0 M KOH against the scan rate, a linear slope, which is equivalent to twice the value of C_{dl}, can be obtained. The double-layer capacitances (C_{dl}) of the samples were estimated by plotting the $\Delta J = Ja - Jc$ against the CV scan rate, where the slope was twice of C_{dl} and can be used to represent the ECSA. ECSA of each electrocatalyst was then calculated by,

$$ECSA = C_{dl}/C_s,$$
 (S1)

Where, Cs is specific capacitance of the alkaline electrolyte (Cs = 0.04 mF cm^{-2}). The roughness factor (RF) was calculated by,

$$RF = ECSA/GSA,$$
 (S2)

Where, GSA is the geometric surface area of the sample.

TOF and active sites calculation of those ZCS@rGO catalyst

The hydrogen TOF per site of the ZCS@rGO catalyst was calculated using the following formula (S1):

TOF per site

$$= \frac{\# \text{ total hydrogen turnover/cm}^2 \text{ geometric area}}{\# \text{ active sites/cm}^2 \text{ geometric area}}$$
(S3)

The total number of hydrogens turn overs were calculated by using the following formula (S3).

$$\# H_{2} = \left(j\frac{mA}{cm^{2}}\right) \left(\frac{\frac{1C}{s}}{1000 \ mA}\right) \left(\frac{1mol \ e^{-}}{96485 \ C}\right) \left(\frac{1mol \ H_{2}}{2 \ mol \ e^{-}}\right) \left(\frac{6.02 \times 10^{23} mol \ H_{2}}{1mol \ H_{2}}\right) 3.12 \times 10^{15} \frac{\frac{H_{2}}{s}}{cm^{2}} \ per \ \frac{mA}{cm^{2}}$$
(S4).

Further, Zn and Co content of ZCS@rGO catalyst was quantified by using ICP-OES analysis was about ~2.41 wt. and 5.48 wt. Accordingly, the density of active sites based on the Zn and Co is:

$$\left(\frac{2.41}{65.4} + \frac{5.48}{58.9}\right) \times \frac{1mmol}{100 mg} \times 3 \frac{mg}{cm^2} \times 6.022 \times 10^{20} \frac{sites}{mmol} = 2.34 \times 10^{18} sites \ cm^{-2}$$
(S5)

For example, TOF of the catalyst at an overpotential of 302 mV was calculated and given below,

$$TOF = \frac{61 \times 3.12 \times 10^{15} \frac{H_2/s}{cm^2}}{2.34 \times 10^{18} sites \ cm^{-2}} = 0.0813 \ s^{-1} \ (S6)$$

Faradaic efficiency

The Faradaic efficiency (η_F) of the water splitting device was determined by water displacement method using lab-made water splitting cell system.¹¹ The volume of evolved O₂ and H₂ gas were measured by collecting of evolved gases in to measuring cylinders during the water splitting at constant current density with different time interval. The theoretical volumes of released O₂ and H₂ gas were calculated using following Faraday's law

$$V_{Theo} = \frac{IRTt}{PzF}$$
(S7)

V_{Theo =} Theoretical volume of evolved gas

- I= working current density (mA cm^{-2})
- T = working temperature (K) and 't' is time interval (s)
- R = the gas constant and 'P' is the working pressure
- F = the Faraday's constant (F = 96485 C)
- z = the number of electrons for generating 1 mol H₂ (z = 2)

Faradaic efficiency (ηF) was determined by ratio of measured gas volume (V_{meas}) and theoretically calculated volumes (V_{Theo}) as given in equation S6

$$\eta F = \frac{V_{meas}}{V_{Theo}} \tag{S8}$$



Fig. S1 (a-b) TEM images of ZCS@rGO catalyst.



Fig. S2 EDS spectrum of ZCS@rGO catalyst.



Fig. S3 (a-b) HR-TEM and (c) fast Fourier transform (FFT) image of CS@rGO catalyst. (d-f) HAADF-STEM-EDX elemental mapping and (g) EDS spectrum of CS@rGO catalyst.



Fig. S4 ICP-OES result; bare chart displays the element composition of (a) ZCS@rGO and (b) CS@rGO catalysts.



Fig. S5 XPS analysis of (a) survey spectrum, (b) O1s, and (c) C1s of ZCS@rGO. The (d) elemental composition of ZCS@rGO catalyst (atomic percentage) from XPS analysis.



Fig. S6 (a) d-orbital splitting in Co^{3+} in CS and (b) crystal structure of spinel CS. (c) d-orbital splitting in Zn^{2+} in ZCS and (b) crystal structure of spinel ZCS.



Fig. S7 Schematic illustration of Jahn-Teller effect in (a) cubic spinel structure and (b) compression (cubic structure). The Jahn-Teller effect in (c) tetragonal spinel structure and (d) elongation for an octahedral complex.



Fig. S8 (a, b) 3d orbital energy levels in Co³⁺ high spin and low spin. (c, d) 3d orbital energy levels in Co²⁺ high spin and low spin.

Table S1. The calculation of crystal field stabilization energy (CFSE).

Spin state	CFSE value	Jhan-Teller effect
Co ³⁺ -high spin	$0.4 \Delta_0$	No
Co ³⁺ -low spin	$2.4 \Delta_0$	No
Co ²⁺ -high spin	$0.8 \Delta_0$	Yes
Co ²⁺ -low spin	$1.8 \Delta_0$	Yes
Zn ²⁺	$0 \Delta_0$	No



Fig. S9 HER performance: LSV curves of CC and GO/CC electrocatalysts.



Fig. S10 Long-term chronopotentiometry curves of ZCS@rGO and CS@rGO at current density of 10 mA cm⁻².



Fig. S11 1st and 1000th CV curves of ZCS@rGO/CC catalysts at a scan rate 100 mV s⁻¹.



Fig. S12 After HER stability test; (a) SEM image of ZCS@rGO. (b, c) SEM-EDAX elemental mapping of ZCS@rGO with respect to Zn-K, Co-K, S-K, and C-K. (d) EDS spectrum of ZCS@rGO catalyst.



Fig. S13 After HER stability; (a) HR-TEM image and (b-d) HR-TEM-EDAX elemental mapping of ZCS@rGO catalyst with respect to Zn-K, Co-K, O-K, and S-K, (e) EDS spectrum of ZCS@rGO/CC catalyst.



Fig. S14 After HER stability test, XPS analysis (a) survey spectrum, (b) C 1s, (c) O 1s, (d) Zn 2p, (e) Co 2p and (f) S 2p (insert table of elemental composition) of ZCS@rGO/CC catalyst.



Fig. S15 Calculation of DOS for Co₃S₄ and ZnCo₂S₄.



Fig. S16 The (a) side view, and (b) top view of Co_3S_4 . The (c) side view, and (d) top view of H*- Co_3S_4 .



Fig. S17 The (a) side view, and (b) top view of $ZnCo_2S_4$. The (c) side view, and (d) top view of H*-ZnCo_2S_4.



Fig. S18 The Gibbs free energy of $ZnCo_2S_4$ (A) and rGO (B).

Table S2. The DFT	calculation study	of Co ₃ S ₄ and	$ZnCo_2S_4$ catalyst.

S.No	Materials	Atomic distance (Å)	Formation	Gibbs free	
			energy (eV)	energy($\Delta G^*(eV)$	
1	Co_3S_4	Co:S=2.26, S:Co=2.13	4.10	_	
2	H*-Co ₃ S ₄	H:S=1.5, Co:S=2.13 4.83		0.894	
3	ZnCo ₂ S ₄	Co:S=2.13, S:Zn=2.26	3.97	_	
4	H*-ZnCo ₂ S ₄	H:S=1.5, Co:S=2.13,	4.68	-0.329	
		S:Zn=2.26			

Electrocatalyst	Electrolytes	Overpotential 10	Tafel slope	Ref.
		mA cm ⁻² (V vs.	mV dec ⁻¹	
		RHE)		
VS/NiCo ₂ S ₄ /NF	1.0 M KOH	187	160	12
CoS ₂	1.0 M KOH	288.5	76.5	13
Co ₃ S ₄ @FNC	1.0 M KOH	176	103	14
CoS _x /Ni ₃ S ₂	1.0 M KOH	204	113.13	15
MnCo ₂ S ₄ /NF	1.0 M KOH	167	136.74	16
CoMnS@NiO/CC	1.0 M KOH	232	147.3	17
NiCo ₂ S ₄	1.0 M KOH	183	70.1	18
NiCo ₂ S ₄ NS/CC	1.0 M KOH	181	130.5	19
NiCo ₂ S ₄ @MoS ₂	1.0 M KOH	194	62	20
ZnCo ₂ S ₄ /NF	1.0 M KOH	185	110.4	21
CuCo ₂ S ₄	1.0 M KOH	158	113	22
CuCo ₂ S ₄ /CC	1.0 M KOH	312	50	23
CuCo ₂ S ₄ /NiCo ₂ S ₄	1.0 M KOH	206	90	24
Ni/NiS/P,N,S@rGO	1.0 M KOH	155	135	25
ZCS@rGO	1.0 M KOH	135	47	This work

 Table S3. Comparison of HER performance of ZCS@rGO with recently reported catalysts.

Reference

- 1. J. Yu, S. Chen, W. Hao and S. Zhang, *ACS Nano*, 2016, **10**, 2500-2508.
- 2. C. Sathiskumar, S. Ramakrishnan, M. Vinothkannan, A. Rhan Kim, S. Karthikeyan and D. J. Yoo, *Nanomaterials*, 2020, **10**, 76.
- 3. V. Mani, S. Shanthi, T.-K. Peng, H.-Y. Lin, H. Ikeda, Y. Hayakawa, S. Ponnusamy, C. Muthamizhchelvan and S.-T. Huang, *Sensors and Actuators B: Chemical*, 2019, **287**, 124-130.
- 4. Z. Fang, L. Peng, Y. Qian, X. Zhang, Y. Xie, J. J. Cha and G. Yu, *J. Am. Chem. Soc.*, 2018, **140**, 5241-5247.
- 5. G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.
- 6. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 7. P. E. Blochl, *Phys. Rev. B Condens. Matter*, 1994, **50**, 17953-17979.
- 8. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
- 9. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 10. J. K. Noorskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2006, **153**, L33.
- 11. D. C. Nguyen, D. T. Tran, T. L. L. Doan, D. H. Kim, N. H. Kim and J. H. Lee, *Adv. Energy Mater.*, 2020, **10**, 1903289.
- Y. Han, S. Sun, J. Xu, X. Zhang, L. Wang, Y. Xu, J. Wu and Z. Wang, *Sustain. Energy Fuels* 2021, 5, 3858-3866.
- 13. Y. Dong, H. Sun and G. Liu, *Sustain. Energy Fuels*, 2021, **5**, 4115-4125.
- 14. X. Zhu, J. Dai, L. Li, D. Zhao, Z. Wu, Z. Tang, L.-J. Ma and S. Chen, *Carbon.*, 2020, **160**, 133-144.
- 15. S. Shit, S. Chhetri, W. Jang, N. C. Murmu, H. Koo, P. Samanta and T. Kuila, *ACS Appl. Mater. Interfaces.*, 2018, **10**, 27712-27722.
- 16. B. Hou, J. Fu, H. Su and X. Du, *ChemistrySelect*, 2019, **4**, 4499-4505.
- 17. Q. Li, Z. Xing, D. Wang, X. Sun and X. Yang, *ACS Catal.*, 2016, **6**, 2797-2801.
- 18. F. Li, R. Xu, Y. Li, F. Liang, D. Zhang, W.-F. Fu and X.-J. Lv, *Carbon.*, 2019, **145**, 521-528.
- 19. W. Zhu, M. Ren, N. Hu, W. Zhang, Z. Luo, R. Wang, J. Wang, L. Huang, Y. Suo and J. Wang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 5011-5020.
- 20. X.-Z. Song, F.-F. Sun, Y.-L. Meng, Z.-W. Wang, Q.-F. Su and Z. Tan, *New J. Chem.*, 2019, **43**, 3601-3608.
- 21. G. Song, Z. Wang, J. Sun, J. Sun, D. Yuan and L. Zhang, *Electrochem. commun.*, 2019, **105**, 106487.
- 22. C. Zequine, S. Bhoyate, F. Wang, X. Li, K. Siam, P. K. Kahol and R. K. Gupta, *J. Alloys Compd.*, 2019, **784**, 1-7.
- 23. C. Ren, Y. Chen, L. Du, Q. Wang, L. Li and G. Tian, *ChemElectroChem*, 2021, 8.
- 24. L. Ma, J. Liang, T. Chen, Y. Liu, S. Li and G. Fang, *Electrochim. Acta*, 2019, **326**, 135002.
- 25. M. B. Z. Hegazy, M. R. Berber, Y. Yamauchi, A. Pakdel, R. Cao and U.-P. Apfel, *ACS Appl. Mater. Interfaces.*, 2021, **13**, 34043-34052.