Supporting information For

Interface engineering strategy of MoS₂/perovskite oxide as

bifunctional catalyst to boost overall water splitting

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Sample Synthesis and methods

Materials

The chemicals used in this experiment are lanthanum (III) nitrate hexahydrate $(La(NO_3)_3 \cdot 6H_2O, 99\%, Aladdin)$, strontium nitrate $(Sr(NO_3)_2, \ge 99.5\%, Sinopharm)$, Cobalt (II) nitrate hexahydrate $(Co(NO_3)_2 \cdot 6H_2O, \ge 99.5\%, Sinopharm)$, citric acid (CA, $\ge 99.5\%$, Sinopharm), ethylene diamine tetraacetic acid (EDTA, $\ge 99.5\%$, Sinopharm), ammonia solution (NH₃·H₂O, 25~28\%, Sinopharm), molybdenum sulfide (MoS₂, 99%, Macklin), potassium hydroxide (KOH, 99.99%, Aladdin), ethanol absolute (C₂H₆O, $\ge 99.7\%$, Sinopharm), carbon black (Cabot Vulcan XC-72R), and Nafion solution (5% in lower aliphatic alcohols and water, Sigma-Aldrich). All reagents were directly used without further refinement. The deionized water was supplied for the entire experiment.

Synthesis of La_{1-x}Sr_xCoO₃

The perovskite oxide $La_{1-x}Sr_xCoO_3$ (x=0, 0.4) was synthesized by sol-gel method and denoted as LC and LSC. Under magnetic stirring, 4 mmol Co(NO₃)₂ 6H₂O, La(NO₃)₃ 6H₂O and Sr(NO₃)₂ according to the stoichiometric ratio were dissolved in 30 ml deionized water, and then 12 mmol CA and 8 mmol EDTA were added to the above solution. The molar ratio of metal ion: CA: EDTA was 1:1.5:1. The pH of the solution was adjusted to 8 with ammonia after thorough agitation. Then the solution was continuously stirred at 90 ° C for 8 h to convert into a gel, and the gel was transferred to Muffle oven and reacted at 250 °C for 5 h to obtain the perovskite precursor. After the obtained precursor was fully ground, the sample was annealed at 800°C for 5 h at the heating rate of 5°C/min to obtain black LC and LSC perovskite powders.

Synthesis of La_{1-x}Sr_xCoO₃/MoS₂

60 mg La_{1-x}Sr_xCoO₃ and 60 mg MoS₂ were mixed in a planetary ball mill for 48 h, zirconia ball was used as grinding medium, in which the weight ratio of perovskite powder to zirconia ball was 1:100, and the ratio of large and small zirconia balls was 1: 6. La_{1-x}Sr_xCoO₃/MoS₂ two-phase heterojunction composite electrocatalyst was obtained at the speed of ball mill of 240 ~ 300 rpm.

Characterization

X-ray powder diffractometer (XRD, D/MAX2500, Cu k α , 1.54056 Å, scanning range 5-90°, 40 kV, 40 mA) was used to qualitatively analyze the crystal phase of the material. The grain size of catalyst surface was characterized by field emission scanning electron microscopy (FESEM, SUPRA-55, Zeiss). The phase, crystal type and grain size of the materials were characterized by transmission electron microscopy (TEM, JEM-2100F, JEOL). X-ray photoelectron spectroscopy analyzer (XPS, ESCALAB 250XI, Thermo) was used to identify the components and analyze the valence state of the material. The obtained spectra were corrected by C1s spectral line with binding energy of 284.8 eV, and the data were fitted by peak software. Static contact angle meter (Dataphysics-OCA20) to obtain the wetting ability of the electrolyte on the different samples. Raman spectra were measured at 532 nm excitation wavelength by laser Raman spectrometer (LabRAM HR Evolution) to investigate the catalytically active sites and structural evolution.

Electrochemical test

The electrocatalytic performance was investigated by CHI 660E electrochemical analyzer. First, 2 mg of perovskite powder and 2 mg of Vulcan XC-72 conductive carbon were dispersed in 375 μ L water and 125 μ L ethanol solution, and then 20 μ L Nafion (0.5 wt%) was added, under ultrasonic treatment for 1 h. The ink (6 μ L) was dropped on the glassy carbon electrode, and the catalyst load on the glassy carbon electrode was 0.327 mg/cm².

All electrochemical tests were performed using a three-electrode system. The glassy carbon electrode loaded with heterojunction composite electrocatalyst was used as working electrode, and carbon rod was used as the counter electrode. The reference electrode was Hg/HgO in alkaline condition, and the electrolyte was 1 mol/L KOH solution; the Ag/AgCl was used as the reference electrode and the electrolyte was 0.5 mol/L H₂SO₄ under acidic conditions. The different reference electrodes are converted to the potential relative to the standard reversible hydrogen electrode (RHE) by using the Nernst equation as follows: E (*vs. RHE*) = E (*vs. Hg/HgO*) + 0.059 pH + 0.059 pH + 0.059 pH + 0.21.

To remove the bubbles and activate the electrodes, cyclic voltammetry (CV) was run at least five times before the electrochemical test until a repeatable curve was observed. The polarization curves of OER and HER were measured by linear sweep voltammetry (LSV). The potential required for 10 mA cm⁻² current density was used to evaluate and compare the electrocatalytic efficiency of the catalysts [1]. According to LSV curve, Tafel curve ($\eta = b \log i + a$) was further fitted, η , a, b, j were over potential, Tafel constant, Tafel slope and current density, respectively. By using CV in the non-Faraday region relative to RHE, a potential window size of 0.1 V was selected, and 20 cycles were scanned at different scan rates (20, 40, 60, 80, 100, 120, 140 mV/s). The slope of current density and sweep rate was viewed as a linear curve of electrochemical double layer capacitance (C_{dl}) . Moreover, the specific capacitance of flat surfaces was usually between 20 and 60 μ F/cm². Here, we assume that it is 60 μ F/cm² [2]. Electrochemical active surface area (ECSA) calculation formula is: $ECSA=C/60 \ \mu F \ cm^{-2}$. The electrochemical impedance spectroscopy (EIS) test was performed by applying an AC voltage of 5 mV in the frequency range of 100 K to 0.1 Hz with PARSTAT3000. The circuit was fitted, where R_S , Q, and R_{CT} correspond to the solution resistance, constant phase element, and charge transfer resistance of the system, respectively. Multi-step chronopotentiometry (CP) was used to explore the change of overpotential under different current densities, and the deviation degree of OER and HER

polarization curves before and after 3000 cycles CV test was compared to characterize the stability of the catalyst, the scanning rate was 100 mV/s. The long-term stability of the catalyst in 16 h was studied by current-time method under the constant current density of 10 mA cm⁻² overpotential. We made a two-electrode device to examine the overall performance of water splitting. The catalyst was suspended on the surface of nickel foam, and then the electrode was prepared by air drying. The stability of catalyst overall water splitting was tested by CP method at 10 mA cm⁻².

Computational details

Density functional theory (DFT) calculations were performed using the Vienna Ab initio simulation package[3,4], with the projected augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) function [5,6]. The kinetic cutoff energy was set to 400 eV for the calculations. The convergence tolerances for energy and force were set to be 10^{-4} eV and 0.03 eV/Å, respectively. To properly include the weak van der Waals (vdW) interactions, the Grimme's dispersion correction (DFT-D3) is employed during the calculations related with surface adsorption [7,8].

The lattice parameters of optimized unit cells were a=b=5.48 Å, c=13.26 Å for LC, and a=b=3.18 Å for 2H-MoS₂, respectively. The values are consistent with the experimentally reported values [9,10]. Based on the XRD measurements, the (110) surface of LC and (002) surface of 2H- MoS_2 was cleaved from the bulk crystal to form LC/MoS_2 heterostructure (HS). Then the fourlayer model of (100) surface of LC/MoS₂ HS was obtained as the active interface for catalysis. As results, the LC ($\overline{1}14$) surface with O termination and MoS₂ (002) surface with S edge acted as the exposure surface. The LSC/MoS₂ HS was modeled by substituting one of the surface La atom into Sr atom. To reduce the computational cost, only the surface layer of LC/MoS₂ HS was allowed for relaxation during structural relaxation (see Figure 7). The structures were relaxed using the Monkhorst–Pack k-point mesh of $2 \times 1 \times 1$ during surface calculations. The adsorption energy of the reaction

$$^{L}ads = E_{X*} - E_{*} - E_{X}$$

where E_{X*} denotes the energy of adsorption system, E* denotes the energy of clean surface, and E_X denotes the energy of the adsorbate. Therefore the smaller value of adsorption energy means the stronger adsorption based on this definition.

The computational hydrogen electrode (CHE) model was applied for the electro-chemical steps. The Gibbs free energy of adsorbed hydrogen ($\Delta G_{\rm H}$) is computed as:[11]

$$\Delta G_H = \Delta E_H + \Delta Z P E - T \Delta S_H$$

where ΔE_{H} is the adsorption energy of hydrogen atom [calculated by E(H*)-E(*)-E(H)], ΔZPE and ΔS_H are the zero-point energy change and the entropy difference between H* and free H atom at room temperature (298.15 K), respectively.

The adsorption energies (ΔE_{ads}) of different oxygen-contained intermediates during OER were separately calculated (at U = 0 and pH = 0) as

$$\Delta E_{OH} = E_{OH*} - E_* - (E_{H_2O} - \frac{1}{2}E_{H_2})$$
$$\Delta E_O = E_{O*} - E_* - (E_{H_2O} - E_{H_2})$$

$$\Delta E_{OOH} = E_{OOH*} - E_* - (2E_{H_2O} - \frac{3}{2}E_{H_2})$$

where E_{X*}, E_X, and E_{*} represent the total energies of the adsorption system, the adsorbate, and the

substrate, respectively. The Gibbs free energy change (ΔG) of each step was defined as

 $\Delta G = \Delta E_{ads} + \Delta Z P E - T \Delta S$

The theoretically determined overpotential (η) is derived from Gibbs free energy differences ΔG_i (i= 1, ..., 4) at each step as

$$\eta = \frac{\max\left(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right)}{e} - 1.23 V$$



Fig. S1 SEM of LC (a), LSC (b), MoS_2 (c), LC/MoS₂ (d), and LSC/MoS₂ (e).



Fig. S2 SEM (a), TEM (b) of LSC.



Fig.S3 XPS results of LSC/MoS₂ full spectrum (a), La 3d (b), Sr 3d (c).



Fig.S4 At 1M KOH, CV curves with different scan rates for LC (a), LSC (b), MoS_2 (c), LC/MoS_2 (d) and LSC/MoS_2 (e) in OER.



Fig.S5 At 1M KOH, (a) current-time curve at 10 mA cm⁻² constant current density for LSC/MoS₂ and (b) LSV polarization curves of LSC/MoS₂ before and after 3000 cycles in OER.



Fig.S6 At 1M KOH, CV curves with different scan rates for LC (a), LSC (b), MoS_2 (c), LC/MoS₂ (d) and LSC/MoS₂ (e) in HER.



Fig.S7 At 1M KOH, (a) current-time curve at 10 mA cm⁻² constant current density for LSC/MoS₂ and (b) LSV polarization curves of LSC/MoS₂ before and after 3000 cycles in HER.



Fig. S8 Electrochemical performance of catalysts under HER test condition in 0.5 H₂SO₄. (a) LSV polarization curves (b) Tafel plots (c) comparison of overpotential η at 10mA cm⁻² and Tafel slope (d) electrochemical double-layer capacity (C_{dl}) and (e) Nyquist plots and (f) the multicurrent step durability test from 10 to 50 mA·cm⁻² for LSC/MoS₂.



Fig.S9 At 0.5 H_2SO_4 , CV curves with different scan rates for LC (a), LSC (b), MoS_2 (c), LC/MoS₂ (d) and LSC/MoS₂ (e) in HER.



Fig.S10 At 0.5 H_2SO_4 , (a) current-time curve at 10 mA cm⁻² constant current density for LSC/MoS₂ and (b) LSV polarization curves of LSC/MoS₂ before and after 3000 cycles in HER.



Fig. S11 The relaxed structures of LSC/MoS₂ HS with different doping site of Sr, as well as the corresponding DFT calculated total energies. LSC/MoS₂ HS-2 is more energetically stable than the LSC/MoS₂ HS-1 based on our DFT calculations, and is selected as the catalytic model in this work.



Fig. S12 The projected density of states (PDOS) profiles of **a** MoS₂ (002), **b** LC/MoS₂ HS and **c** LSC/MoS₂ HS. The p-band center (ε_p) positions of S atoms (green color) and O atoms (red color) are pointed out by dash arrow.



Fig. S13 The Bader charge distribution on surface S atoms and O atoms of LC/MoS_2 HS and LSC/MoS_2 HS.



Fig. S14 XRD comparison of LSC/MoS2 before and after reaction



Fig. S15 TEM comparison of LSC/MoS $_2$ before (a) and after (b) reaction

Perovskite	O 1s			Area ratio		
electrocatalyst		O ^{2–}	$\Omega_{2}^{2}/\Omega^{2}$	OH-/Oa	Н.О	O22–/O -
electrocataryst		0	O_2 / O	011/02	1120	O2-+OH-/O2+H2O
IC	Position [eV]	528.81	529.96	531.17	532.00	0.051
LC	Proportion [%]	37.64	4.82	31.63	25.91	0.031
LSC	Position [eV]	528.81	529.60	531.17	532.15	0 149
	Proportion [%]	21.55	12.95	40.39	25.11	01115
LC/MoS ₂	Position [eV]	530.62	531.31	532.02	532.66	0.282
	Proportion [%]	17.93	22.00	32.20	27.87	0.202
LC/MoS ₂	Position [eV]	530.62	531.55	532.27	533.05	0.307
	Proportion [%]	16.13	23.50	30.50	29.87	

Table 1 The relative concentration of different oxygen species in O 1s XPS

Table 2 ECSA values for different materials of OER in alkaline electrolyte

Catalyst	C (F/g)	ECSA (m ² /g)
LC	7.80	13.00
LSC	7.49	12.49
MoS_2	11.16	18.60
LC/MoS_2	16.51	27.52
LSC/MoS ₂	19.72	32.87

Table 3 Fitting parameters for EIS results of OER in alkaline electrolyte

Catalyst	R _S /Error	Q/Error	n/Error	R _{CT} /Error
LC	9.443, 1.162	0.0034530, 2.400	0.8293, 1.060	727.6, 8.797
LSC	10.62, 2.416	0.0006496, 5.465	0.8369, 1.592	671.4, 5.290
MoS_2	10.92, 2.317	0.0014880, 5.299	0.8539, 1.847	446.5, 6.559
LC/MoS ₂	33.27, 2.164	0.0027490, 14.89	0.7210, 6.006	77.17, 7.581
LSC/MoS ₂	11.91, 1.569	0.0033770, 9.748	0.7602, 3.176	24.84, 2.896

Catalyst	C (F/g)	ECSA (m²/g)
LC	13.07	21.79
LSC	17.22	28.70
MoS_2	22.23	37.05
LC/MoS ₂	28.24	47.07
LSC/MoS ₂	40.52	67.53

Table 4 ECSA values for different materials of HER in alkaline electrolyte

 Table 5 Fitting parameters for EIS results of HER in alkaline electrolyte

Catalyst	R _S /Error	Q/Error	n/Error	R _{CT} /Error
LC	16.13, 1.275	0.0007310, 2.656	0.9017, 0.897	1146, 3.995
LSC	16.09, 5.916	0.0003291, 11.72	0.8287, 3.107	548.0, 6.613
MoS_2	10.88, 2.565	0.0016730, 8.031	0.8165, 2.701	258.3, 8.211
LC/MoS ₂	9.835, 2.142	0.0023740, 7.879	0.7576, 2.669	132.1, 5.854
LSC/MoS ₂	15.87, 1.159	0.0010330, 10.35	0.7851, 2.604	16.25, 2.267

Table 6 ECSA values for different materials of HER in acidic electrolyte

Catalyst	C (F/g)	ECSA (m ² /g)
LC	6.56	10.93
LSC	12.57	20.95
MoS_2	5.87	9.79
LC/MoS ₂	28.07	46.79
LSC/MoS ₂	32.28	53.80

Catalyst	R _S /Error	Q/Error	n/Error	R _{CT} /Error
LC	13.94, 0.901	0.0002843, 3.883	0.9011, 0.882	314.5, 2.312
LSC	15.58, 0.630	0.0002761, 3.133	0.8919, 0.693	278.4, 1.763
MoS_2	13.34, 0.756	0.0003417, 4.056	0.8674, 0.874	96.56, 1.108
LC/MoS ₂	9.363, 1.048	0.0004537, 7.570	0.8346, 1.546	46.60, 1.963
LSC/MoS ₂	9.413, 1.123	0.0005518, 9.947	0.7872, 2.010	18.21, 1.988

Table 7 Fitting parameters for EIS results of HER in acidic electrolyte

Table 8 ICP-AES analysis of element content before and after reaction of $La_{0.6}Sr_{0.4}CoO_3/MoS_2$

Sample	La (mg L ⁻¹)	Sr (mg L ⁻¹)	Co (mg L ⁻¹)	Mo (mg L ⁻¹)	S (mg L ⁻¹)	Composition
Before	0.325	0.229	0.53	1.07	2.24	$La_{0.61}Sr_{0.43}CoO_3/MoS_{2.09}$
After	0.314	0.205	0.517	1.04	1.99	$La_{0.6}Sr_{0.4}CoO_{3}/MoS_{1.91}$

Table 9 Overall water splitting activity comparison for catalysts in this work with previously reported ones in 1 M KOH.

	Voltage (V) at	C. Lataria	Source	
Catalyst	10 mA cm ⁻²	Substrate		
LSC/MoS ₂	1.48	Ni foam	This work	
Pt/C RuO ₂	1.58	Ni foam	This work	
NdBaMn ₂ O _{5.5}	1.67	Ni foam	ACS Catal., 2018, 8(1): 364-371.	
$SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta}$	1.68	Ni foam	Adv. Energy Mater., 2017, 7(8): 1602122.	
$La_{0.5}Sr_{0.5}CoO_{3\!-\!\delta}$ and $MoSe_2$	1.67	Ni foam	J. Mater. Chem. A, 2019, 7(46): 26607-26617.	
$La_{0.1}Sr_{0.9}Fe_{0.5}Co_{0.475}P_{0.025}O_{3-\delta}$	1.57	Ni foam	ACS Mater. Lett., 2021, 3(8): 1258-1265.	
NiCo ₂ S ₄	1.58	Ni foam	Adv. Funct. Mater. 2019, 29, 1807031.	
$PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta} @FeOOH$	1.638	Ni foam	ACS Appl. Mater. Inter., 2018, 10(44): 38032.	
$La_{0.8}Sr_{0.2}Cr_{0.69}Ni_{0.31}O_{3-\delta}\!/Ni_2P$	1.7	Ni foam	Electrochim. Acta, 2019, 318: 120-129.	
$La_{0.7}Y_{0.3}Co_{0.5}Ni_{0.5}O_{3}$	1.63	Ni foam	Mater. Lett., 2023, 332: 133532.	
NiMoP/NiFeP	1.57	Ni foam	Appl. Catal. B Environ., 2021, 297: 120434.	
CuCo ₂ S ₄ /NiCo ₂ S ₄	1.66	Ni foam	Electrochim. Acta, 2019, 326: 135002.	
$Zr_{0.012}Ni_{4.3}O_{0.68}$	1.55	Ni foam	Fuel, 2023, 333: 126538.	
$La_{0.9}Sr_{0.1}CoO_{3}/Ti_{3}C_{2}T_{x}$	1.59	Ni foam	Adv. Funct. Mater., 2023, 33(21): 2215061.	
LSC-N-GQDs-MoSe ₂	1.57	Ni foam	Nano Energy, 2022, 96: 107117.	
Ni ₂ P/Ni ₅ P ₄	1.56	Ni foam	Inorg. Chem., 2023, 62(16): 6518-6526.	
Ni_3S_2/MoS_2	1.62	Ni foam	Int. J. Hydrogen Energy, 2022, 47(13): 8165.	

Ni ₃ S ₂ /FeNi ₂ S ₄	1.55	Ni foam	Chem. Eng. J., 2022, 427: 131944.
$CoS_{1.25}Se_{0.75}$	1.67	Ni foam	J. Colloid Interf. Sci., 2023, 630: 580-590.
(Ni,Co)Se ₂ /CoSe ₂	1.56	Ni foam	Appl. Surf. Sci., 2022, 592: 153352.
Co ₃ S ₄ /Ni ₃ S ₂ @PPy	1.52	Ni foam	J. Colloid Interf. Sci., 2022, 618: 1-10.
MoS_2/NiS_2	1.59	Ni foam	Appl. Catal. B: Environ. 2019, 253, 131-139.
CoSe/Co(OH) ₂	1.65	Ni foam	Compos. Part B-Eng., 2022, 236: 109823.
Co ₄ Ni ₁ S/CC	1.60	Ni foam	ACS Appl. Mater. Inter., 2022, 14(8): 10277.

References

- [1]. Z. Y. Lu, W. W. Xu, W. Zhu, Q. Yang, X. D. Lei, J. F. Liu, Y. P. Li, X. M. Sun, X. Duan, Three-dimensional NiFe layered double hydroxide film for high-efficiency oxygen evolution reaction, Chem. Commun. 50 (2014) 6479-6482.
- [2]. Y. Lu, A. Ma, Y. F. Yu, R. Tan, C. W. Liu, P. Zhang, D. Liu, J. Z. Gui, Engineering oxygen vacancies into LaCoO₃ perovskite for efficient electrocatalytic oxygen evolution, ACS Sustainable Chem. Eng. 7 (2018) 2906-2910.
- [3]. G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169-11186.
- [4]. G. Kresse and D. Joubert, Fromultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. B 59 (1999) 1758-1775.
- [5]. P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953-17979.
- [6]. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865-3868.
- [7]. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010), 154104.
- [8]. S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, J. Comput. Chem. 32 (2011) 1456-1465.
- [9]. G. Thornton, B. C. Tofield, A. W. Hewat, A neutron diffraction study of LaCoO₃ in the temperature range 4.2<T<1248K, J. Solid State Chem. 61 (1986) 301-307.</p>
- [10]. M. Li, J. L. Shi, L. Q. Liu, P. Yu, N. Xi, Y. C. Wang, Experimental study and modeling of atomic-scale friction in zigzag and armchair lattice orientations of MoS₂, Sci. Technol. Adv. Mater. 17 (2016) 189-199.
- [11]. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, J. Phys. Chem. B 108 (2004) 7886-17892.