1. Experimental Section

1.1. Synthesis of LDH-0

GF was synthesized following a templated chemical vapor deposition method by using Mg(OH)₂ derived MgO flakes as the templates, methane as the carbon source, and pyridine as the nitrogen source. More details can be found in our previous work.¹ LDH-0 was synthesized via a urea-assisted precipitation using GF as the substrate. 100 mg GF was firstly dispersed into 100 mL N-methylpyrrolidone (NMP) under sonication for 30 min to form a homogeneous suspension. 0.873 g Ni(NO₃)₂·6H₂O, 0.404 g Fe(NO₃)₃·9H₂O, and 7.00 g urea were dissolved in 35 mL deionized water. The two suspensions were mixed and sonicated for another 30 min. After that, the mixture was kept at 100°C under continuous magnetic stirring for 12.0 h and then cooled to room temperature. LDH-0 was finally obtained after filtration, washing with deionized water, and freeze-drying for 12 h.

1.2. Synthesis of LDH-x under anionic regulation

The anionic regulated LDH-*x* were synthesized in Li–S cells as the reactor. LDH-0 was coated on a Celgard 2400 polypropylene (PP) membrane and assembled in Li–S punch cells for the electrochemical assisted anionic regulation. Specifically, 80.0 mg LDH-0 and 8.0 mg Nafion binder were dispersed in 4.0 mL ethanol by ultrasonic treatment for 5 min. The as-obtained suspension was filtered through a piece of rectangular PP separator (40 mm \times 70 mm) and subsequently dried at room temperature for 24 h.

The cathode was composed of sulfur, conductive carbon nanotubes (CNT), and poly(vinylidene fluoride) (PVDF) binder. Sulfur and CNT were firstly mixed in a batch with a weight ratio of 7:3. The obtained composite was then mixed with the PVDF binder with a weight

ratio of 9:1 in NMP under sonication and stirring to form a homogeneous suspension. The suspension was then coated on an Al current collector and dried at 60°C for 12 h. The sulfur cathodes for the Li–S punch cells were cut into rectangles with a size of 40 mm \times 70 mm. The areal sulfur content and areal loading was 63 wt.% in the composite and 1.2 mg cm⁻², respectively.

Li metal anodes were also cut into the same rectangular shape. A layer-by-layer process was used to alternate the cathodes and the anodes with LDH-0 coated PP membranes acting as the separator in Li–S punch cells. The LDH-0 side of the separator faced the sulfur cathode. The electrolyte was the mixture of 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v/v=1:1) with 1.0 mol L⁻¹ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 2 wt.% lithium nitride (LiNO₃). Electrolyte was added to each punch cell at the amount of 2 mL during assembling.

After the assembly of the punch cells, galvanostatic charge/discharge were set at 0.02 mA cm^{-2} within a potential range of 2.11–2.35 V. After *x* cycles (*x* = 1, 2, 5, 10), LDH-*x* was obtained by disassembling the punch cell, subsequently washing with the DOL/DME (v/v=1:1) mixture solvent several times to remove extra polysulfide and finally dried at room temperature.

1.3. Material characterization:

The morphology characterization was performed by a JSM 7401F (JEOL Ltd., Tokyo, Japan) scanning electron microscope (SEM) operated at 3.0 kV and a JEM 2010 (JEOL Ltd., Tokyo, Japan) transmission electron microscope (TEM) operated at 120.0 kV. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was conducted on a FEI Tecnai G2 F20 TEM operated at 300.0 kV. Energy-dispersive X-ray spectrometer (EDS) analysis was carried out by an Oxford Instrument energy dispersive X-ray spectrometer.

X-ray diffraction (XRD) patterns was collected using a Bruker D8 Advanced diffractometer with Cu-K_{α} radiation at 40.0 kV and 120 mA as the X-ray source. X-ray photoelectron spectroscopy (XPS) measurements was carried out by Escalab 250xi, with all samples cleaned with argon plasma in advance. All XPS spectra were calibrated using carbon 1s line at 284.6 eV.

1.4. Electrochemical evaluation:

Electrochemical measurements were performed using a three-electrode system controlled with an electrochemical workstation (CHI 760E, CH Instrument, USA). A saturated calomel electrode (SCE) and a platinum sheet electrode served as the reference and counter electrode, respectively. All potentials measured were calibrated to reversible hydrogen electrode (RHE) using the following equation:

$$E_{\rm RHE} = E_{\rm SCE} + 0.224 \text{ V} + 0.0592 \text{ pH}$$
(1)

The overpotential was calculated by the following equation:

$$Overpotential = E_{RHE} - 1.229 V$$
 (2)

The working electrode was a rotating disk electrode, where the disk electrode is a glass carbon disk with a diameter of 5.0 mm (Pine Research Instrument, USA). The fabrication of the working electrode was carried out following a drop-casting method. Typically, 10.0 mg electrocatalyst was added in the mixture of 1.90 mL ethanol and 100 μ L Nafion solution (5.0 wt.% in ethanol), followed by 1.0 h sonication for homogeneous dispersion. Then 10.0 μ L of the suspension was pipetted onto the disk electrode, which was mechanically polished and ultrasonically washed in advance. After solvent evaporation for 5 min in air, the working electrode was ready for further electrochemical evaluation. The areal loading of the electrocatalyst is 0.25 mg cm⁻².

All electrochemical evaluations were tested in O₂-saturated 0.10 M KOH electrolyte at room temperature. Throughout the tests, the rotating disk electrode was rotated at 1600 rpm. Linear sweep voltammetry (LSV) was tested at a scan rate of 10.0 mV s⁻¹ with 95% *iR*compensation and a potential range from 0.00 to 0.75 V vs SCE.

Tafel slopes were calculated based on the data of the LSV curves according to the Tafel equation:

$$\eta = b \log(j/j_0) \tag{3}$$

where η is the overpotential, b is the Tafel slope, j is the disk current density, and j₀ is the exchange current density.

The stability of the electrocatalysts was evaluated using the chronoamperometric method performed at a constant potential (ca. 0.52 and 0.43 V vs SCE for 0.1 and 1.0 M KOH, respectively) to reach an initial current density of 10.0 mA cm^{-2} , and the 1.0 M KOH electrolyte was replaced periodically.

The electrochemical active surface area (ECSA) was determined by double-layer capacity (Cdl). Cdl was measured by capacitive current dependent on the scan rate of cyclic voltammetry (CV). CV was tested with a potential window of 0.000 to 0.050 V vs SCE and at the scan rates of 10, 20, 40, 60, 80, 100 mV s⁻¹. Then linear fitting of the charging current density differences $(\Delta j = j_a - j_b)$ at 0.025 V vs SCE against the scan rates was done. Cdl was half of the slope, which is used to represent ECSA. The electrochemical impedance spectroscopy (EIS) test was performed on the working electrodes at 0.51 V vs SCE. The spectra were collected in a frequency range from 10⁻² to 10⁶ Hz with an amplitude of 5.0 mV.

1.5. Evaluation of lithium sulfide nucleation and Li₂S₆ symmetric cells:

Firstly, electrodes with LDH-0 or LDH-10 coated on Al foil current collectors were fabricated for further evaluation of lithium sulfide nucleation and Li₂S₆ symmetric cells. The electrode slurry was prepared by mixing LDH-0 or LDH-10 with PVDF and CNT with a mass ratio of 5:1:5 in NMP and sonicating for 1.0 h, followed by stirring for 12.0 h. The slurry was then coated onto Al foil with an areal loading of 0.20 mg cm⁻² and dried at 60°C for 12.0 h. The electrodes were obtained after punched into disks with a diameter of 13.0 mm.

Typical two-electrode 2025 coin cells were used to investigate the nucleation of lithium sulfide. The anode was a piece of Li foil, the separator was Celgard 2400 PP membrane, and the as-obtained LDH-0 or LDH-10 loading electrode served as the cathode. The applied Li₂S₈ electrolyte was obtained by dissolving Li₂S and sulfur with a molar ratio of 7:1 in tetraglyme with extra 1.0 mol L⁻¹ LiTFSI under continuous magnetic stirring for 3 days. The concentration of Li₂S₈ was 2.5 mol_[S] L⁻¹. 20 μ L blank electrolyte without Li₂S₈ was dropped onto the lithium anode, and 20 μ L of the as-obtained Li₂S₈ electrolyte was added to the cathode side. The assembled cells were firstly galvanostatically discharged to 2.06 V at 0.10 mA. Followed by the galvanostatic discharge, the cells were potentiostatically discharged at 2.05 V for the nucleation of Li₂S until the current was below 10⁻⁵ A.

For the assembly of Li₂S₆ symmetric cells, two identical electrodes were assembled into a standard 2025 coin cell with a Celgard 2400 PP membrane as the separator and 40 μ L Li₂S₆ electrolyte. The Li₂S₆ electrolyte was obtained by mixing Li₂S and sulfur with a molar ratio of 1:5 in the mixture of DOL/DME (v/v=1:1) under continuous magnetic stirring for 3 days. The concentration of Li₂S₆ was 3.0 mol_[S] L⁻¹. The electrolyte also contained 0.50 mol L⁻¹ LiTFSI. Cyclic voltammetry (CV) was carried out on a Solartron 1470E electrochemical workstation for

kinetic study. CV was performed with a scan rate of 50 mV s⁻¹ at a voltage window between -0.7 and 0.7 V.

1.6. Fabrication of LDH-0 and LDH-10 separator:

LDH-0 separator was prepared by coating an LDH-0 interlayer on the Celgard 2400 PP membrane separator *via* filtration. Typically, 9.0 mg LDH-0, 9.0 mg CNT, and 2.0 mg PVDF were dispersed in 40 mL NMP under sonication for 4.0 h to form a homogeneous suspension. Then, the suspension was filtered through the Celgard 2400 PP membrane with a diameter of 4.0 cm. After dried at room temperature overnight, the membrane with coated LDH-0 was punched into LDH-0 separators with a diameter of 17.0 mm. LDH-10 separator was fabricated following otherwise identical methods but using LDH-10 as the interlayer.

1.7. Assembly of Li–S cells and electrochemical evaluation:

Li–S cells were assembled using the above obtained LDH-0 or LDH-10 separators. The sulfur cathodes were fabricated using sulfur/carbon composites. Typically, 60.0 mg CNT and 140.0 mg sulfur were mixed in a batch. The composite was then mixed with PVDF binder at a weight ratio of 9:1 in NMP under sonication and stirring to form a homogeneous slurry. The slurry was then coated on Al foils, dried at 60°C for 12.0 h. The sulfur cathodes were obtained after punched into small disks with a diameter of 13.0 mm. The areal sulfur loading was 1.2 mg cm⁻². The sulfur content was 63 wt.% in the sulfur composite.

For electrochemical evaluation, standard 2025 coin cells were applied using the above prepared sulfur cathodes, Li metal foil anodes, and LDH-0 or LDH-10 separators. The interlayer side was in contact with the sulfur cathode. The electrolyte was the mixture of DOL/DME

(v/v=1:1) with 1.0 mol L⁻¹ LiTFSI and 2 wt.% LiNO₃. The electrolyte volume was 20 μ L, corresponding to an electrolyte/sulfur ratio of 12.5 μ L(electrolyte)/mg(sulfur).

After the assembly of the Li–S cells, galvanostatic measurements were carried out on a Neware multichannel battery cycler within a potential range of 1.7–2.8 V under the current density of 0.2 C (1 C = 1672 mA g⁻¹).

2. Supplementary Figures



Fig. S1. Morphology characterization of GF. a) SEM, b) TEM, and c) high-resolution TEM images of GF.



Fig. S2. Morphology characterization of LDH-0. a) SEM, b) TEM, and c) high-resolution TEM images of LDH-0.



Fig. S3. XRD patterns of LDH-0.



Fig. S4. Elemental composition analysis of LDH-0. (A) XPS survey spectrum and (B) EDS patterns of LDH-0.



Fig. S5. Morphology characterization of LDH-1. a) SEM, b) TEM, and c) high-resolution TEM images of LDH-1.



Fig. S6. Morphology characterization of LDH-5. a) SEM, b) TEM, and c) high-resolution TEM images of LDH-5.



Fig. S7. Morphology characterization of LDH-10. a) SEM, b) TEM, and c) high-resolution

TEM images of LDH-10.



Fig. S8. Elemental composition analysis of LDH-1. a) XPS survey spectrum and b) EDS patterns of LDH-1.



Fig. S9. Elemental composition analysis of LDH-5. a) XPS survey spectrum and b) EDS patterns of LDH-5.



Fig. S10. Elemental composition analysis of LDH-10. a) XPS survey spectrum and b) EDS patterns of LDH-10.



Fig. S11. a) HAADF-STEM image, b) and c) corresponding elemental mapping of LDH-10.



Figure S12. Tafel plots of the LDH-x electrocatalysts.



Figure S13. EIS of the LDH-x electrocatalysts.



Figure S14. ECSA profiles of the LDH-x electrocatalysts.



Fig. S15. Chronoamperometric response of the LDH-10 electrocatalyst in 1.0 M KOH electrolyte for long-term stability evaluation.



Figure S16. Polarization curves of Li–S cells with LDH-0 or LDH-10 electrocatalysts.

3. Supplementary Tables

Sample	Method	Relative amount of elements (at.%)					
		Ni	Fe	0	S	С	Ν
GF	XPS	0.3	0.3	5.2	0.2	92.2	1.8
	EDS	-	-	0.0	-	75.3	20.0
LDH-0	XPS	17.2	6.4	38.9	0.6	30.7	6.3
	EDS	26.8	9.3	24.3	0.0	21.3	0.0
LDH-1	XPS	9.7	4.6	32.2	6.3	44.5	2.7
	EDS	24.6	8.7	11.5	6.2	27.6	0.0
LDH-5	XPS	9.6	4.3	37.9	9.6	35.4	3.3
	EDS	29.0	9.9	7.6	14.9	9.9	0.0
LDH-10	XPS	10.7	5.0	36.3	10.7	34.2	3.2
	EDS	21.9	8.5	14.1	12.9	26.8	0.0

Table S1. Composition comparison of the samples.

Electrocatalyst	η ₁₀ (mV)	η ₂₀ (mV)
LDH-0	318	353
LDH-1	299	326
LDH-5	294	318
LDH-10	286	312
Ir/C	403	-

Table S2. OER reactivity of the electrocatalysts.

Sample	Electrolyte	Mass loading (mg cm ⁻²)	η10 (mV)	Reference
LDH-10	0.1 M KOH	0.25	286	This work
nNiFe LDH/NGF	0.1 M KOH	0.25	337	1
α-Ni(OH)2 HS	0.1 M KOH	0.2	331	2
CoP-MNA	0.1 M KOH	6.2	290	3
Co ₂ B	0.1 M KOH	0.21	360	4
Co4N	1 M KOH	0.82	257	5
G@N-MoS ₂	0.1 M KOH	0.2	390	6
Bi-S,S'-CNT	1 M KOH	0.23	350	7
Co-POC	0.1 M KOH	0.10	470	8
Ni@NC	0.1 M KOH	0.4	390	9
LiCoO2	1 M KOH	0.32	430	10

Table S3. OER reactivity comparison of the anionic regulated electrocatalyst and other reported
 electrocatalysts.

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