

Anion-activated dual redox in amorphous CoS₂ hollow nanoleaves for advanced magnesium storage cathodes

Lin Ran^{1,§}, Zhen Qin^{1,§}, Jianni Li¹, Fei Xu², Daohong Zhang^{1,3}(✉), Ting Li^{1,3}(✉)

¹ Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, South-Central Minzu University, Wuhan 430074, China

² Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China

³ Guangdong Provincial Laboratory of Chemistry and Fine Chemical Engineering Jieyang Center, Jieyang 515200, China

[§] Lin Ran and Zhen Qin contributed equally to this work.

Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909136>

<https://www.sciopen.com/journal/1998-0124> on Aug. 20, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, 18, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Research Article

Anion-activated dual redox in amorphous CoS₂ hollow nanoleaves for advanced magnesium storage cathodes

Lin Ran^{1,§}, Zhen Qin^{1,§}, Jianni Li¹, Fei Xu², Daohong Zhang^{1,3*}, and Ting Li^{1,3*}

¹ Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, South-Central Minzu University, Wuhan 430074, China

² Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China

³ Guangdong Provincial Laboratory of Chemistry and Fine Chemical Engineering Jieyang Center, Jieyang 515200, China

[§] Lin Ran and Zhen Qin contributed equally to this work.

Received: 4 June 2026; Revised: 8 August 2026; Accepted: 20 August 2026

*Address correspondence to Ting Li, liting@mail.scuec.edu.cn; Daohong Zhang, daohong.zhang@scuec.edu.cn

Cite this article: Nano Research, 2026, 19, 94909136

<https://doi.org/10.26599/NR.2026.94909136>

Abstract: Rechargeable magnesium batteries (RMBs) are promising candidates for sustainable energy-storage technologies, yet their advancement has been constrained by the scarcity of high-performance cathode materials. While conversion-type cathodes circumvent the structural limitations of Mg-intercalation mechanisms, most existing conversion cathodes depend exclusively on the redox activity of transition metal cations, whose capacity is inherently restricted by the reversibility of metal-ion oxidation states. Herein, we report amorphous CoS₂ hollow nanoleaves (*a*-CoS₂) derived from cobalt-based metal-organic frameworks, which host a dual

redox Mg-storage mechanism wherein sulfur anions and cobalt cations undergo simultaneous and reversible redox reactions. Coupled with the abundant anionic sites, hollow architecture and amorphous structure, the α -CoS₂ cathode delivers a high reversible capacity of 195 mAh g⁻¹ at 50 mA g⁻¹, remarkable rate capability of 76.1 mAh g⁻¹ at 1.0 A g⁻¹, and outstanding long-term cyclability (74.6% capacity retention after 300 cycles at 200 mA g⁻¹), which are significantly outperforming amorphous CoS (α -CoS) and crystalline CoS₂ (c -CoS₂). Mechanistic studies confirm the reversible reconstruction of S–S bonds during magnesiation/demagnesiation, along with valence evolution of cobalt ions. This work establishes an anion-activated dual redox chemistry that transcends the limitations of conventional cation-only redox paradigm, providing new design principle for high-capacity cathode materials in multivalent-ion batteries.

Keywords: rechargeable magnesium batteries, cathode materials, anion-activated, amorphous cobalt sulfide, dual redox chemistry.

1. Introduction

The rapid deployment of renewable energy technologies has created a pressing demand for large-scale energy-storage systems to ensure grid stability and energy dispatchability [1]. Among emerging electrochemical energy-storage solutions, rechargeable Mg batteries (RMBs) have attracted considerable interest due to several inherent advantages of Mg element [2]. With high earth abundance, the Mg metal anode exhibits a low redox potential (–2.37 V vs. SHE), a high theoretical volumetric capacity (3833 mAh cm⁻³), and crucially, a low dendritic growth tendency, which significantly enhances operational safety [3-7]. Nevertheless, the development of practical RMBs has been substantially hindered by limitations in cathode materials. The high charge density of divalent Mg²⁺ cations results in strong

Coulombic interactions with host lattice anions, which not only restricts the availability of reversible Mg^{2+} intercalation sites but also leads to sluggish ion diffusion kinetics [8-10].

Unlike conventional Mg-intercalation mechanism, conversion-type Mg-storage reactions circumvent structural constraints through phase transformation processes [11]. This mechanism enables multi-electron transfer, offering high specific capacity by fully utilizing the redox activity of transition metals [12]. Various transition metal chalcogenides have been explored as conversion cathodes for RMBs, including copper-based chalcogenides (CuS [13,14], CuSe [15,16], and Cu_{2-x}Se [17]), cobalt-based chalcogenides (CoS [18], $\text{Co}_{0.85}\text{Se}$ [19], and CoSe_2 [20,21]), and nickel-based selenides ($\text{Ni}_{0.85}\text{Se}$ [22] and NiSe_2 [23]). However, the capacity of these materials relies predominantly on the redox of transition metal cations, which is fundamentally constrained by the reversibility of the metal ion's oxidation states [24]. Furthermore, the bond-breaking and structural reconstruction inherent to conversion reactions often lead to sluggish kinetics and unsatisfactory cycling stability [11].

Recent studies have revealed that anions in metal polysulfides and polyselenides (e.g., FeS_2 [25], TiS_3 [26], MoS_3 [27], VS_4 [28,29], Cu_3VS_4 [30], CoSe_x [31] and Cu_3VSe_4 [32]) can actively participate in redox reactions during magnesiation/demagnesiation, leading to significantly enhanced specific capacities. This cooperative cation-anion redox mechanism opens new avenues for designing high-capacity RMB cathodes [24, 33]. In particular, cobalt disulfide (CoS_2) is a promising candidate for Mg storage. Its disulfide anions (S_2^{2-}) exhibit lower charge density, reducing Coulombic interaction with Mg^{2+} , while the reversible cleavage and reformation of disulfide (S–S) bonds enable redox cycling between S_2^{2-} and S^{2-} . These dual redox-active centers offer a pathway to high capacity and improved kinetics.

In the present study, we synthesized unique amorphous cobalt sulfide hollow

nanoleaves with different S/Co molar ratios derived from cobalt-based metal-organic frameworks (Co-MOFs). The amorphous structure provides disordered pathways for ion diffusion, mitigating crystalline lattice constraints, while the hollow architecture accommodates volume changes and alleviates structural stress during cycling. Electrochemical Mg-storage performance reveals that amorphous CoS_2 (*a*- CoS_2) delivers a reversible capacity of 195 mAh g^{-1} at 50 mA g^{-1} and 76.1 mAh g^{-1} at 1.0 A g^{-1} , with 74.6% capacity retention after 300 cycles at 200 mA g^{-1} , significantly outperforming both amorphous CoS (*a*- CoS) and crystalline CoS_2 (*c*- CoS_2). Kinetic analyses indicate lower charge-transfer resistance and a higher Mg^{2+} diffusion coefficient for *a*- CoS_2 . Mechanistic studies confirm reversible structural evolution involving $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{S}_2^{2-}/\text{S}^{2-}$ redox couples. These results highlight the potential of anion-activated dual redox chemistry and provide valuable insights for designing high-capacity cathodes for next-generation multivalent energy-storage systems.

2. Experimental

2.1 Materials synthesis

Synthesis of Co-MOF nanoleaves: 4 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 32 mmol of 2-methylimidazole (2-MIM) were dissolved in 80 mL of distilled water. The $\text{Co}(\text{NO}_3)_2$ solution was then rapidly added to the 2-MIM solution, followed by 30 min of magnetic stirring and aging for 12 h at room temperature. The resulting Co-MOF nanoleaves were collected by centrifugation and freeze-dried for 48 h.

Synthesis of a-CoS, a-CoS₂ and c-CoS₂ hollow nanoleaves: 0.15 g of Co-MOF was mixed with different amounts of thioacetamide (0.05 g and 0.30 g), corresponding to raw Co/S molar ratios of 1:2 and 1:12, respectively. The mixtures were dispersed in 40 mL of anhydrous ethanol and ultrasonicated for 30 min. The homogeneous mixture was sealed in a Teflon-lined autoclave (100 mL) and heated for 6 h at 180°C . Then the solid products were collected via centrifugation,

thoroughly washed with ethanol and distilled water, and freeze-dried for 48 h, resulting in amorphous CoS (*a*-CoS) and amorphous CoS₂ (*a*-CoS₂) samples. Additional samples with raw Co/S molar ratios of 1:6 and 1:15 were fabricated similarly. The crystalline CoS₂ (*c*-CoS₂) was obtained by annealing the *a*-CoS₂ sample for 2 h at 350 °C with a heating rate of 2 °C min⁻¹ under an argon atmosphere.

2.2 Structural characterizations

The structural characteristics were analyzed with X-ray diffraction (XRD, Bruker-D8-Advance, Cu K α radiation), Confocal Raman spectroscopy (Horiba XploRA Plus, 532 nm laser excitation), and X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, with the C1s peak at 284.6 eV used for calibration). Nitrogen adsorption-desorption isotherms were obtained on Micromeritics ASAP 2460 analyzer. The elemental compositions of cobalt and sulfur were quantified by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 730 Series) and further confirmed through thermogravimetric analysis (TGA, NETZSCH-TG209-F3) performed from 40 to 700 °C in air at 10 °C min⁻¹. Preparation of the samples for the ICP test was dissolved ~30 mg powder in 5 mL aqua regia (HNO₃/HCl=1:3, v/v) and heated at 80 °C for 2 h. The solution was diluted to 25 mL with ultrapure water and analyzed by ICP-OES; the Co/S molar ratio was calculated from the Co and S concentrations. Morphology was observed with scanning electron microscope (SEM, Hitachi SU-8010) and scanning transmission electron microscope (STEM, Thermo Fisher Talos F200X). For ex-situ structural characterizations, the electrodes were carefully disassembled and rinsed with anhydrous dimethoxyethane (DME) in an argon-filled glovebox (Mikrouna Super, H₂O and O₂ < 0.1 ppm) prior to analysis.

2.3 Electrochemical characterizations

The electrodes were fabricated by mixing 60 wt.% active material, 30 wt.% conductive carbon (Super P), and 10 wt.% polyvinylidene fluoride (PVDF) binder,

which were coated onto carbon cloth. The Mg^{2+} electrolyte was prepared by dissolving 3 mmol of magnesium bis(hexamethyldisilazide) ($\text{Mg}(\text{HMDS})_2$, Sigma-Aldrich, 97%), 6 mmol of AlCl_3 (Alfa Aesar, 99.999%), and 3 mmol of MgCl_2 (Alfa Aesar, 99%) in 10 mL of dehydrated tetraglyme. CR2032 coin cells were assembled using the prepared electrode as the cathode (with a loading mass of $\sim 1.5 \text{ mg cm}^{-2}$ and a diameter of 12 mm), polished magnesium foil as the anode, glass fiber separator (Whatman GF/A), and the as-prepared Mg^{2+} electrolyte in the argon-filled glovebox. Galvanostatic charge/discharge tests were carried out on LAND battery testers within a voltage window of 0.1–2.5 V. Cyclic voltammetry (CV) measurements were performed using an electrochemical workstation (CHI 660e, ChenHua, China). Galvanostatic intermittent titration technique (GITT) was conducted with a constant current pulse of 50 mA g^{-1} for 10 min followed by a 30 min relaxation period. Electrochemical impedance spectroscopy (EIS) was carried out on an Ivium-n-Stat instrument (Netherlands) with voltage amplitude of 5 mV from 100 kHz to 10 mHz.

3. Result and discussion

Amorphous cobalt sulfide hollow nanoleaves with different anion composition were synthesized via a liquid-phase anion-exchange strategy using Co-MOFs as sacrificial templates (**Fig. 1a**). The Co-MOF precursor, characterized by XRD and TGA (**Fig. S1**) and containing 13.3 wt% Co^{2+} [34], was synthesized at room temperature from Co^{2+} and 2-methylimidazole (2-MIM) at a 1:8 molar ratio, then sulfidized under controlled Co/S stoichiometries. A low sulfur ratio ($\text{Co/S} = 1:2$) yielded predominantly amorphous CoS (*a*-CoS), while a high ratio ($\text{Co/S} = 1:12$) led to the domination of amorphous CoS_2 (*a*- CoS_2). Subsequent thermal annealing of *a*- CoS_2 at 350°C under argon produced crystalline CoS_2 (*c*- CoS_2). XRD analyses (**Figs. 1b and S2**) confirm the amorphous nature of all as-synthesized samples (Co/S

= 1:2, 1:6, 1:12, 1:15), while the annealed *c*-CoS₂ exhibits sharp diffraction peaks indexed to the cubic phase (JCPDS No. 19-0362), verifying successful crystallization. Thermogravimetric analyses (**Fig. 1c**) determine Co/S molar ratios of approximately 1:0.995, 1:1.913, and 1:1.891 for *a*-CoS, *a*-CoS₂, and *c*-CoS₂, respectively, confirming their near-stoichiometric compositions. The overlapping curves of *a*-CoS₂ and *c*-CoS₂ indicate that annealing primarily induced crystallization without significant compositional change. ICP-OES analysis (**Table S1**) corroborates these findings, yielding Co/S molar ratios of 1:0.93 and 1:1.92 for *a*-CoS and *a*-CoS₂ samples, respectively. Raman spectroscopy (**Fig. 1d**) reveals vibrational modes of Co–S bonds in *a*-CoS (468, 514, 676 cm⁻¹) [35,36]. In contrast, both *a*-CoS₂ and *c*-CoS₂ exhibit characteristic peaks at 302 cm⁻¹ (E_g, librational vibrations) and 389 cm⁻¹ (A_g, in-phase stretching vibrations) for S–S bonds, confirming the presence of disulfide (S₂²⁻) species [35,37]. Phase evolution studies reveal a progressive transition from CoS to CoS₂ with increasing sulfidation ratio (**Fig. S3**), which ultimately yields a CoS₂-dominant phase, demonstrating the thermodynamic stability of both CoS and CoS₂. Nitrogen physisorption measurements (**Fig. 1e**) showed that thermal annealing enhanced both crystallinity and porosity, increasing the BET surface area from 19.89 m² g⁻¹ (*a*-CoS₂) to 45.39 m² g⁻¹ (*c*-CoS₂). XPS spectra provided insights into the surface chemistry and redox-active sites. Co 2p spectra (**Fig. 1f**) indicated the presence of mixed Co³⁺ (778.9 and 794.1 eV) and Co²⁺ (781.6 and 797.4 eV) oxidation states in both *a*-CoS and *a*-CoS₂ [36,38], with a higher proportion of Co³⁺ in the latter. The S 2p spectra (**Fig. 1g**) of *a*-CoS displayed peaks corresponding to S²⁻ species (162.2 and 163.5 eV) and S–O bonds (168.9 eV) [35]. Crucially, the spectra of *a*-CoS₂ exhibited additional peaks (162.8 and 164.5 eV) assigned to disulfide (S₂²⁻), directly evidencing the presence of S–S bonds [35,39]. This finding confirms that both cationic (Co³⁺/Co²⁺) and anionic (S₂²⁻/S²⁻) sites possess redox activity, establishing the foundation for the proposed synergistic redox mechanism.

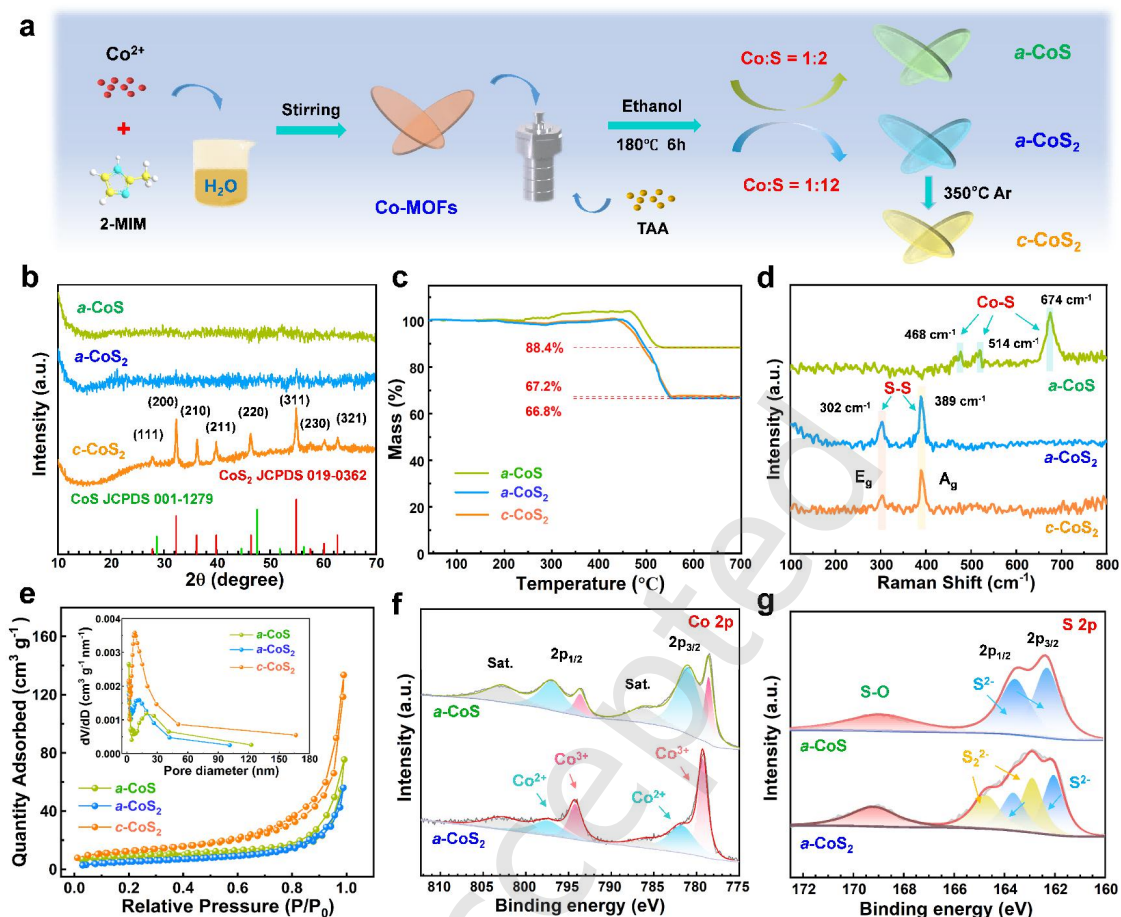


Figure 1. (a) Schematic illustration of the synthesis process, (b) XRD patterns, (c) TGA curves, (d) Raman spectra, (e) N_2 adsorption-desorption isotherm curves and pore distributions of *a*-CoS, *a*-CoS₂ and *c*-CoS₂ samples. XPS spectra of (f) Co 2p, (g) S 2p for *a*-CoS and *a*-CoS₂ samples.

The microstructures of the synthesized cobalt sulfides were characterized by SEM and TEM. As shown in **Figs. 2a** and **S4**, the Co-MOF precursor exhibits smooth, compact leaf-like morphologies with dimensions of approximately 2 μm in width, 4 μm in length, and 150 nm in thickness (**Fig. S4**), and its solid interior is confirmed by TEM (**Fig. 2e**). After sulfidation, the *a*-CoS (**Figs. 2b** and **2f**), *a*-CoS₂ (**Figs. 2c** and **2g**), and samples prepared with other Co/S ratios (**Fig. S5**) retain the leaf-like morphology of the precursor but develop a rougher surface and a distinct hollow interior, as clearly visible in **Figs. 2f** and **2g**. TEM images of sheet edges (**Figs. 2i** and **2k**) and a cross-sectional SEM image (**Fig. 2j**) reveal comparable shell thicknesses of ~ 40 nm for both *a*-CoS (**Fig. 2i**) and *a*-CoS₂ (**Figs. 2j** and **2k**). The morphology and shell thickness remain largely unchanged after calcination, as seen

in the SEM and TEM images of *c*-CoS₂ (**Figs. 2d, 2h, and 2l**). HRTEM and SAED patterns indicate that the shells of *a*-CoS (**Fig. 2m**) and *a*-CoS₂ (**Figs. 2n and 2o**) consist of amorphous nanoparticles (10–20 nm in size). In contrast, *c*-CoS₂ displays well-defined lattice fringes with a spacing of 0.277 nm, corresponding to the (200) plane of crystalline CoS₂ (**Fig. 2p**). HAADF-STEM images and EDS elemental mappings (**Figs. 2q, 2r and S6**) demonstrate the uniform distribution of Co and S throughout the shell layers in all three samples. EDS spectra further yield S/Co atomic ratios of 0.97, 1.98, and 1.96 for *a*-CoS, *a*-CoS₂, and *c*-CoS₂, respectively (**Fig. S7**), consistent with the TGA and ICP analysis. Additional samples prepared with precursor ratios of 1:6 and 1:15 show S/Co molar ratios of 1.61 and 2.11, respectively (**Fig. S8**).

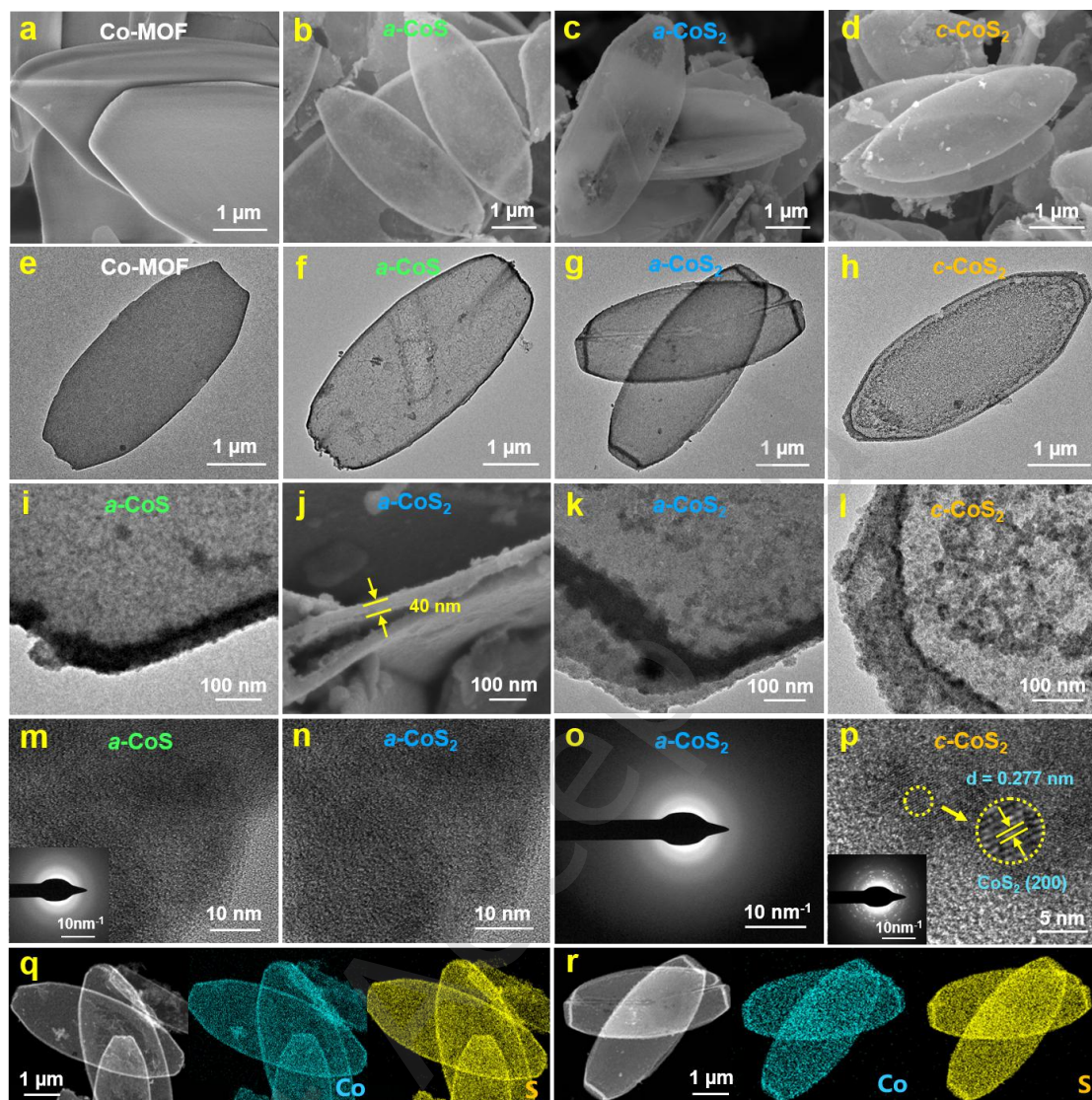


Figure 2. SEM images of (a) Co-MOFs, (b) *a*-CoS, (c,j) *a*-CoS₂ and (d) *c*-CoS₂. TEM images of (e) Co-MOFs, (f,i) *a*-CoS, (g,k) *a*-CoS₂ and (h,l) *c*-CoS₂. HRTEM images of and corresponding SAED patterns of (m) *a*-CoS, (n,o) *a*-CoS₂. (p) *c*-CoS₂. HAADF STEM images and EDS element mapping images of (q) *a*-CoS and (r) *a*-CoS₂.

The Mg-storage performance of *a*-CoS, *a*-CoS₂, and *c*-CoS₂ electrodes was evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. As shown in **Fig. 3a**, the CV profiles of *a*-CoS and *a*-CoS₂ electrodes recorded at 0.1 mV s⁻¹ after activation reveal that the *a*-CoS₂ electrode exhibits a pair of broad redox peaks around 0.95 V and 2.2 V, along with significantly higher current densities across the entire potential window, indicating enhanced electrochemical activity and superior Mg-storage capability compared to the *a*-CoS

electrode (the initial five-cycle CV curves for *c*-CoS₂ and other electrodes are provided in **Fig. S9**). According to subsequent ex-situ XRD analysis (**Fig. 5a**), the *c*-CoS₂ electrode discharged to 0.9 V is dominated by CoS, indicating S-S bond cleavage and Co³⁺→Co²⁺ reduction. The CV of *a*-CoS₂ exhibits a markedly stronger reduction peak at 1.0 V than that of *a*-CoS, along with two anodic peaks at 1.9 and 2.2 V, whereas *a*-CoS displays only a weak anodic peak at 2.2 V (**Fig. 3a**). Accordingly, the 1.0 V cathodic peak is assigned to coupled S₂²⁻→S²⁻ and Co³⁺→Co²⁺ reductions; the 1.9 V anodic peak corresponds to reversible S-S bond reformation, and the 2.2 V anodic peak mainly originates from Co²⁺→Co³⁺ re-oxidation.

Figs. 3b and **S10** present the corresponding charge/discharge profiles at 50 mA g⁻¹. *a*-CoS₂ delivers initial discharge/charge capacities of 81/38 mAh g⁻¹, with poorly defined voltage plateaus in the early cycles. After 50 cycles, however, it achieves a reversible capacity of 191.2 mAh g⁻¹, featuring a distinct discharge plateau near 1.0 V and significantly reduced polarization. In contrast, *a*-CoS exhibits consistently low capacities and featureless charge/discharge profiles throughout cycling (**Fig. S10a**). **Fig. 3c** compares the cycling stability of the three electrodes. *a*-CoS₂ reaches a maximum capacity of 195 mAh g⁻¹ after an activation period of about 20 cycles and retains 169.8 mAh g⁻¹ after 100 cycles, corresponding to a capacity retention of 87.1%. *a*-CoS delivers a much lower capacity, retaining only 79.4 mAh g⁻¹ after 100 cycles. Although the crystalline *c*-CoS₂ eventually attains a comparable maximum capacity to *a*-CoS₂, it requires a prolonged activation process and shows capacity fading to 146 mAh g⁻¹ after 100 cycles. Furthermore, cobalt sulfide electrodes synthesized with Co/S molar ratios of 1:6 and 1:15 exhibit similar charge/discharge behavior to *a*-CoS₂ (**Fig. S11**) but deliver lower capacities and inferior cycling stability.

The rate capabilities of *a*-CoS, *a*-CoS₂, and *c*-CoS₂ were evaluated at various current densities. As shown in **Figs. 3d** and **S12**, *a*-CoS₂ demonstrates superior rate

performance (with corresponding charge/discharge profiles in **Fig. 3e**), delivering a reversible capacity of 76.1 mAh g⁻¹ even at 1 A g⁻¹, compared to only 29 and 63.6 mAh g⁻¹ for *a*-CoS₂ and *c*-CoS₂, respectively. A comparison with previously reported chalcogenide RMB cathodes [18,40-49] (**Fig. 3f and Table S2**) highlights the competitive advantage of *a*-CoS₂. Long-term cycling at 200 mA g⁻¹ (**Fig. 3g**) shows that *a*-CoS₂ reaches a capacity of 119.7 mAh g⁻¹ after a 50-cycle activation and maintains 74.6% capacity retention after 300 cycles. In contrast, *a*-CoS delivers a significantly lower capacity (68 mAh g⁻¹), while *c*-CoS₂, despite reaching a comparable capacity after a longer activation, suffers from substantial decay, retaining only 53.1% after 300 cycles. All electrodes exhibit an activation process, likely driven by structural transformation and progressive grain refinement, which collectively enlarge the active interfacial area. These results demonstrate that the amorphous structure's isotropic bonding and abundant defects collectively shorten Mg²⁺ diffusion pathways, accommodate volume changes, and relieve internal strain during cycling, thereby enabling faster activation and superior cycling stability. Electrochemical impedance spectroscopy (**Fig. 3h and Table S3** for equivalent circuit fitting results) reveals that the charge-transfer resistance (*R*_{ct}) of *a*-CoS₂ is significantly lower than that of *a*-CoS in both the 1st and 50th cycles, and the initial *R*_{ct} of *c*-CoS₂ is also higher than that of *a*-CoS₂, indicating superior Mg-storage activity and faster kinetics for *a*-CoS₂. This enhancement is attributed to the electrochemically active S₂²⁻ ions enabling synergistic anion-cation redox, as well as the amorphous structure which facilitates shorter Mg²⁺ diffusion pathways and enhances structural stability compared to the crystalline counterpart.

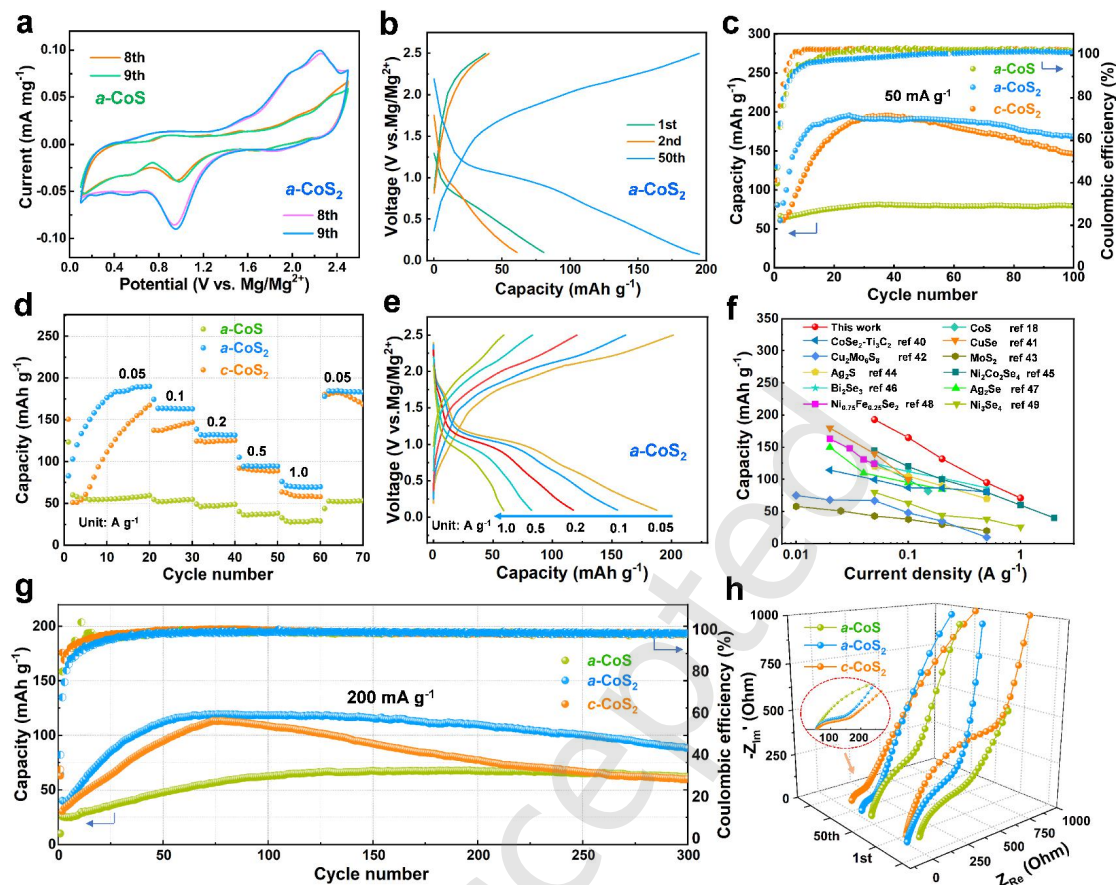


Figure 3. (a) CV curves of *a*-CoS and *a*-CoS₂ electrodes at 0.1 mV s⁻¹ after activation. (b) Charge/discharge curves of *a*-CoS₂ electrode at 50 mA g⁻¹. (c) Cycling performance at 50 mA g⁻¹ and (d) rate capabilities of *a*-CoS, *a*-CoS₂ and *c*-CoS₂ electrodes. (e) Charge/discharge curves at various current densities and (f) a comparison of rate capability of *a*-CoS₂ electrode with reported RMB cathodes. (g) long-term cycling performance at 200 mA g⁻¹ and (h) electrochemical impedance spectra (EIS) of *a*-CoS, *a*-CoS₂ and *c*-CoS₂ electrodes at the first and 50th cycles.

The Mg-storage kinetics were further investigated by CV and galvanostatic intermittent titration technique (GITT). **Figs. 4a** and **S13** present the CV curves of *a*-CoS, *a*-CoS₂, and *c*-CoS₂ at scan rates ranging from 0.1 to 1.5 mV s⁻¹. The peak currents increase with scan rate, and linear relationships between the peak currents and the square root of the scan rate are observed for both oxidation and reduction peaks of all three electrodes (**Fig. 4b** and **S14**). The calculated apparent solid-state diffusion coefficients ($D_{\text{Mg}^{2+}}$, summarized in **Table S4**) for *a*-CoS₂ are 0.87×10^{-11} (peak C at 0.97 V) and 2.18×10^{-11} cm² s⁻¹ (peak A at 2.23 V), approximately twice those of *a*-CoS and *c*-CoS₂. Surface-related pseudocapacitive contributions may also

influence the Mg-storage behavior. Linear fitting of $\log$ (peak current) versus $\log$ (scan rate) (**Fig. S15**) with different scan rates yields b values (details are given in Supporting Information) ranging from 0.6 to 0.9 for all three electrodes, indicating a hybrid diffusion-controlled and surface capacitive storage mechanism. This mixed behavior arises from the unique hollow architecture, which facilitates rapid Mg^{2+} transport and enhances interfacial reaction kinetics. GITT analysis (**Figs. 4c and 4d**) further confirms that the $D_{\text{Mg}^{2+}}$ values for $a\text{-CoS}_2$ are consistently higher than those for $c\text{-CoS}_2$ and $a\text{-CoS}$ throughout the charge/discharge process. This enhancement is attributed to the polyanionic structure dispersing negative charge density and weakening the interaction with Mg^{2+} , thereby lowering the diffusion barrier, while the amorphous nature shortens the ion diffusion pathways, collectively improving the Mg-storage kinetics.

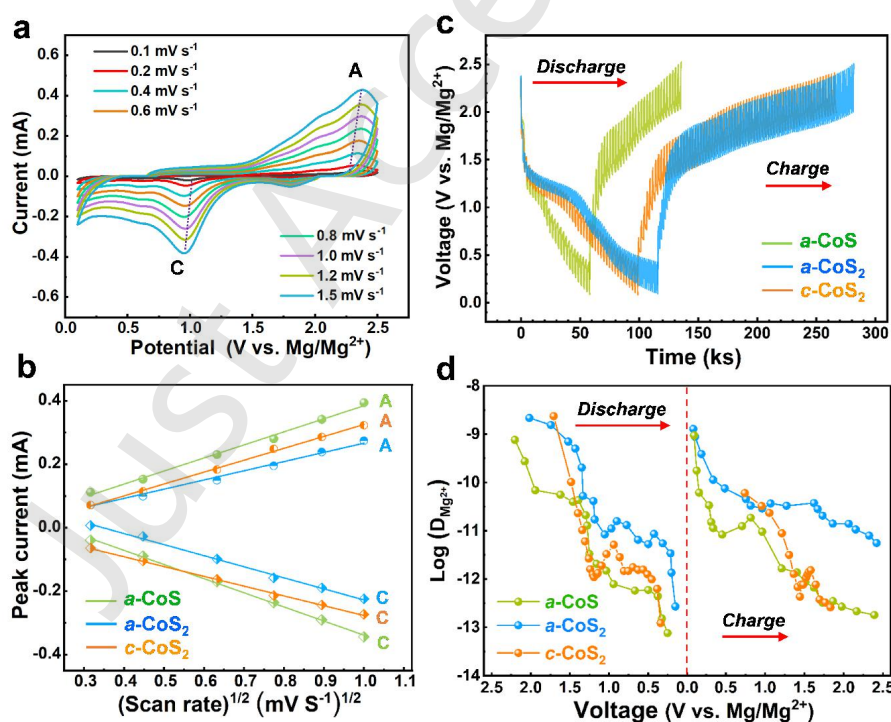


Figure 4. (a) CV curves of $a\text{-CoS}_2$ electrode at different scan rates. (b) Linear relationship of peak current (i) vs. square root of scan rate ($v^{1/2}$), (c) GITT curves at constant current pulse of 50 mA g^{-1} , (d) calculated Mg^{2+} diffusion coefficients of $a\text{-CoS}$, $a\text{-CoS}_2$ and $c\text{-CoS}_2$ electrodes.

The Mg-storage mechanisms of $a\text{-CoS}$ and $a\text{-CoS}_2$ were investigated using

ex-situ XRD, Raman, XPS, and TEM. Phase evolution during cycling was first tracked by XRD using the crystalline *c*-CoS₂ (**Fig. 5a**). The pristine electrode shows distinct CoS₂ diffraction peaks. Upon discharging to 1.75 V, these peaks weaken while new peaks emerge at 28.6° and 47.5° (CoS) and at 34.5° (MgS), indicating conversion to CoS and MgS. Further discharge to 0.9 V leads to the attenuation of CoS signals and the emergence of new peaks at 29.9° and 51.9°, corresponding to the formation of Co₉S₈. At full discharge (0.1 V), CoS₂ peaks vanish, leaving Co₉S₈ and MgS as dominant phases. The charging process reverses this evolution, with CoS₂ peaks gradually reappearing and dominating again at 2.5 V, confirming the reversible reformation of CoS₂. Ex-situ Raman on *a*-CoS₂ (**Fig. 5b**) corroborates these phase changes. The characteristic S–S bond vibrations of CoS₂ (302, 389 cm⁻¹) [37] disappear upon discharge, replaced by peaks for CoS (469, 512, 678 cm⁻¹) [36,39], Co₉S₈ (195, 666 cm⁻¹) [36,39,50], and MgS (523 cm⁻¹) [51]. These signals reverse upon charging, with the S–S vibrations fully recovering at 2.5 V, confirming the reversible cleavage and reformation of disulfide bonds. The Raman spectra for *a*-CoS (**Fig. 5c**) show only a partially reversible transformation involving Co₉S₈, highlighting a different reaction pathway.

XPS analysis provides direct evidence of valence-state changes (**Figs. 5d and 5e**). For *a*-CoS₂, the Co 2p spectrum in the discharged state shows a significant decrease in the Co³⁺ signal (778.9 and 794.1 eV) and a pronounced increase in Co²⁺ (781.6 and 797.4 eV), which reverts to a Co³⁺-dominated state upon full charge, confirming the reversible Co³⁺↔Co²⁺ redox couple. Concurrently, the S 2p spectrum shows a decrease in the S₂²⁻ peaks (162.8 and 164.5 eV) and an increase in S²⁻ peaks (162.2 and 163.5 eV) upon discharge, with recovery to the initial state upon charge, verifying the reversible S₂²⁻↔S²⁻ transformation and the active participation of anions. For *c*-CoS₂, the ex-situ XPS reveals nearly identical evolution in the Co 2p and S 2p spectra relative to *a*-CoS₂ (**Fig. S16**), confirming both electrodes follow the same dual-redox mechanism. In stark contrast, the XPS spectra for *a*-CoS reveal

only the reversible $\text{Co}^{3+} \leftrightarrow \text{Co}^{2+}$ redox, with no significant change in the S 2p spectrum, indicating a cation-only redox process. Notably, $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ reduction is more pronounced in *a*-CoS than in *a*-CoS₂ upon discharge, because the additional $\text{S}_2^{2-}/\text{S}^{2-}$ redox activity in *a*-CoS₂ shares charge compensation with the cobalt center, thereby attenuating the apparent extent of cobalt reduction. The Raman and XPS data collectively demonstrate reversible S-S bond cleavage and reformation, confirming the essential, synergistic contribution of both cationic ($\text{Co}^{3+}/\text{Co}^{2+}$) and anionic ($\text{S}_2^{2-}/\text{S}^{2-}$) redox couples to the high capacity and rapid kinetics of *a*-CoS₂.

Microstructural evolution was further examined by TEM and HRTEM. *a*-CoS₂ electrode maintains its integrated leaf-like morphology after 50 cycles (**Fig. 5f and S17**), whereas *c*-CoS₂ electrode exhibits severe morphological degradation and particle cracking (**Fig. S18**). The HRTEM image (**Fig S17b**) confirms that the *a*-CoS₂ electrode remains its fully amorphous structure after cycling, exhibiting no discernible lattice fringes or crystalline domains. Consistently, the post-cycling XRD patterns (**Fig. S19**) exhibit broad, featureless diffraction humps, further corroborating the structural stability of the amorphous hollow nanoleaves. HRTEM of the fully discharged state (**Fig. 5g**) reveals lattice fringes corresponding to CoS ($d = 0.191$ nm, (102) plane), MgS ($d = 0.260$ nm, (200) plane), and Co₉S₈ ($d = 0.176$ nm, (440) plane). In the fully charged state (**Fig. 5h**), lattice fringes with a spacing of 0.167 nm, indexed to the CoS₂ (311) plane, are observed, consistent with the XRD results. EDS elemental mapping visually confirms the reversible magnesiation/demagnesiation process, namely Mg is uniformly distributed within the nanosheets in the discharged state (**Fig. 5i**) but significantly diminished in the charged state (**Fig. 5j**). Based on these comprehensive analyses, the conversion reaction mechanism is summarized in **Fig. 5k**. Discharge involves Mg^{2+} intercalation, S-S bond cleavage (S_2^{2-} to S^{2-}), and Co^{3+} reduction, stepwise forming CoS/MgS and ultimately Co₉S₈/MgS. The charge process reverses these steps, demonstrating a stepwise, reversible anion-cation co-redox mechanism that

underpins the high-performance Mg storage in anion-rich CoS₂.

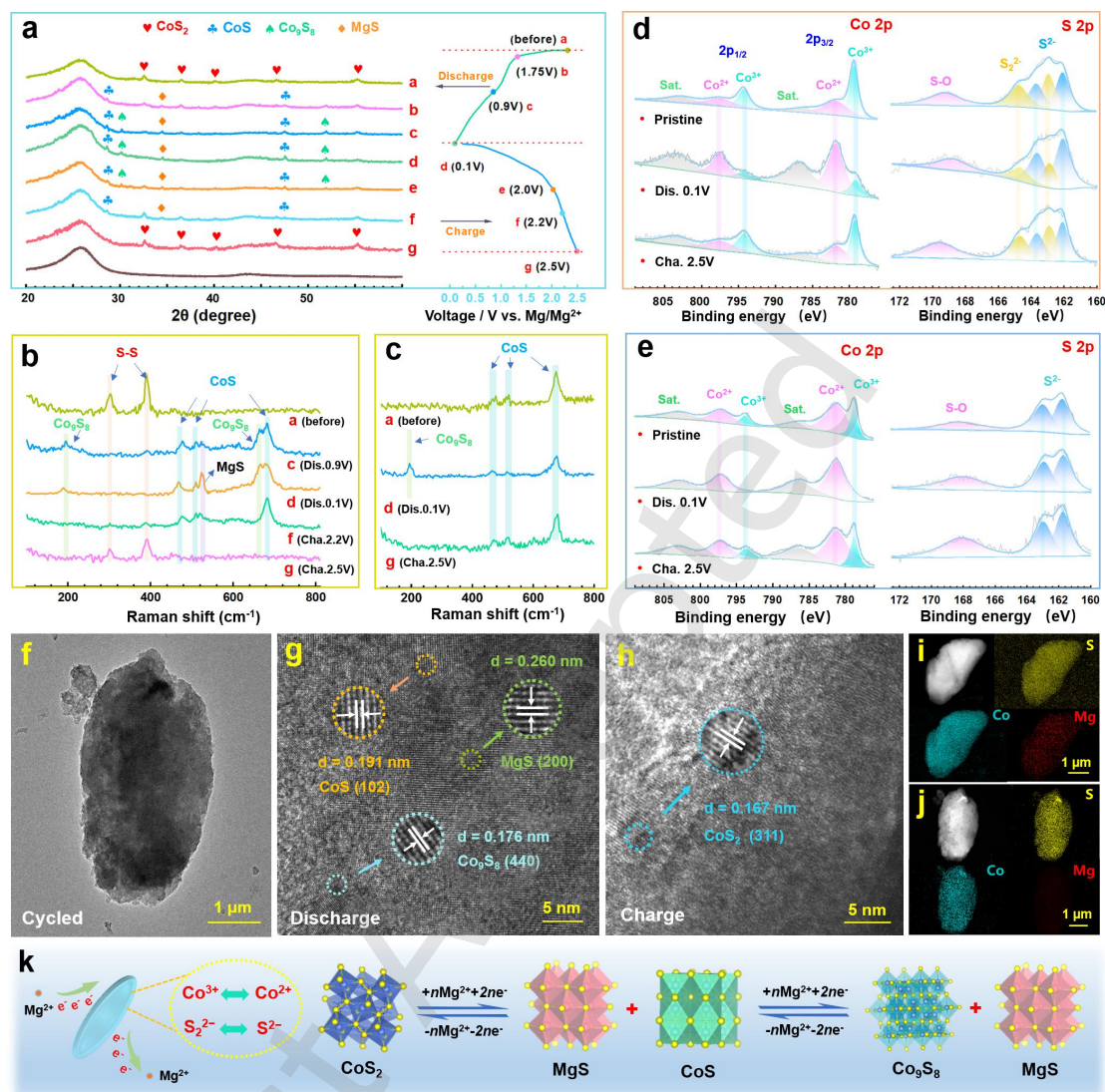


Figure 5. (a) Ex-situ XRD patterns of *c*-CoS₂ electrode at different discharge/charge states. Ex-situ Raman spectra of (b) *a*-CoS₂ and (c) *a*-CoS. Ex-situ Co 2p and S 2p XPS spectra of (d) *a*-CoS₂ and (e) *a*-CoS electrodes at discharge/charge states. (f) TEM image of *a*-CoS₂ electrode after 50 cycles. HRTEM images and EDS mapping images of *a*-CoS₂ electrode at (g,i) discharged state and (h,j) charged state. (k) Schematic illustration of magnesium-storage mechanism of CoS₂ electrode.

4. Conclusions

In this study, we derived amorphous cobalt sulfide hollow nanoleaves from Co-MOF templates as high-performance RMB cathodes. Compared to amorphous CoS (containing only S²⁻) and crystalline CoS₂, the amorphous *a*-CoS₂ demonstrates significantly enhanced Mg-storage activity, kinetics, and cycling stability.

Specifically, it delivers a reversible capacity of 195 mAh g⁻¹ at 50 mA g⁻¹ and 76.1 mAh g⁻¹ at 1 A g⁻¹, with a capacity retention of 74.6% after 300 cycles at 200 mA g⁻¹. Kinetic analyses reveal lower charge-transfer resistance and higher Mg²⁺ diffusion coefficients for α -CoS₂. These superior properties are attributed to its unique structural design, namely the polyanionic (S₂²⁻) framework offers abundant redox-active sites, while the amorphous hollow nanosheet architecture enlarges the reaction interface, shortens Mg²⁺ diffusion pathways, and accommodates volume changes during conversion reactions. Mechanistic studies confirm a reversible conversion mechanism involving the synergistic redox couples of Co³⁺/Co²⁺ and S₂²⁻/S²⁻. This work establishes an anion- activated synergistic redox chemistry, providing a new direction for designing high-capacity cathode materials for next-generation multivalent-ion batteries.

Electronic Supplementary Material: Supplementary material (XRD, TG, ICP-OES, Raman, SEM, TEM, CV, charge/discharge curves, performance comparison, impedance simulation results, calculation of Mg²⁺ diffusion coefficients and pseudo-capacitive capacity contribution, ex situ XRD, XPS, TEM analyses) is available in the online version.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 52572287, 52172266), Hubei Provincial Natural Science Foundation (2024AFB750), Funds for the Central Universities of South-Central Minzu University (CZZ25004 and CZD24001) and Fund for Academic Innovation Teams of South-Central Minzu University (XTZ24012).

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Lin Ran: Investigation, Data Curation, Writing-Original Draft. **Zhen Qin:** Investigation, Validation, Writing - Review & Editing. **Jianni Li:** Investigation. **Fei Xu:** Writing - Review & Editing. **Daohong Zhang:** Supervision, Funding acquisition, Project administration. **Ting Li:** Conceptualization, Visualization, Supervision, Funding acquisition, Writing - Review & Editing.

Use of AI statement

None

References

- [1] Muldoon, J.; Bucur, C. B.; Gregory, T. Quest for nonaqueous multivalent secondary batteries: Magnesium and beyond. *Chem. Rev.* **2014**, *114*, 11683-11720.
- [2] Liang, Y.; Dong, H.; Aurbach, D.; Yao, Y. Current status and future directions of multivalent metal-ion batteries. *Nat. Energy* **2020**, *5*, 646-656.
- [3] Saha, P.; Datta, M. K.; Velikokhatnyi, O. I.; Manivannan, A.; Alman, D.; Kumta, P. N. Rechargeable magnesium battery: Current status and key challenges for the future. *Prog. Mater. Sci.* **2014**, *66*, 1-86.
- [4] Zhang, J.; Zhang, Z.; Zhou, H.; Liu, J.; Du, A.; Dong, S.; Zhou, X.; Wang, Q.; Li, G.; Cui, G. Critical ingredients revitalize magnesium-metal batteries: rationality and challenges. *Adv. Mater.* **2025**, *37*, 2417652.
- [5] Hao, Y.; Wang, D.; Chen, Y.; Tong, L.; Tong, Y.; Huang, G.; Xu, C.; Li, Q.; Qu, B.; Pan, F.; Wang, J. An ultra-thin composite magnesium anode with controlled (002) facet orientation by heterogeneous epitaxial electrodeposition for highly stable lean-magnesium metal batteries. *Acta. Mater.* **2025**, *293*, 121107.
- [6] Chen, Y.; Tang, Z.; Yue, J.; Qu, B.; Wu, J.; Wu, G.; Tong, L.; Shi, K.; Wei, Q.; Huang, G.; Zhou, X.; Peng, D-L.; Wang, J.; Pan, F. Design of a stress-free magnesium anode with a functional interface layer towards practical Ah-level

- pouch cell. *eScience*. **2026**, *19*, 100609.
- [7] Xu, K.; Qi, X.; Zhao, X. Boron-based electrolytes for rechargeable magnesium batteries: From design principles to the optimization of $\text{Mg}[\text{B}(\text{hfip})_4]_2$ via additives and solvation modulations. *Rev. Mat. Res.* **2025**, *1*, 100129.
- [8] Mao, M.; Gao, T.; Hou, S.; Wang, C. A critical review of cathodes for rechargeable Mg batteries. *Chem. Soc. Rev.* **2018**, *47*, 8804.
- [9] Li, Z.; Häcker, J.; Fichtner, M.; Zhao-Karger, Z. Cathode materials and chemistries for magnesium batteries: Challenges and opportunities. *Adv. Energy Mater.* **2023**, *13*, 2300682.
- [10] Tong, L.; Zhang, Y.; Zhang, J.; Chen, Y.; Shen, X.; Lian, X.; Deng, R.; Li, Q.; Paillard, E.; Qu, B.; Wang, J. P2-type Mn-based oxide cathode for chlorine-free Mg-Na hybrid battery devices. *ACS. Energy. Lett.* **2025**, *10*, 5144-5155.
- [11] Zhang, Z.; Dong, S.; Cui, Z.; Du, A.; Li, G.; Cui, G. Rechargeable magnesium batteries using conversion-type cathodes: A perspective and minireview. *Small Methods* **2018**, *2*, 1800020.
- [12] Liu, Y.; Qu, B.; Li, S.; Lian, X.; Luo, Y.; Shen, X.; Xu, C.; Wang, J.; Pan, F. Recent advances and prospects of chalcogenide cathodes for rechargeable magnesium batteries. *Adv. Funct. Mater.* **2024**, *34*, 2405586.
- [13] Mao, M.; Gao, T.; Hou, S.; Wang, F.; Chen, J.; Wei Z.; Fan, X.; Ji, X.; Ma, J.; Wang, C. High-energy-density rechargeable Mg battery enabled by a displacement reaction. *Nano Lett.* **2019**, *19*, 6665-6672.
- [14] Su, Q; Wang, W; Chen, J.; Ji, J.; Wang, W.; Ren, W.; Zhang, L.; Xie, J.; An. Q. The out-of-plane C-S Bonds boosting reversible redox in copper sulfide cathodes for ultradurable magnesium battery. *Adv. Funct. Mater.* **2025**, *35*, 2419594.
- [15] Zhang, Y.; Zhu, Y.; Wang, Z.; Peng, H.; Yang, X.; Cao, Y.; Du, C.; Ma, X.; Cao, C. Pulverization-tolerant CuSe nanoflakes with high (110) planar orientation for high-performance magnesium storage. *Adv. Funct. Mater.* **2021**, *31*, 2104730.
- [16] Shen, Y.; Wang, Y.; Miao, Y.; Li, Q.; Zhao, X.; Shen, X. Anion-incorporated Mg-ion solvation modulation enables fast magnesium storage kinetics of conversion-type cathode materials. *Adv. Mater.* **2023**, *35*, 2208289.
- [17] Chen, D.; Zhang, Y.; Li, X.; Shen, J.; Chen, Z.; Cao, S-a.; Li, T.; Xu, F.

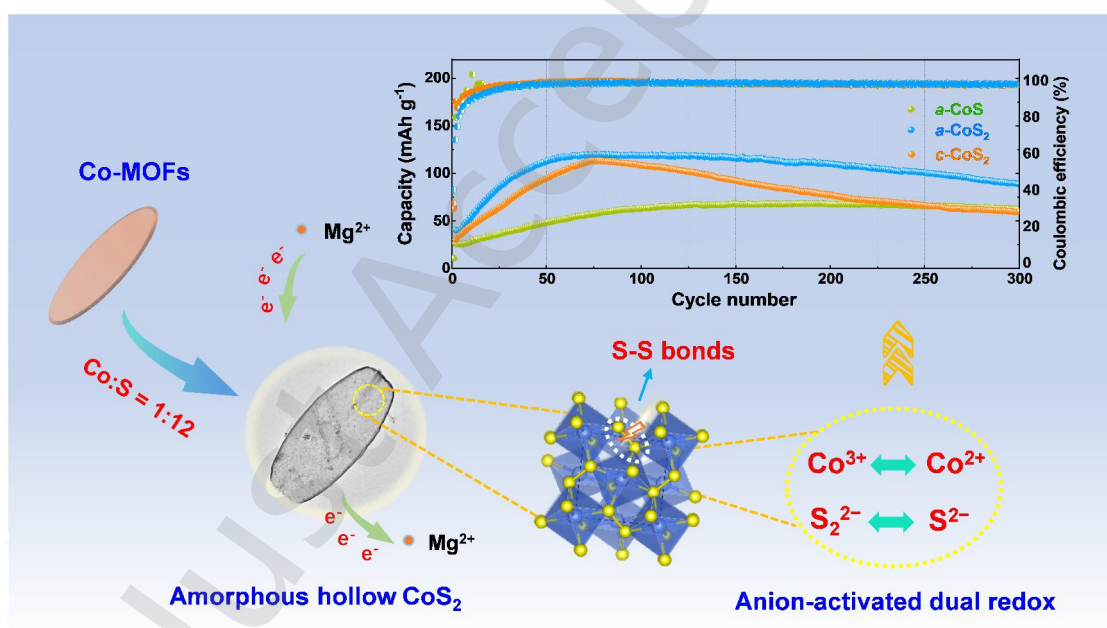
- Nanosheets assembling hierarchical starfish-like Cu_{2-x}Se as advanced cathode for rechargeable Mg batteries. *Chem. Eng. J.* **2020**, *384*, 123235.
- [18] He, D.; Wu, D.; Gao, J.; Wu, X.; Zeng, X.; Ding, W. Flower-like CoS with nanostructures as a new cathode-active material for rechargeable magnesium batteries. *J. Power Sources.* **2015**, *294*, 643-649.
- [19] Chen, D.; Du, F.; Cao, S-a.; Li, T.; Xu, F. $\text{Co}_{0.85}\text{Se}$ hollow polyhedrons entangled by carbon nanotubes as a high-performance cathode for magnesium secondary batteries. *Chem. Eng. J.* **2022**, *428*, 129545.
- [20] Chen, D.; Zhang, Y.; Li, X.; Shen, J.; Chen, Z.; Cao, S-a.; Li, T.; Xu, F. CoSe_2 hollow microspheres, nano-polyhedra and nanorods as pseudocapacitive Mg-storage materials with fast solid-state Mg^{2+} diffusion kinetics. *Nanoscale*, **2019**, *11*, 23173-23181.
- [21] Zhang, H-a.; Xiao, P.; Hu, C.; Tao, D.; Zhang, D.; Cao, Y.; Li, T.; Xu, F. Favorable orthorhombic phase cobalt diselenide cathode for rechargeable Mg batteries: Elucidating the significant impact of crystal structure on conversion-type Mg-storage reactions. *Adv. Funct. Mater.* **2025**, *35*, 2426006.
- [22] Chen, D.; Shen, J.; Li, X.; Cao, S-a.; Li, T.; Luo, W.; Xu, F. $\text{Ni}_{0.85}\text{Se}$ hexagonal nanosheets as an advanced conversion cathode for Mg secondary batteries. *J. Energy Chem.* **2020**, *48*, 226-323.
- [23] Hu, C.; Ran, L.; Zhang, H-a.; Cui, S.; Xu, F.; Zhang, D. H.; Li, T. In-situ generated elemental selenium nanograins cooperated with NiSe_2 microspheres for significantly enhanced magnesium-storage performance. *Chem. Eng. J.* **2023**, *478*, 147440.
- [24] Xue, X.; Huang, T.; Zhang, Y.; Qi, J.; Wei, F.; Sui, Y.; Jin, Z. Cationic-anionic redox chemistry in multivalent metal-ion batteries: Recent advances, reaction mechanism, advanced characterization techniques, and prospects. *Adv. Funct. Mater.* **2023**, *33*, 2306377.
- [25] Shen, Y.; Zhang, Q.; Wang, Y.; Gu, L.; Zhao, X.; Shen, X. A pyrite iron disulfide cathode with a copper current collector for high-energy reversible magnesium-ion storage. *Adv. Mater.* **2021**, *33*, 2103881.
- [26] Wang, J.; Tan, X.; Ng, M-F.; Wu, G.; Yang, G.; Ghosh, T.; Lim, C. Y. J.; Busayaporn, W.; Limphirat, W.; Kaewsuwan, D.; Chinnadurai, D.; Xing, Z.; Liu, H.; Ren, Y.; Yan, Q.; Seh, Z. W. Hybrid redox chemistry in defective

- titanium polyanion nanobelt cathodes for advanced magnesium-ion batteries. *Adv. Funct. Mater.* **2026**, *36*, e12519.
- [27] Zhang, Y.; Chen, D.; Li, X.; Shen, J.; Chen, Z.; Cao, S.-a.; Li, T.; Xu, F. a-MoS₃@CNT nanowire cathode for rechargeable Mg batteries: a pseudocapacitive approach for efficient Mg-storage. *Nanoscale* **2019**, *11*, 16043-16051.
- [28] Dey, S.; Lee, J.; Britto, S.; Stratford, J. M.; Keyzer, E. N.; Dunstan, M. T.; Cibir, G.; Cassidy, S. J.; Elgaml, M.; Grey, C. P. Exploring cation-anion redox processes in one-dimensional linear chain vanadium tetrasulfide rechargeable magnesium ion cathodes. *J. Am. Chem. Soc.* **2020**, *142*, 19588-19601.
- [29] Reupert, A.; Schleicher, H.; Hu, Y.; Fuchs, S.; Dillenz, M.; Borca, C. N.; Huthwelker, T.; Groß, A.; Fichtner, M.; Li, Z. Solid-state synthesis of phase-pure micron-sized patronite vanadium tetrasulfide toward practical magnesium batteries. *Small Struct.* **2025**, *6*, 2400518.
- [30] Tao, D.; Ran, L.; Li, T.; Cao, Y.; Xu, F. 3D Tunnel copper tetrathiovanadate nanocube cathode achieving ultrafast magnesium storage reactions through a charge delocalization and displacement mechanism. *ACS Nano*. **2024**, *18*, 28810-28821.
- [31] Li, T.; Ran, L.; Li, H.; Zhang, D.; Xu, F. Amorphous cobalt polyselenides with hyperbranched polymer additive as high-capacity magnesium storage cathode materials through cationic and anionic co-redox mechanism. *Small* **2024**, *20*, 2400903.
- [32] Tao, D.; Li, T.; Tang, Y.; Gui, H.; Cao, Y.; Xu, F. Cu₃VSe₄ Cathode for rechargeable magnesium batteries: Favorable chemical and electronic structures inducing intercalation and displacement reactions. *Adv. Funct. Mater.* **2024**, *34*, 2411223.
- [33] Wang, S.; Zhao, X. Minireview on metal-chalcogenide cathode materials with dual-redox centers for magnesium-metal-anode-based batteries: Recent progress and future directions. *Energy. Fuels.* **2023**, *37*, 18441-18455.
- [34] Shu, T.; Wang, H.; Li, Q.; Feng, Z.; Wei, F.; Yao, K. X.; Sun, Z.; Qi, J.; Sui, Y. Highly stable Co₃O₄ nanoparticles/carbon nanosheets array derived from flake-like ZIF-67 as an advanced electrode for supercapacitor. *Chem. Eng. J.* **2021**, *419*, 129631.

- [35] Ma, D.; Hu, B.; Wu, W.; Liu, X.; Zai, J.; Shu, C.; Tsega, T. T.; Chen, L.; Qian, X.; Liu, T. L. Highly active nanostructured CoS₂/CoS heterojunction electrocatalysts for aqueous polysulfide/iodide redox flow batteries. *Nat. Commun.* **2019**, *10*, 3367.
- [36] Yin, B.; Cao, X.; Pan, A.; Luo, Z.; Dinesh, S.; Lin, J.; Tang, Y.; Liang, S.; Cao, G. Encapsulation of CoS_x nanocrystals into N/S co-doped honeycomb-like 3D porous carbon for high-performance lithium Storage. *Adv. Sci.* **2018**, *5*, 1800829.
- [37] Guo, Y.; Shang, C.; Wang, E. An efficient CoS₂/CoSe₂ hybrid catalyst for electrocatalytic hydrogen evolution. *J. Mater. Chem. A.* **2017**, *5*, 2504.
- [38] Han, X.; Wu, X.; Deng, Y.; Liu, J.; Lu, J.; Zhong, C.; Hu, W. Ultrafine Pt nanoparticle-decorated pyrite-type CoS₂ nanosheet arrays coated on carbon cloth as a bifunctional electrode for overall water splitting. *Adv. Energy Mater.* **2018**, *8*, 1800935.
- [39] Lu, Q.; Yu, J.; Zou, X.; Liao, K.; Tan, P.; Zhou, W.; Ni, M.; Shao, Z. Self-catalyzed growth of Co, N-codoped CNTs on carbon-encased CoS_x surface: A noble-metal-free bifunctional oxygen electrocatalyst for flexible solid Zn-air batteries. *Adv. Funct. Mater.* **2019**, *29*, 1904481.
- [40] Liu, F.; Wang, T.; Liu, X.; Jiang, N.; Fan, L-Z. High-performance heterojunction Ti₃C₂/CoSe₂ with both intercalation and conversion storage mechanisms for magnesium batteries. *Chem. Eng. J.* **2021**, *426*, 130747.
- [41] Yang, S.; Ji, F.; Wang, Z.; Zhu, Y.; Hu, K.; Ouyang, Y.; Wang, R.; Ma, X.; Cao, C. Microwave-assisted synthesis of CuSe nano-particles as a high-performance cathode for rechargeable magnesium batteries. *Electrochim. Acta.* **2019**, *324*, 134864.
- [42] Murgia, F.; Antitomaso, P.; Stievano, L.; Monconduit, L.; Berthelot, R. Express and low-cost microwave synthesis of the ternary Chevrel phase Cu₂Mo₆S₈ for application in rechargeable magnesium batteries. *J. Solid State Chem.* **2016**, *242*, 151-154.
- [43] Liang, Y.; Yoo, H. D.; Li, Y.; Shuai, J.; Calderon H. A.; Hernandez, F. C. R.; Grabow, L. C.; Yao, Y. Interlayer-expanded molybdenum disulfide nanocomposites for electrochemical magnesium storage. *Nano Lett.* **2015**, *15*, 2194-2202.

- [44] Zhang, Y.; Li, X.; Shen, J.; Chen, Z.; Cao, S-a.; Li, T.; Xu, F. Rechargeable Mg batteries based on a Ag₂S conversion cathode with fast solid-state Mg²⁺ diffusion kinetics. *Dalton Trans.* **2019**, *48*, 14390.
- [45] Zhang, Y.; Li, T.; Cao, S-a.; Luo, W.; Xu, F. NiCo₂Se₄ Hierarchical microflowers of nanosheets and nanorods as pseudocapacitive Mg-storage materials. *ACS Sustainable Chem. Eng.* **2020**, *8*, 2964-2972.
- [46] Chen, D.; Zhang, Y.; Shen, J.; Li, X.; Chen, Z.; Cao, S-a.; Li, T.; Xu, F. Facile synthesis and electrochemical Mg-storage performance of Sb₂Se₃ nanowires and Bi₂Se₃ nanosheets. *Dalton Trans.* **2019**, *48*, 17516.
- [47] Ha, J. H.; Lee, B.; Kim, J. H.; Cho, B. W.; Kim, S-O.; Oh, S. H. Silver chalcogenides (Ag₂X, X=S, Se) nanoparticles embedded in carbon matrix for facile magnesium storage via conversion chemistry. *Energy Storage Mater.* **2020**, *27*, 459-465.
- [48] Zhou, L.; Xiong, F.; Tan, S.; An, Q.; Wang, Z.; Yang, W.; Tao, Z.; Yao, Y.; Chen, J.; Mai, L. Nickel-iron bimetallic diselenides with enhanced kinetics for high-capacity and long-life magnesium batteries. *Nano Energy.* **2018**, *54*, 360-366.
- [49] Wei, L.; Lian, R.; Zhao, Y.; Meng, Y.; He, L.; Yu, Y.; Chen, G.; Wei, Y. Experimental investigation and first-principles calculations of a Ni₃Se₄ cathode material for Mg-ion batteries. *ACS Appl. Mater. Interfaces.* **2020**, *12*, 9316-9321.
- [50] Yang, T.; Qi, Y.; Zhong, W.; Tao, M.; Guo, B.; Wu, Y.; Bao, S-J.; Xu, M. A strategy for polysulfides/polyselenides protection based on Co₉S₈@SiO₂/C host in Na-SeS₂ batteries. *Adv. Funct. Mater.* **2021**, *31*, 2001952.
- [51] Luo, T.; Wang, Y.; Elander, B.; Goldstein, M.; Mu, Y.; Wilkes, J.; Fahrenbruch, M.; Lee, J.; Li, T.; Bao, J. L.; Mohanty, U.; Wang, D. Polysulfides in magnesium-sulfur batteries. *Adv. Mater.* **2024**, *36*, 2306239.

Table of Contents (TOC)



MOF-derived amorphous CoS_2 hollow nanoleaves with a dual anionic/cationic redox Mg-storage mechanism deliver a high reversible capacity of 195 mAh g^{-1} at 50 mA g^{-1} , an outstanding rate capability, and durable cyclability with 74.6% capacity retention.

Electronic Supplementary Material

Anion-activated dual redox in amorphous CoS₂ hollow nanoleaves for advanced magnesium storage cathodes

Lin Ran^{1,§}, Zhen Qin^{1,§}, Jianni Li¹, Fei Xu², Daohong Zhang^{1,3*}, and Ting Li^{1,3*}

¹ Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications, South-Central Minzu University, Wuhan 430074, China

² Key Laboratory of Hydraulic Machinery Transients, Ministry of Education, School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China

³ Guangdong Provincial Laboratory of Chemistry and Fine Chemical Engineering Jieyang Center, Jieyang 515200, China

[§] Lin Ran and Zhen Qin contributed equally to this work.

*Address correspondence to Ting Li, liting@mail.scuec.edu.cn; Daohong Zhang, daohong.zhang@scuec.edu.cn

Supporting information to <https://doi.org/10.26599/NR.2026.94909136>

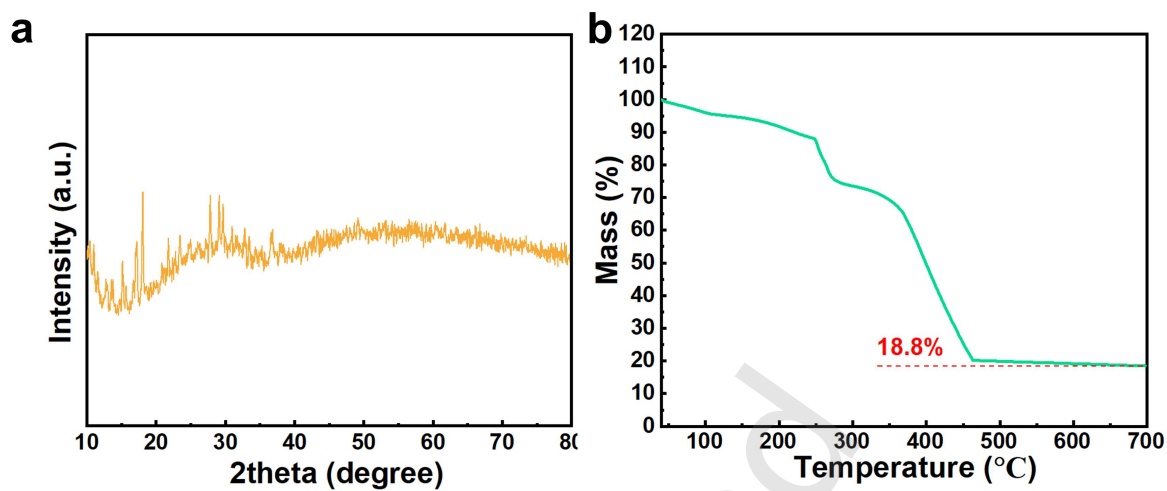


Figure S1. (a) XRD pattern and (b) TGA curve of Co-MOFs.

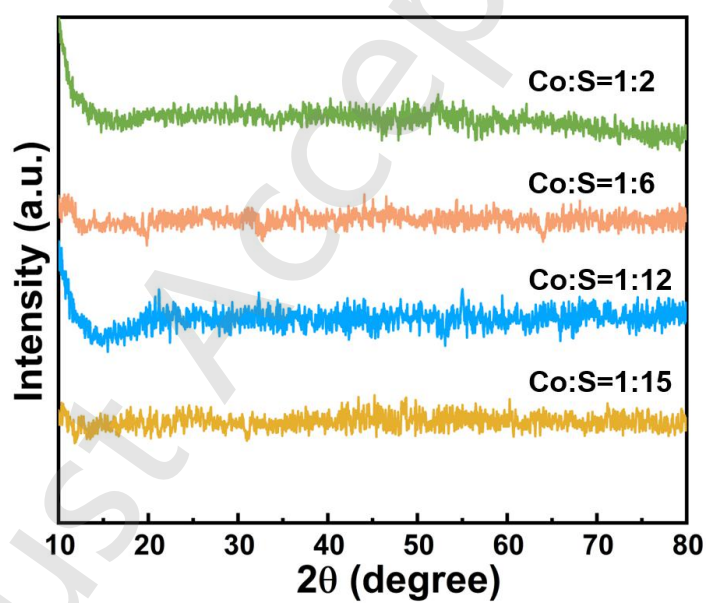


Figure S2. XRD patterns of samples prepared with different Co/S raw ratios.

Table S1. ICP-OES analysis results of *a*-CoS and *a*-CoS₂ samples

Sample	Element content		Element ratio
	Co ($\mu\text{g mg}^{-1}$)	S ($\mu\text{g mg}^{-1}$)	Co/S
<i>a</i> -CoS	476.647	241.160	1:0.93
<i>a</i> -CoS ₂	359.745	375.770	1:1.92

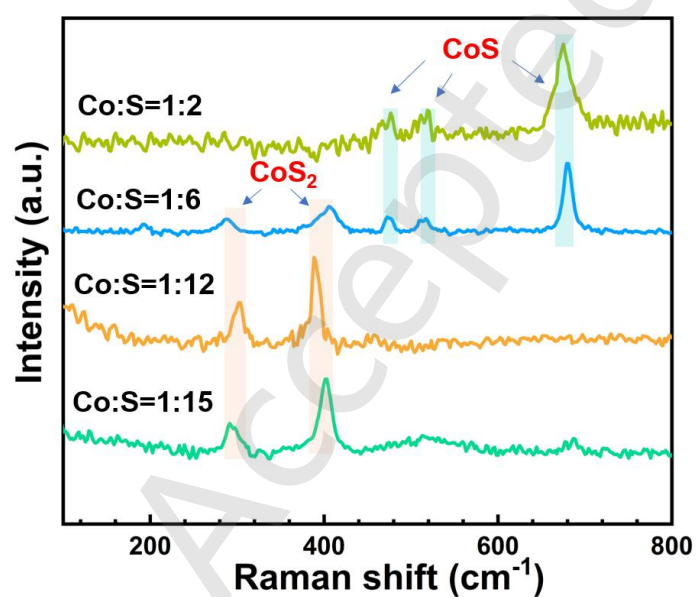


Figure S3. Raman spectra of samples prepared with different Co/S raw ratios.

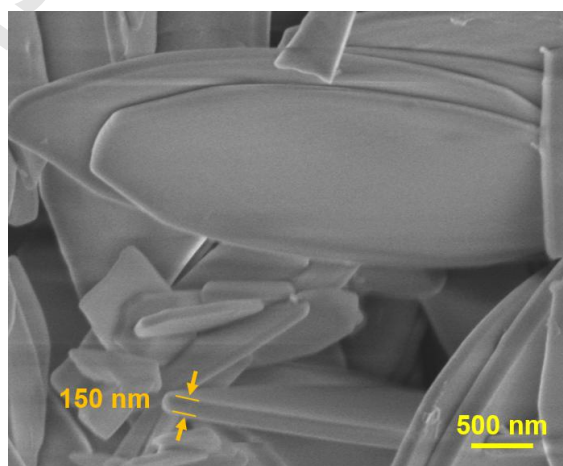


Figure S4. SEM image of Co-MOFs.

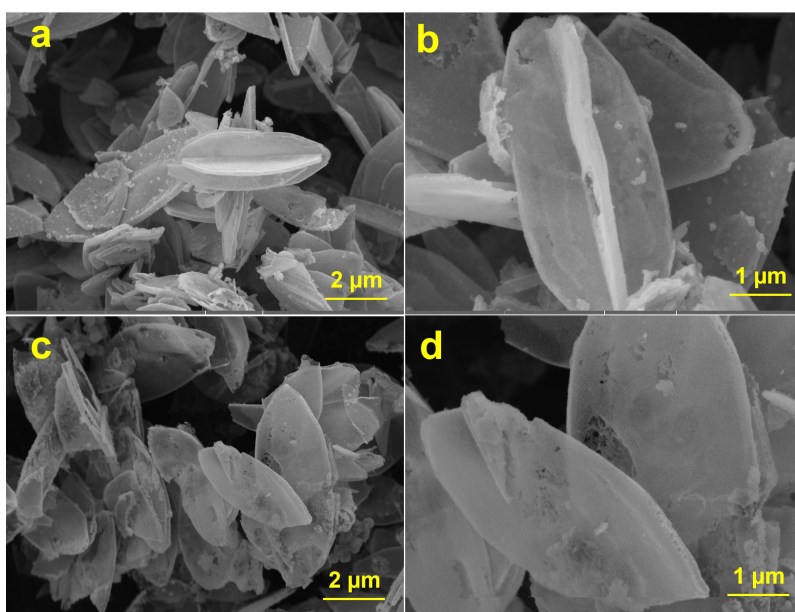


Figure S5. SEM images of the samples prepared with Co/S raw ratios of (a,b) 1:6, (c,d) 1:15.

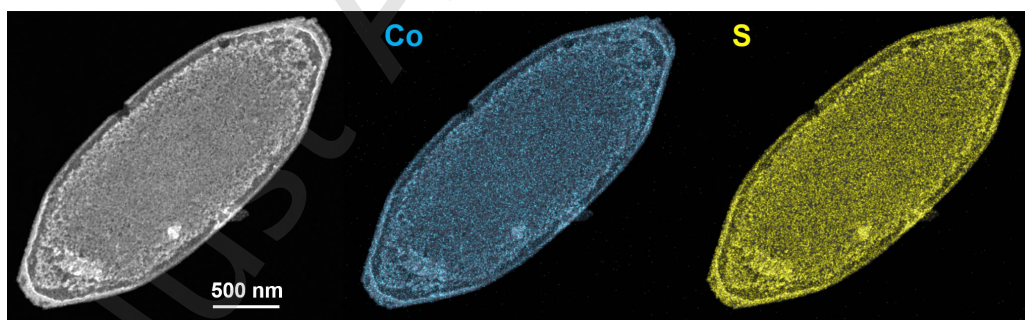


Figure S6. HAADF STEM image and EDS element mapping images of *c*-CoS₂ sample.

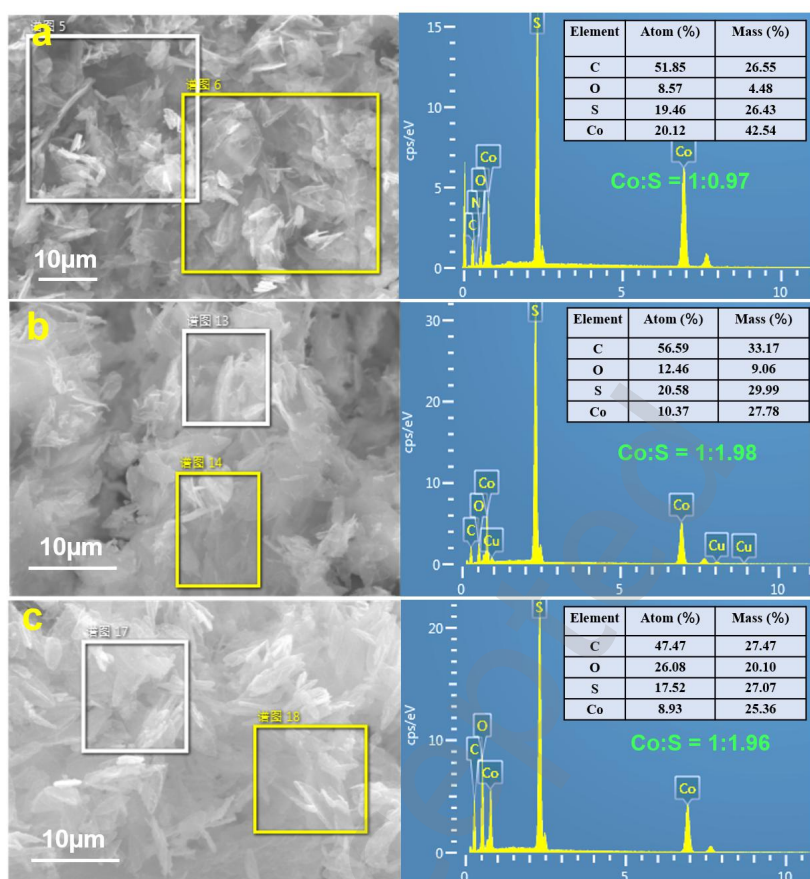


Figure S7. EDS spectra of (a) *a*-CoS, (b) *a*-CoS₂ and (c) *c*-CoS₂.

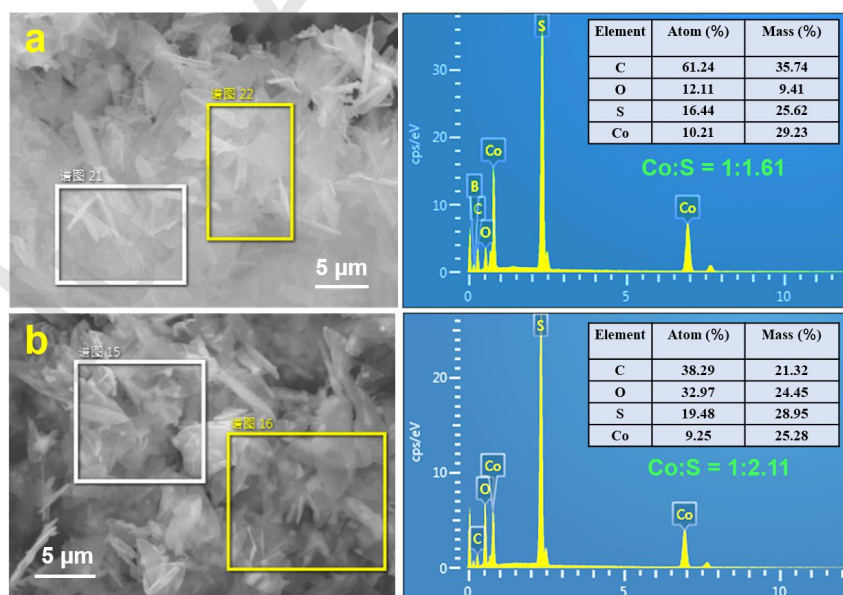


Figure S8. EDS spectra of the samples prepared with Co/S raw ratios of (a) 1:6, (b) 1:15.

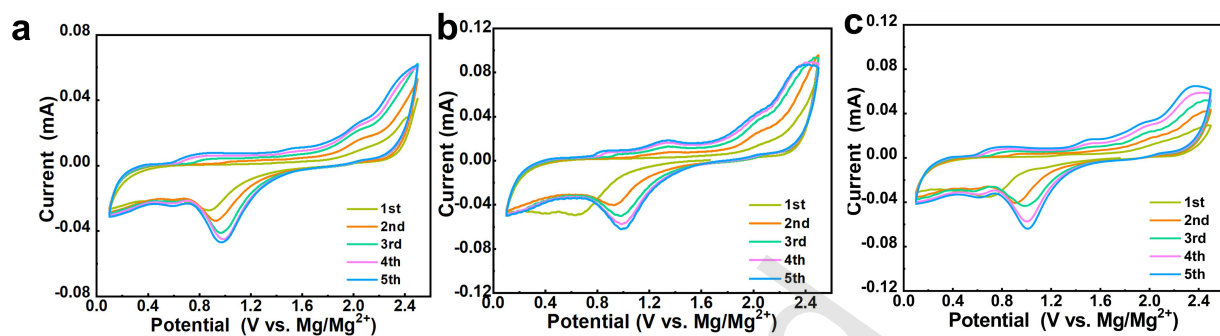


Figure S9. CV curves of (a) *a*-CoS, (b) *a*-CoS₂ and (c) *c*-CoS₂ cathodes at a scan rate of 0.1 mV s⁻¹ between 0.1 and 2.5 V

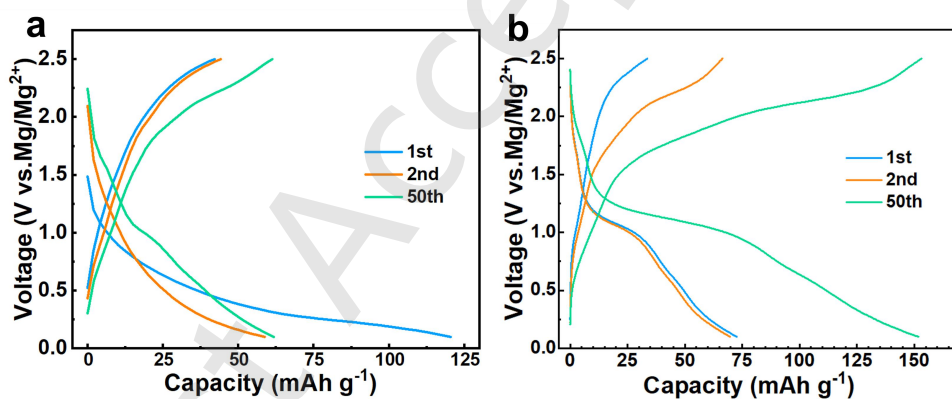


Figure S10. Charge/discharge profiles of (a) *a*-CoS and (b) *c*-CoS₂ cathodes at 50 mA g⁻¹ between 0.1 and 2.5 V.

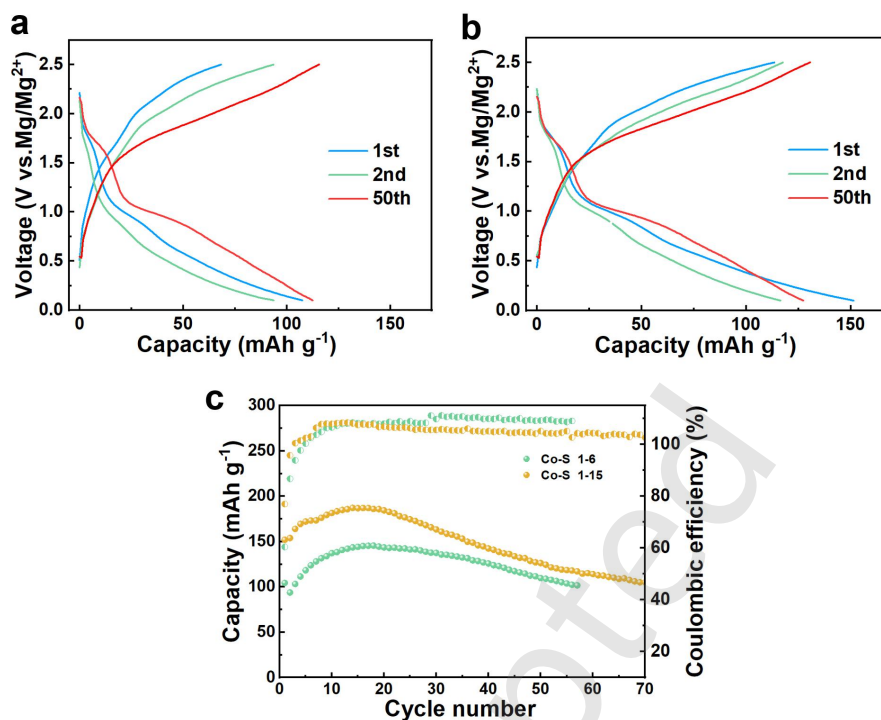


Figure S11. Charge/discharge curves of electrodes with Co/S raw ratios of (a) 1:6, (b) 1:15. (c) Cycling performance of electrodes with Co/S raw ratios of 1:6 and 1:15.

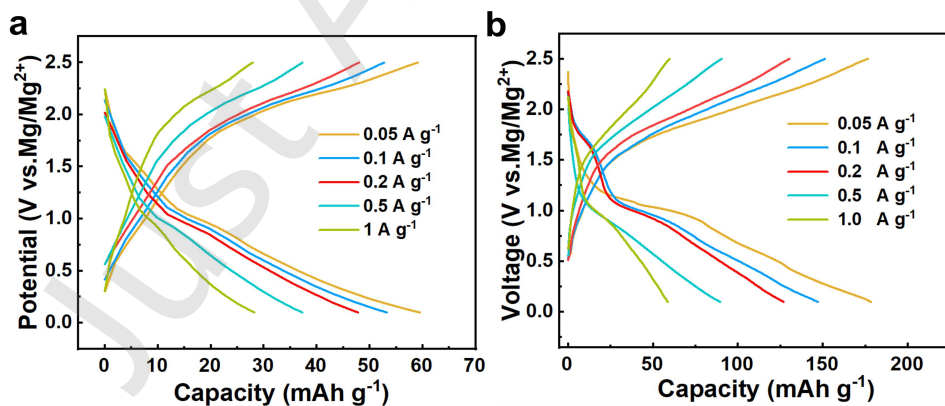


Figure S12. Charge/discharge curves of (a) *a*-CoS and (b) *c*-CoS₂ cathodes at various current densities.

Table S2 Comparison of Mg-storage capacity of as-prepared *a*-CoS₂ cathode with previous reported chalcogenide cathodes.

Materials	Electrolyte	Voltage range(V)	Current density (mA g ⁻¹)	Capacity (mAh g ⁻¹)	Ref
a-CoS ₂	Mg(HMDS) ₂ -AlCl ₃ -MgCl ₂ /G4	0.1~2.5	50	195.1	This work
			1000	71.5	This work
CoS	0.25 M Mg(AlCl ₂ EtBu) ₂ /THF	0.1-2.0	50	125	[1]
			150	112	[1]
Mo ₆ S ₈	2(PhMgCl)-AlCl ₃ /THF	0.5~1.75	20	92.0	[2]
			120	51.5	[2]
TiS ₂	1 M Mg(ClO ₄) ₂ /ACN	0.1~2.0	50	97	[3]
MoS ₂	0.25 M Mg(AlCl ₂ EtBu) ₂ /THF	0.01~2.2	50	76.0	[4]
VS ₂	0.4 M (PhMgCl) ₂ -AlCl ₃ /THF	0.5-2.0	120	64.5	[5]
			600	41.5	[5]
Cu ₂ MoS ₄	Mg(HMDS) ₂ -AlCl ₃ -MgCl ₂ /G4	0.2-2.7	50	180	[6]
			1000	45	[6]
WS ₂	1.3 M Mg(AlCl ₂ EtBu) ₂ /THF	0.01-2.5	20	82.5	[7]
VS ₄	2(PhMgCl)-AlCl ₃ /THF	0.2-2.2	50	75	[8]
			300	60	[8]
Ag ₂ S	Mg(HMDS) ₂ -AlCl ₃ -MgCl ₂ /G4	0.1-2.5	50	120	[9]
			500	75	[9]
NiCo ₂ Se ₄	Mg(HMDS) ₂ -AlCl ₃ -MgCl ₂ /G4	0.01~2.8	50	145	[10]
			2000	40	[10]
H-CoSe ₂	Mg(HMDS) ₂ -AlCl ₃ -MgCl ₂ /G4	0.01~2.6	50	110	[11]
			5000	77.6	[11]
Co _{0.85} Se/CNTs	Mg(HMDS) ₂ -AlCl ₃ -MgCl ₂ /G4		50	194	[12]

Table S3 EIS simulation results of α -CoS, α -CoS₂ and c -CoS₂ cathodes at the 1st and 50th cycles using the equivalent circuit as below.

Cycle	α -CoS		α -CoS ₂		c -CoS ₂	
	R_s (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{ct} (Ω)
1 st	60.2	752.7	12.5	522.9	58.2	899.7
50 th	16.9	545.5	52.1	90.4	89.6	82.9

R_s and R_{ct} are the resistances of solid electrolyte interface (SEI) film and charge transfer, respectively.

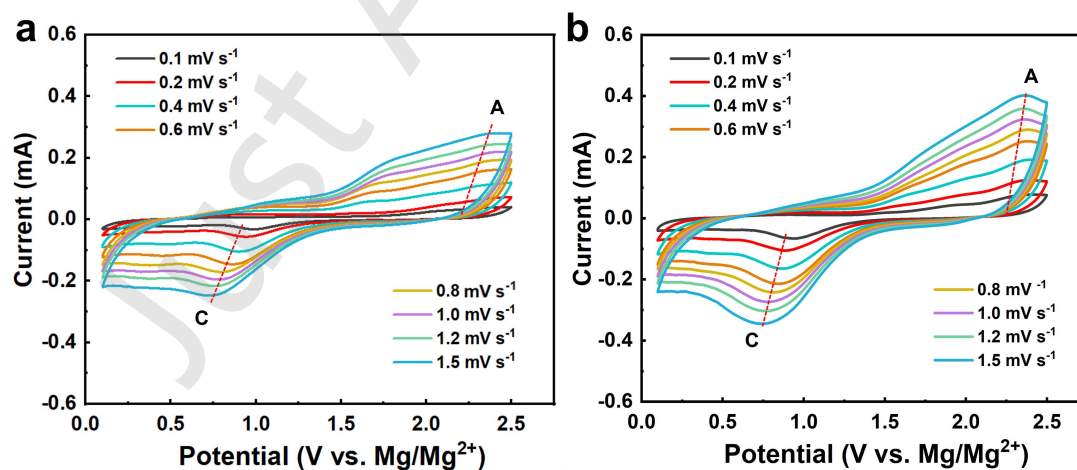


Figure S13. CV curves of (a) α -CoS and (b) c -CoS₂ cathodes at different scan rates.

Table S4 Calculation results of apparent Mg^{2+} diffusion coefficients ($D_{\text{Mg}^{2+}}$) from CV.

Peak	<i>a</i> -CoS		<i>a</i> -CoS ₂		<i>c</i> -CoS ₂	
	$i_p/v^{1/2}$	$D (\times 10^{-11} \text{ cm}^2 \text{ s}^{-1})$	$i_p/v^{1/2}$	$D (\times 10^{-11} \text{ cm}^2 \text{ s}^{-1})$	$i_p/v^{1/2}$	$D (\times 10^{-11} \text{ cm}^2 \text{ s}^{-1})$
C	0.0123	0.6155	0.0175	0.8704	0.0096	0.5816
A	0.0201	1.1836	0.0372	2.1813	0.0117	1.0267

The Mg^{2+} diffusion coefficient is calculated by the following equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C_0 \quad (\text{S1})$$

where i_p is the peak current (A), n is the number of electrons per molecule during the reaction, A is the contact area between the electrode and electrolyte, D is the diffusion coefficient of Mg^{2+} ($\text{cm}^2 \text{ s}^{-1}$), C_0 is the concentration of Mg^{2+} in the electrode material (mol m^{-3}), and v is the scan rate (V s^{-1}).

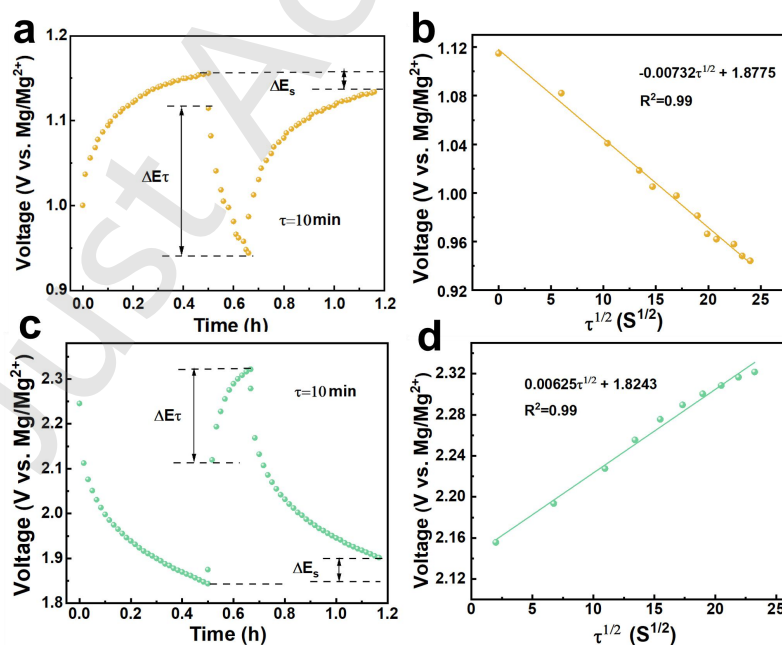


Figure S14. A single GITT titration and the corresponding linear behavior of E vs. $\tau^{1/2}$ relationship of *a*-CoS₂ electrode (a, b) discharged from 1.11 V to 0.95 V, (c, d) charged from 2.10 V to 2.32 V.

The Mg-ion diffusion coefficients ($D_{\text{Mg}^{2+}}$) can be calculated based on the following equation:

$$D_{\text{Mg}^{2+}} = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad (\text{S2})$$

where V_m , M_B and m_B are the molar volume, the molar mass and the weight of the compound, respectively, A is the active surface area of the electrode, τ is the charging or discharging time within one procedure, ΔE_τ and ΔE_s represent the total voltage change during the current pulse and the steady-state voltage change at the plateau potential, respectively.

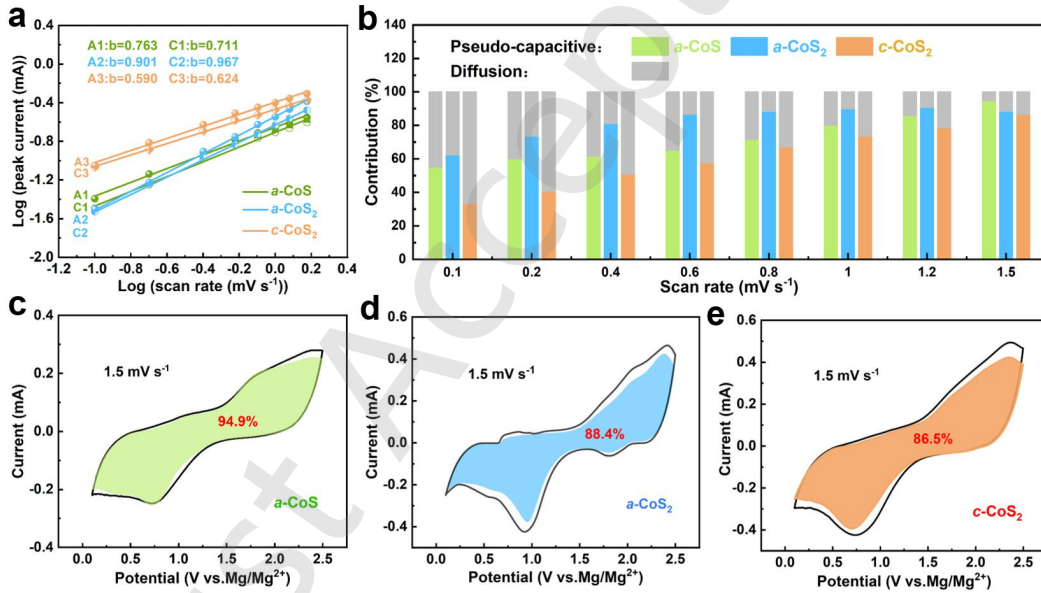


Figure S15. (a) Linear relationship of log (peak current) versus log (scan rate) plots of the redox peaks and (b) pseudo-capacitive capacity contribution comparison at different scan rates of *a*-CoS, *a*-CoS₂ and *c*-CoS₂. Pseudo-capacitive capacity contribution of (c) *a*-CoS, (d) *a*-CoS₂ and (e) *c*-CoS₂ at 1.5 mV s⁻¹.

The b value is calculated by following equation:

$$i = av^b \quad (\text{S3})$$

here i is current, a is a constant and v is the sweep rate. The b -value can change from 0.5 (semi-infinite diffusion) to 1 (capacitive processes).

The pseudocapacitive contribution is calculated following the equation:

$$i = k_1v + k_2v^{1/2} \quad (\text{S4})$$

where k_1 and k_2 are coefficients of capacitive and diffusion contribution, respectively.

The k_1 -values could be acquired by following the equation through the linear

relationship of $i/v^{1/2}$ versus $v^{1/2}$ at fixed potentials.

$$i/v^{1/2} = k_1 v^{1/2} + k_2 \quad (S5)$$

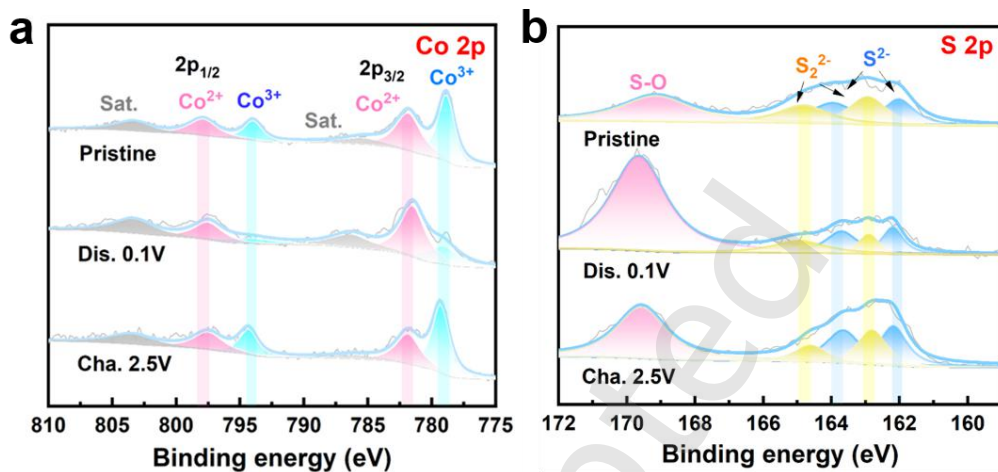


Figure S16. Ex-situ (a) Co 2p and (b) S 2p XPS spectra of *c*-CoS₂ electrodes at discharge/charge states.

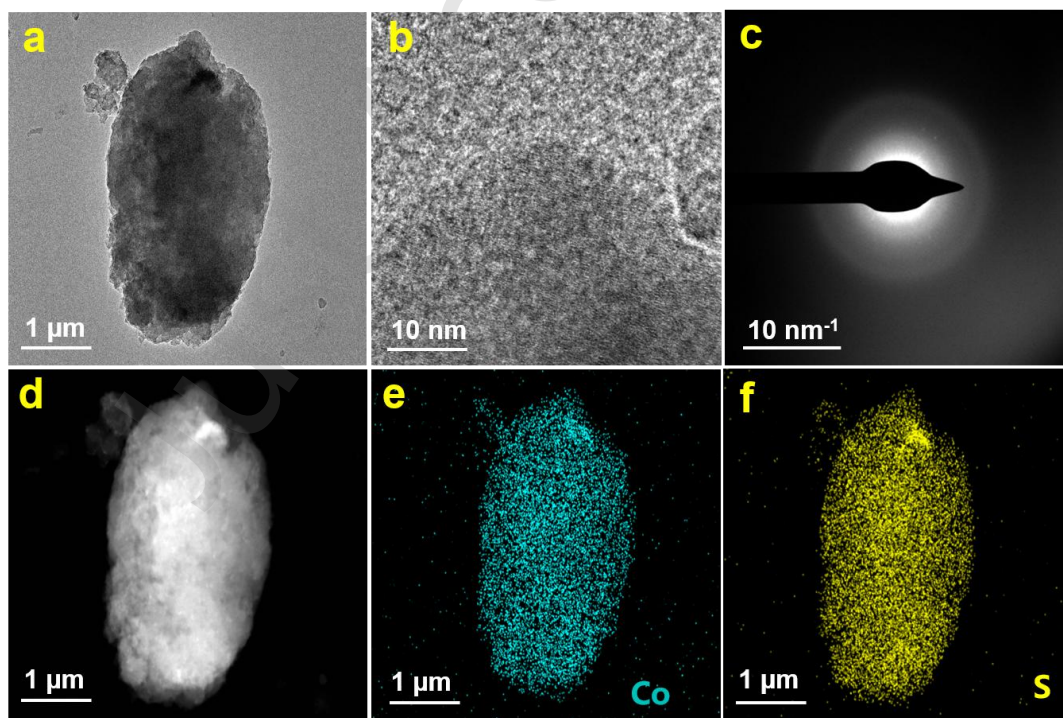


Figure S17. (a) TEM image, (b) HRTEM image, (c) corresponding SAED pattern, (d-f) HAADF STEM image and EDS element mapping images of *a*-CoS₂ electrode after 50 cycles.

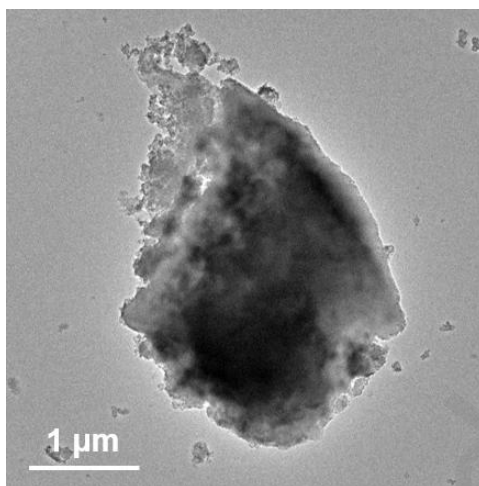


Figure S18. TEM image of *c*-CoS₂ electrode after 50 cycles.

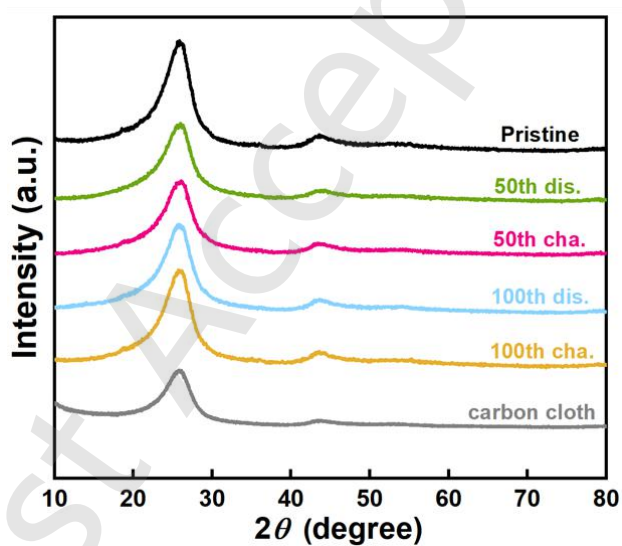


Figure S19. Ex-situ XRD patterns of *a*-CoS₂ electrode at discharge and charge states after 50 and 100 cycles

References

- [1] He, D.; Wu, D.; Gao, J.; Wu, X.; Zeng, X.; Ding, W. Flower-like CoS with nanostructures as a new cathode-active material for rechargeable magnesium batteries. *J. Power Sources*. **2015**, *294*, 643-649.
- [2] Saha, P.; Jampani, P. H.; Datta, M. K.; Hong, D.; Gattu, B.; Patel, P.; Kadakia, K. S.; Manivannan, A.; Kumta, P. N. A rapid solid-state synthesis of electrochemically active chevrel phases (Mo_6T_8 ; T=S, Se) for rechargeable magnesium batteries. *Nano Res.* **2017**, *10*, 4415-4435.
- [3] Tao, Z-L.; Xu, L-N.; Gou, X-L.; Chen, J.; Yuan, H-T. TiS_2 nanotubes as the cathode materials of Mg-ion batteries. *Chem. Commun.* **2004**, 2080-2081.
- [4] Liu, Y.; Jiao, L.; Wu, Q.; Zhao, Y.; Cao, K.; Liu, H.; Wang, Y.; Yuan, H. Synthesis of rGO-supported layered MoS_2 for high-performance rechargeable Mg batteries. *Nanoscale*. **2013**, *5*, 9562-9567.
- [5] Wang, M.; Yagi, S. Redox behavior of VS_2 nanosheets in Grignard reagent-based electrolyte. *Mater. Lett.* **2020**, *273*, 127914.
- [6] Zhang, Y.; Li, T.; Cao, S-a.; Luo, W.; Xu, F. Cu_2MoS_4 hollow nanocages with fast and stable Mg^{2+} -storage performance. *Chem. Eng. J.* **2020**, *387*, 124125.
- [7] Latha, M.; Biswas, S.; Rani, J. V. Application of WS_2 -G composite as cathode for rechargeable magnesium batteries. *Ionics*. **2020**, *26*, 3395-3404.
- [8] Li, Z.; Ding, S.; Yin, J.; Zhang, M.; Sun, C.; Meng, A. Morphology-dependent electrochemical performance of VS_4 for rechargeable magnesium battery and its magnesiation/ demagnesiation mechanism. *J. Power Sources*. **2020**, *451*, 227815.
- [9] Zhang, Y.; Li, X.; Shen, J.; Chen, Z.; Cao, S-a.; Li, T.; Xu, F. Rechargeable Mg batteries based on a Ag_2S conversion cathode with fast solid-state Mg^{2+} diffusion kinetics, *Dalton Trans.* **2019**, *48*, 14390-14397.
- [10] Zhang, Y.; Li, T.; Cao, S-a.; Luo, W.; Xu, F. NiCo_2Se_4 Hierarchical microflowers of nanosheets and nanorods as pseudocapacitive Mg-storage materials. *ACS Sustainable Chem. Eng.* **2020**, *8*, 2964-2972.
- [11] Chen, D.; Zhang, Y.; Li, X.; Shen, J.; Chen, Z.; Cao, S-a.; Li, T.; Xu, F. CoSe_2 hollow microspheres, nano-polyhedra and nanorods as pseudocapacitive Mg-storage materials with fast solid-state Mg^{2+} diffusion kinetics. *Nanoscale*, **2019**, *11*, 23173-23181.
- [12] Chen, D.; Du, F.; Cao, S-a.; Li, T.; Xu, F. $\text{Co}_{0.85}\text{Se}$ hollow polyhedrons entangled by carbon nanotubes as a high-performance cathode for magnesium secondary batteries. *Chem. Eng. J.* **2022**, *428*, 129545.