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Monolayer MoS₂ Fabricated by In Situ Construction of Interlayer Electrostatic Repulsion Enables Ultrafast Ion Transport in Lithium-Ion Batteries

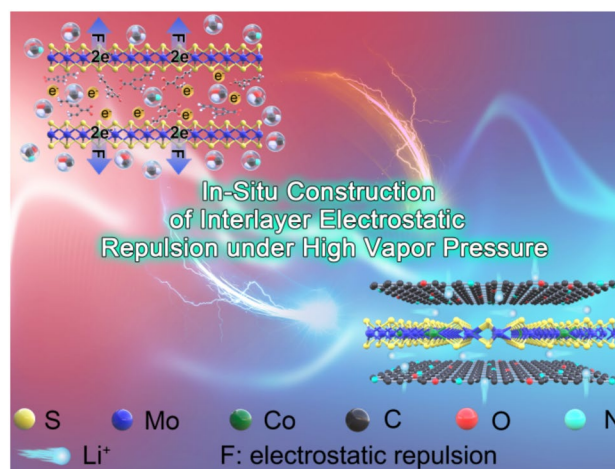
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HIGHLIGHTS

- In-situ construction of electrostatic repulsion between MoS₂ interlayers is first proposed to successfully prepare Co-doped monolayer MoS₂ under high vapor pressure.
- The doped Co atoms radically decrease bandgap and lithium ion diffusion energy barrier of monolayer MoS₂ and can be transformed into ultrasmall Co nanoparticles (~2 nm) to induce strong surface-capacitance effect during conversion reaction.
- The Co doped monolayer MoS₂ shows ultrafast ion transport capability along with ultrahigh capacity and outstanding cycling stability as lithium-ion-battery anodes.

ABSTRACT High theoretical capacity and unique layered structures make MoS₂ a promising lithium-ion battery anode material. However, the anisotropic ion transport in layered structures and the poor intrinsic conductivity of MoS₂ lead to unacceptable ion transport capability. Here, we propose in-situ construction of interlayer electrostatic repulsion caused by Co²⁺ substituting Mo⁴⁺ between MoS₂ layers, which can break the limitation of interlayer van der Waals forces to fabricate monolayer MoS₂, thus establishing isotropic ion transport paths. Simultaneously, the doped Co atoms change the electronic structure of monolayer MoS₂, thus improving its intrinsic conductivity. Importantly, the doped Co atoms can be converted into Co nanoparticles to create a space charge region to accelerate ion transport. Hence, the Co-doped monolayer MoS₂ shows ultrafast lithium ion transport capability in half/full cells. This work presents a novel route for the preparation of monolayer MoS₂ and demonstrates its potential for application in fast-charging lithium-ion batteries.



KEYWORDS Monolayer MoS₂; Interlayer electrostatic repulsion; Co atoms doping; Surface-capacitance effect; Fast-charging lithium-ion batteries

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1 Introduction

Lithium-ion batteries (LIBs) have been extensively commercialized in portable electronics and electrical vehicles (EVs) [1]. Over the past decade, graphite has shown great success as the dominant anode material. However, its small interlayer distance (0.334 nm) and anisotropic ion transport channel have severely limited further advancement of the ion transport rate, which is unable to reach the requirements of fast-charging LIBs for EVs [2]. Moreover, its advancement in fast-charging LIBs has also been delayed owing to its low theoretical capacity [3]. To explore alternatives to graphite, high-performance anode materials such as metals [4], transition metal dichalcogenides (MoS₂, etc.) [5–9], transition metal oxides [10], metal selenides (In₂Se₃, etc.) [11], SiO_x (x < 2) [12–14], and graphene [15] have been investigated, which are critical to break the fast-charging bottleneck of graphite LIBs.

MoS₂ with interlayer spacing of 0.62 nm and lithium-ion storage capacity of 670 mAh g⁻¹ looks very attractive [6, 7]. But the anisotropic ion transport channels caused by the layered nanostructure and poor electrical conductivity (EC) due to its inherent semiconducting properties cause unacceptable ion transport performance in fast-charging LIBs [9]. Based on these limitations, strategies such as designing MoS₂ nanostructure [16, 17], enlarging MoS₂ interlayer spacing [18], doping MoS₂ [19], reducing MoS₂ layers number [20], and fabricating composites of MoS₂/carbon [6, 7, 9] have been proposed. Although these routes have greatly improved the lithium-ion transport capability of MoS₂, the anisotropic ion transport features due to the native layered structure of MoS₂ are not fundamentally changed, which inevitably leads to the same ion transport capability. The fabrication of monolayer MoS₂ can be considered as the most effective route to circumvent the tricky problem due to the completely open ion transport pathway owing to the disappearance of layered structure [21]. The current preparation routes of monolayer MoS₂ can be divided into two categories: (i) substrate growth, including chemical vapor deposition [21], epitaxy method [22], magnetron sputtering [23], etc.; (ii) bulk exfoliation, including scotch tape method [24], liquid ultrasonic method [25], chemically exfoliated method [26], etc. The first category is the synthesis of monolayer MoS₂ membrane, not powder, which is inappropriate as LIB anode. The latter can achieve monolayer MoS₂

powder but has low monolayer performance. Furthermore, the obtained monolayer MoS₂ powder, which suffers from severe agglomeration, must be dispersed in solution and their poor EC is not improved, which is disadvantageous for application in fast-charging LIBs. In order to handle this tricky problem, the interoverlapped structure of monolayer MoS₂ and monolayer carbon has been successfully constructed by solvothermal [27, 28] and with the help of CTAB [29], which can prevent monolayer MoS₂ agglomeration and improve its EC. However, such interoverlapping structure reintroduces anisotropic ion transport features between monolayer MoS₂ and monolayer carbon, which is unfavorable for the full reflection of intrinsic ion transport capability of monolayer MoS₂. With the aim of solving this problem, monolayer MoS₂/carbon composites, in which monolayer MoS₂ is uniformly dispersed into carbon matrix, have been synthesized by electrospinning [30], dual-template route [31], and emulsion-templated solvothermal route [32]. This completely eliminates anisotropic ion transport features, thus obtaining high capacity (1267 mAh g⁻¹ at 0.1 A g⁻¹) and good rate capability (60.6% capacity retention at 10 A g⁻¹ relative to the capacity obtained at 0.1 A g⁻¹). Although the electrochemical performances of MoS₂ have been improved in these researches, some problems are still waiting to be solved. Generally, under the same areal capacity, higher specific capacity makes active materials with less mass loading, thus resulting in thinner electrodes, which certainly increases the ion transport rate throughout the electrode. However, the addition of low-capacity carbon materials inevitably reduces the capacity of the composites, which has an adverse effect on rate performances. The introduction of active materials with high capacity has been the key to solving this problem. Additionally, the intrinsic semiconductor properties of monolayer MoS₂ have not been fundamentally changed, which certainly decreases ion transport capability in basal plane of monolayer MoS₂. For these problems, it is vital and urgent to seek a new preparative technology of monolayer MoS₂ to spur monolayer MoS₂ application in fast-charging LIBs.

Herein, we report a facile route that Co²⁺ in situ substitution of Mo⁴⁺ induces negative charges in MoS₂ to in situ construction of electrostatic repulsion in the interlayer of MoS₂ under high-pressure vapor phase, along with vast gaseous groups insertion, can effectively separate MoS₂ layers, thus obtaining monolayer MoS₂. Meanwhile, the gaseous groups can be transformed into N,O codoped carbon

substrate to effectively suppress agglomeration and re-stacking of Co-doped monolayer MoS₂, thus obtaining the unique nanostructure that Co-doped monolayer MoS₂ uniformly dispersed into N, O codoped carbon matrix (CoMoS₂/C). As LIB anode, the CoMoS₂/C has the following advantages: i) monolayer MoS₂ with fully exposed basal planes has an open Li⁺ transport path owing to the disappearance of anisotropic ion transport path in layered structure, thus ensuring ultrafast lithium-ion transport capability; ii) a maximized contact area of monolayer MoS₂ and C can sufficiently improve the EC of MoS₂, thus accelerating the charge transfer rate; iii) Co doping fundamentally changes the electronic structure of monolayer MoS₂ to enhance its intrinsic EC, thereby remarkably accelerating the charge transport; iv) Co-doped monolayer MoS₂ can be transformed into small superparamagnetic Co and Mo nanoparticles (~2 nm) during the conversion reaction, which can create a space charge region to accelerate charge transfer. The i-iv superiorities enable CoMoS₂/C with ultrahigh capacity (1512.9 mAh g⁻¹ at 0.1 A g⁻¹) and ultrafast ion transport capability (1063.3 mAh g⁻¹ at 20 A g⁻¹) in half cells. Moreover, an energy density of 136.2 Wh kg⁻¹ is acquired at 4 C in full cells with 76.6% retention corresponding to 0.1 C. Our work indicates that the in situ construction of electrostatic repulsion in the interlayer is a very effective route for the fabrication of monolayer MoS₂ and reveals the application potential of Co-doped monolayer MoS₂ in fast-charging LIBs.

2 Experimental Section

2.1 Samples Synthesis

The samples were fabricated using mixed precursor of Cobalt bis (2-ethylhexanoate), (NH₄)₂MoS₄, and N,N-dimethylformamide (DMF) in a fixed total mass of 1.6 g with different mass ratio of 0:1:0, 0:1:3, 3:4:9, 5:4:7, and 7:4:5 to synthesize MoS₂, MoS₂/C, CoMoS₂/C-I, CoMoS₂/C-II, CoMoS₂/C-III, respectively, in a self-made device that can be sealed. The devices were heated to 520 °C for 20 min in a tube furnace with an Ar flow and then experienced natural cooling.

2.2 Characterizations

The obtained materials were tested by scanning electron microscopy (SEM, FEI Quanta 450 FEG),

thermogravimetric analysis (TGA, Pyris I, PerkinElmer), elemental analyzer (EA, PerkinElmer 2400 Series II), X-ray diffraction (XRD, D/max-2500/PC, Rigaku), X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB Xi⁺), Raman spectroscopy (Horiba LabRam HR Evolution), electron spin resonance spectroscopy (ESR, Renishaw RM-1000), photoluminescence spectra (PL, Bruker EMX-plus), Brunner–Emmet–Teller method (ASAP 2020, HD88), transmission electron microscopy (TEM, Hitachi HT7700) with an energy-dispersive spectroscopy (EDS), and physical property measurement system (PPMS-14L, Quantum Design).

2.3 Electrochemical Measurements

2.3.1 Half Cells

The working electrodes were made by spreading slurries of MoS₂-based composites, acetylene black (AB), and polyvinylidene fluoride (PVDF) with a mass ratio of 8:1:1 on Cu foil and dried at 100 °C under vacuum with a time of 12 h. Working electrode, counter/reference electrode (lithium foil), separator (Celgard 2400), and electrolyte were assembled in 2032 coin-type cells, with the active mass of 1.5 mg cm⁻². The lithium-ion storage performances were tested by Land CT2001A battery system at 0.1–20 A g⁻¹ with a voltage window of 0.01 to 3 V (*vs.* Li/Li⁺). A CHI 760D electrochemical workstation was used to test cyclic voltammetry (CV) at 0.1–1 mV s⁻¹ with the same voltage window and electrochemical impedance spectroscopy (EIS) from 10⁵ to 10⁻² Hz with 5 mV amplitude.

2.3.2 Full Cells

Coin-type full cells were assembled with LiFePO₄ cathode made by spreading the slurries of 95.0 wt% LiFePO₄, 2.5 wt% PVDF, and 2.5 wt% AB on Al foil and CoMoS₂/C-II anode with a N/P ratio of ~1.06, in which the active mass loading of anodes and cathodes are 2.0 and 16.4 mg cm⁻², respectively. Other components are the same as those of half cells. Before packaging, the anode was pre-cycled (3 cycles at 0.1 A g⁻¹) to ameliorate its first Coulombic efficiency (CE). The performances were tested at 0.1–4 C (1 C = 170 mA g⁻¹) with a voltage window of 1.0 to 4.0 V at 30 °C.

2.4 Simulation Method

Density functional theory (DFT) is executed in view of Vienna Ab-initio Simulation Package. Interactions between e^- and Li^+ are detailed by Projected Augmented-Wave potentials, meanwhile exchange–correlation interactions are calculated by executing Perdew–Burke–Ernzerhof pseudo-potentials of Generalized Gradient Approximation. DFT-D3 method is applied to determine the van der Waals (vdW) interaction. Plane-wave energy cutoff and convergence threshold are considered as 450 eV, and 1.0×10^{-5} eV in energy and 0.02 eV per Angstrom in force, respectively. Brillouin zone is sampled with $4 \times 4 \times 1$ k-points. A vacuum space of 3 nm is inserted in z direction to prevent interactions between periodic images. Migration energy barrier of Li^+ is calculated by executing climbing image nudged elastic band (CI-NEB) method, and the force is approximate to 0.3 eV nm^{-1} .

3 Results and Discussion

3.1 Materials Analysis and Formation Mechanism

Figure S1 displays the morphology of the obtained samples, where pure MoS_2 exhibits bulk morphology with size of over ten microns (Fig. S1a, b). Clearly, MoS_2/C exhibits spherical shape with sub-micron size and maintains the morphology of nanosheets (Fig. S1c). This indicates that MoS_2 is not completely embedded in carbonaceous materials due to the low mass of carbon materials arising from DMF [9]. Differently, the $CoMoS_2/C$ samples show no obvious flaky morphology (Fig. S1d–f) due to the increase in mass of carbon materials (confirmed by TGA curves below) arising from cobalt bis (2-ethylhexanoate) and DMF, which fully wraps the MoS_2 nanosheets. Clearly, the $CoMoS_2/C$ -III also exhibits the appearance of a peculiar bulk with a size of ~ 200 nm marked with yellow circles (Fig. S1f), which is attributed to the formation of Co_3S_4 (confirmed below) due to the excessive addition of $C_{16}H_{30}CoO_4$. The microstructures are observed via TEM, in which the pure MoS_2 is multilayered (~ 15 layers) with a d -spacing of 0.62 nm (Fig. S2). After bringing in DMF, few-layered MoS_2 (~ 5 layers) with an enlarged d -spacing of ~ 0.96 nm and distributed into the carbon substrate is obtained in MoS_2/C (Fig. S3). After drawing into a small amount of $C_{16}H_{30}CoO_4$, few-layered MoS_2 (~ 5

layers) with a larger d -spacing (1.16 nm) and distributed into the carbon substrate are attained in $CoMoS_2/C$ -I (Fig. S4). As the amount of $C_{16}H_{30}CoO_4$ continues to increase, the intrinsic layered structure of MoS_2 completely disappears, so monolayer MoS_2 is formed in $CoMoS_2/C$ -II (Fig. 1). After bringing in excess $C_{16}H_{30}CoO_4$, the Co_3S_4 is formed besides monolayer MoS_2 (Fig. S5). The results indicate that monolayer MoS_2 can be successfully fabricated by varying the amount of organic ionic liquid ($C_{16}H_{30}CoO_4$ containing one positively charged Co^{2+} and two negatively charged $(CH_3)_2C(CH_2)_4COOH^-$) in the solution of $(NH_4)_2MoS_4$ and DMF. It should be noted that the source mass of Co and DMF is simultaneously changed, which is mainly from the perspective of ensuring the experimental safety and the success of monolayer MoS_2 synthesis. Since the maximum capacity of our reaction device is 5 mL, according to our experience in vapor-phase high-pressure reaction, the total volume of added liquid cannot exceed 30% of the total capacity. Otherwise, the pressure of the vapor phase generated by liquid pyrolysis would exceed the maximum resistance pressure of the device, which causes safety hazards. In addition, the pressure of the vapor phase generated in the reaction is also important for the synthesis of monolayer MoS_2 . Although the mass ratio of cobalt bis (2-ethylhexanoate)/ $(NH_4)_2MoS_4$ /DMF remains unchanged, the decrease in total mass leads to a low vapor pressure that is insufficient to form monolayer MoS_2 (Fig. S6). Therefore, appropriate total precursor mass and liquid volume are very important for experimental safety and synthesis of monolayer MoS_2 . Based on the above discussion, the samples are synthesized with the same total mass of the precursors, and with the increase in the mass of Co source, and the mass of DMF decreases.

Accordingly, the formation mechanism of monolayer MoS_2 should be explored, as shown in Fig. 1a–d. Specifically, in a sealed vessel, with the increase in temperature, the pyrolysis of $(NH_4)_2MoS_4$, DMF, and $C_{16}H_{30}CoO_4$ starts (Fig. 1a), during which $(NH_4)_2MoS_4$ can be decomposed into NH_3 , H_2S , and MoS_2 [9]; DMF can be decomposed into $OHCN$, $OHC\cdot$, $\cdot CH_3$, etc. [9]; the negatively charged carbon chain in $C_{16}H_{30}CoO_4$ can be decomposed into $OHC\cdot$, $\cdot CH_3$, etc. The production of vast gases and gaseous groups leads to high vapor pressure in the sealed vessel [33], which can drive the produced gaseous groups and Co^{2+} into the nucleating and growing MoS_2 interlayers (Fig. 1b). The in situ replacement of a Mo^{4+} by a Co^{2+} leaves two negative

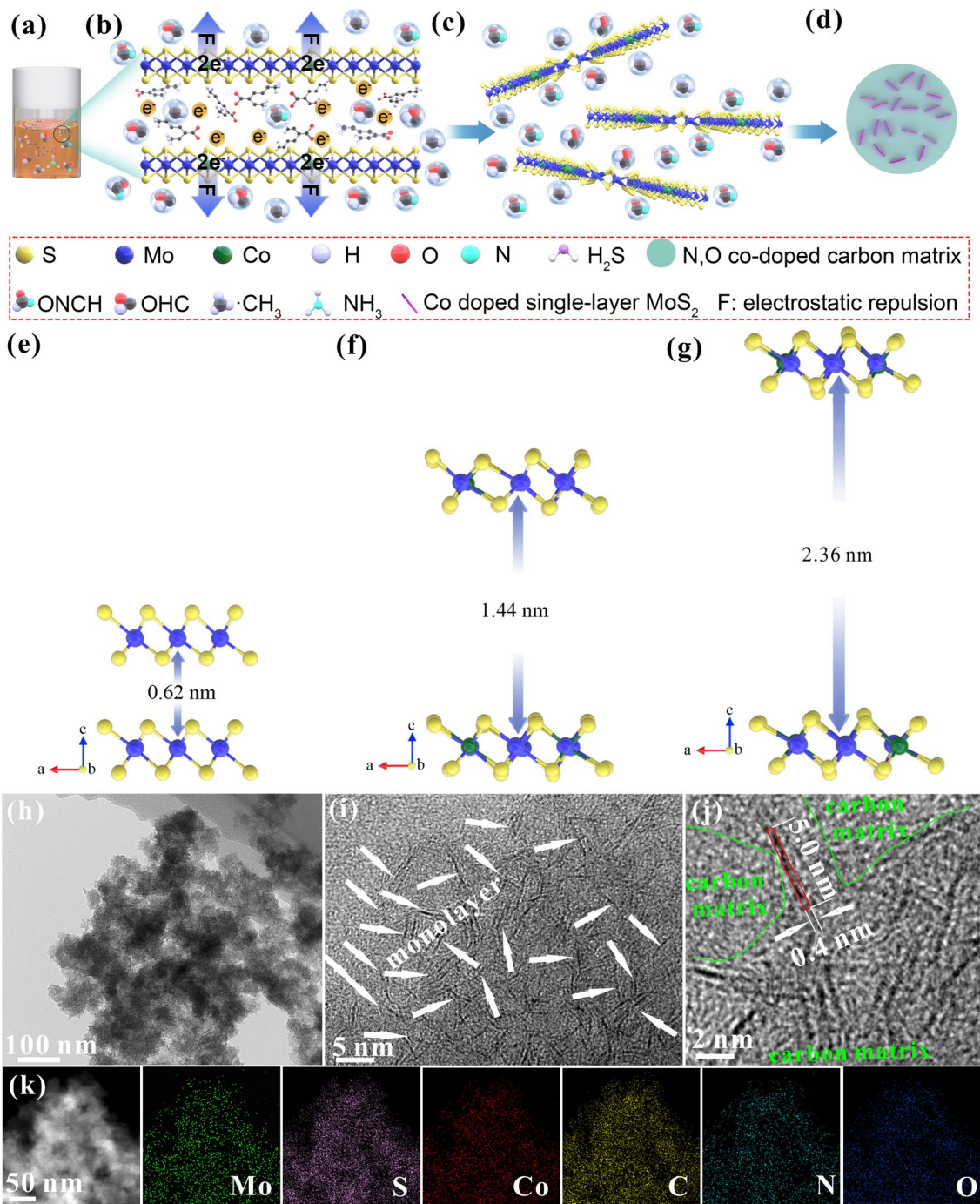


Fig. 1 a–d Schematic diagram of formation process of monolayer MoS₂. DFT results of e pure MoS₂, f Co-doped MoS₂ with a Co/Mo atomic ratio of 1/5, and g Co-doped MoS₂ with a Co/Mo atomic ratio of 1/2. h TEM image, i, j HRTEM images, and k HAADF and its EDS mapping images of CoMoS₂/C-II

charges on the MoS₂ layers, which creates an electrostatic repulsion force between MoS₂ base plane and the two negatively charged groups initially coordinated to the Co²⁺, thus increasing the interlayer spacing (Fig. 1b). By increasing the

amount of Co²⁺ doping, the electrostatic repulsive force can be further increased, and after reaching a threshold value that makes the interlayer van der Waals force disappear completely, it brings about the formation of MoS₂ monolayer

(Fig. 1c). Moreover, the gaseous groups produced by the pyrolysis of precursors insert the MoS₂ interlayer, which facilitates the effective separation of monolayer MoS₂. Meanwhile, the gaseous groups are filled around the monolayer MoS₂, which effectively prevents their agglomeration and re-stacking. With the further increase in temperature, higher vapor-phase pressure can be generated, which can induce the transformation of carbon-containing gaseous groups to solid carbon materials (Fig. 1d).

To confirm the mechanism by which the electrostatic repulsion force can be in situ built after introducing Co²⁺ into MoS₂ lattice, the DFT calculations are performed. The equilibrium interlayer spacing of adjacent MoS₂ with different additional charge concentrations caused by Co doping is investigated and acted as the basis for the construction of MoS₂ model. Specifically, when a Co²⁺ replaces a Mo⁴⁺ of the MoS₂ layers in the doping form, the MoS₂ layers carry two negative charges. Meanwhile, the donor (cobalt bis (2-ethylhexanoate)) of one Co²⁺ provides two negative charges in the interlayer and two loads on MoS₂ layers, leaving four charges for the model. The electrostatic repulsions are triggered via the accumulated negative charges to augment *d*-spacing of MoS₂. MoS₂ retains an interlayer spacing of 0.62 nm (Fig. 1e). Co-doped MoS₂ model with the Co/Mo atomic ratio of 1/5 is constructed and the corresponding negative charges are introduced to the model (Fig. 1f). It is worth noting that the MoS₂ interlayer distance calculated from the model should be lower than the experimental result in CoMoS₂/C-II. This is because the latter is motivated by a combination of gaseous group insertion and interlayer electrostatic repulsion instead of only electrostatic repulsion for the former. However, the calculated interlayer distance (1.44 nm) is slightly higher than 1.16 nm of CoMoS₂/C-II under a similar amount of Co doping (based on XPS results below). This may be due to the volume shrinkage arising from the conversion from gas to solid phase under high vapor-phase pressure and the incomplete insertion of negatively charged gaseous groups in the interlayer. Continuing to increase the amount of Co atoms and negative charges in the model (1/2, atomic ratio of Co/Mo), the interlayer distance is further increased to 2.36 nm (Fig. 1g), which signals the formation of monolayer MoS₂ [34]. The DFT results fully identify the validity of the interlayer electrostatic repulsion in enhancing the interlayer spacing of MoS₂, even in fabrication of monolayer MoS₂. As observed in the TEM images (Fig. 1h–j), Co-doped monolayer MoS₂ (Fig. 1i,

pointed by white arrows) with a linear size of ~5.0 nm, breadth size of 0.4 nm, dispersed in the carbon matrix (circled by green line) (Fig. 1j) is fabricated. High-angle annular dark field (HAADF) and corresponding EDS elemental mapping images (Fig. 1k) display that six elements are uniformly released from the composite, signifying the homogeneous dispersion of the Co-doped monolayer MoS₂ into N,O codoped carbon substrate. The carbon materials are diffuse, indicating that they are amorphous, as confirmed by the XRD pattern below.

Figure 2a displays XRD patterns in which the diffraction peaks for pure MoS₂ belong well to 2H-MoS₂ (JCPDS:37-1492), where the diffraction peaks at ~14.2, 33.5, and 58.5° correspond to (002), (100), and (110) of MoS₂ crystal planes, respectively. Clearly, the diffraction peak of the (002) crystal plane for MoS₂/C shifts to 9.0°, which corresponds to *d*-spacings of ~0.96 nm calculated by Bragg's Law ($2d \sin\theta = n\lambda$), further confirming the enlargement of the interlayer spacing. Obviously, compared with the MoS₂/C, the diffraction peak of the (002) plane of the CoMoS₂/C-I shifts to 7.8°. This indicates a larger interlayer spacing (1.16 nm), confirming the role of Co doping enhancement in increasing the *d*-spacings. Interestingly, the (002) plane of CoMoS₂/C-II and CoMoS₂/C-III completely disappears, which belongs to the feature of monolayer MoS₂ [30, 32] and further confirms the formation of monolayer MoS₂. Besides, the CoMoS₂/C-III shows the peaks of Co₃S₄ (JCPDS No. 02-1338) to further testify the formation of Co₃S₄. Clearly, no obvious diffraction peaks of carbon materials appear in the XRD pattern, which indicates that the carbon materials are amorphous. Figure 2b exhibits Raman spectroscopy, in which all the obtained samples show E_{2g}^1 (~378 cm⁻¹) and A_{1g} (~401 cm⁻¹) Raman peaks of MoS₂ [9]. This further confirms the presence of MoS₂. Besides the pure MoS₂, all other samples show the peaks of disordered carbon (~1367 cm⁻¹, D-band) and ordered graphitic carbon (~1600 cm⁻¹, G-band) of carbon materials [14], further confirming the formation of carbon in these samples. The frequency differences between E_{2g}^1 and A_{1g} vibrations are related to the layer number of MoS₂, which are 27.2, 24.6, 23.7, 20.6, and 20.6 cm⁻¹ for pure MoS₂, MoS₂/C, CoMoS₂/C-I, CoMoS₂/C-II, and CoMoS₂/C-III, respectively (Fig. S7). In previous reports [35–38], the frequency differences were >27.0, 23.4–26.7, ~22.0, and 20.3–20.7 cm⁻¹ corresponding to the multilayered, few-layered (3–6 layers), bilayered, and monolayer MoS₂, respectively. The results

further demonstrate the presence of multilayered MoS₂ in pure MoS₂, few-layered MoS₂ in MoS₂/C and CoMoS₂/C-I, and monolayer MoS₂ in CoMoS₂/C-II and CoMoS₂/C-III. Moreover, the disorder degree of graphitic structure can be validated by the intensity ratios of D and G peaks (I_D/I_G) [14, 39, 40], which are 0.83, 0.91, 0.96, and 0.99 for MoS₂/C, CoMoS₂/C-I, CoMoS₂/C-II, and CoMoS₂/C-III, respectively. Noticeably, the I_D/I_G ratio shows an upward trend with increasing C₁₆H₃₀CoO₄ amount. This may be because the carbon-containing gaseous groups arising from the pyrolysis of C₁₆H₃₀CoO₄ have a greater tendency to transform into disordered carbon under high vapor pressure, thus increasing the ratio I_D/I_G . So high I_D/I_G values suggest the presence of extensive defects in carbon materials. Moreover, the defects in MoS₂ can be evidenced by the ESR (Fig. S8a) and PL spectra (Fig. S8b). Compared with pure MoS₂, the ESR spectra of MoS₂/C and CoMoS₂/C show

a stronger characteristic peak intensity ($g = 2.003$). This confirms the presence of abundant non-intrinsic defects in MoS₂ [41]. Moreover, the PL spectra show that the MoS₂/C and CoMoS₂/C have a lower emission peak intensity at ~ 625.0 nm compared to pristine MoS₂, which is related to bandgap transition of MoS₂. This indicates the effective prevention of free electron-hole pairs due to the presence of defects [42]. Especially, a stronger peak intensity in ESR and a lower peak intensity in PL of the CoMoS₂/C samples than MoS₂/C are owing to Co doping. The above results suggest that compared with pure MoS₂, vast defects exist in MoS₂/C and CoMoS₂/C samples, which is advantageous for charge transfer and storage.

From the XPS survey spectra (Fig. S9), all samples show their proper element signals besides MoS₂, in which the presence of C and O should be due to adventitious impurities [9]. Besides, by fitting the XPS survey peaks, the atomic

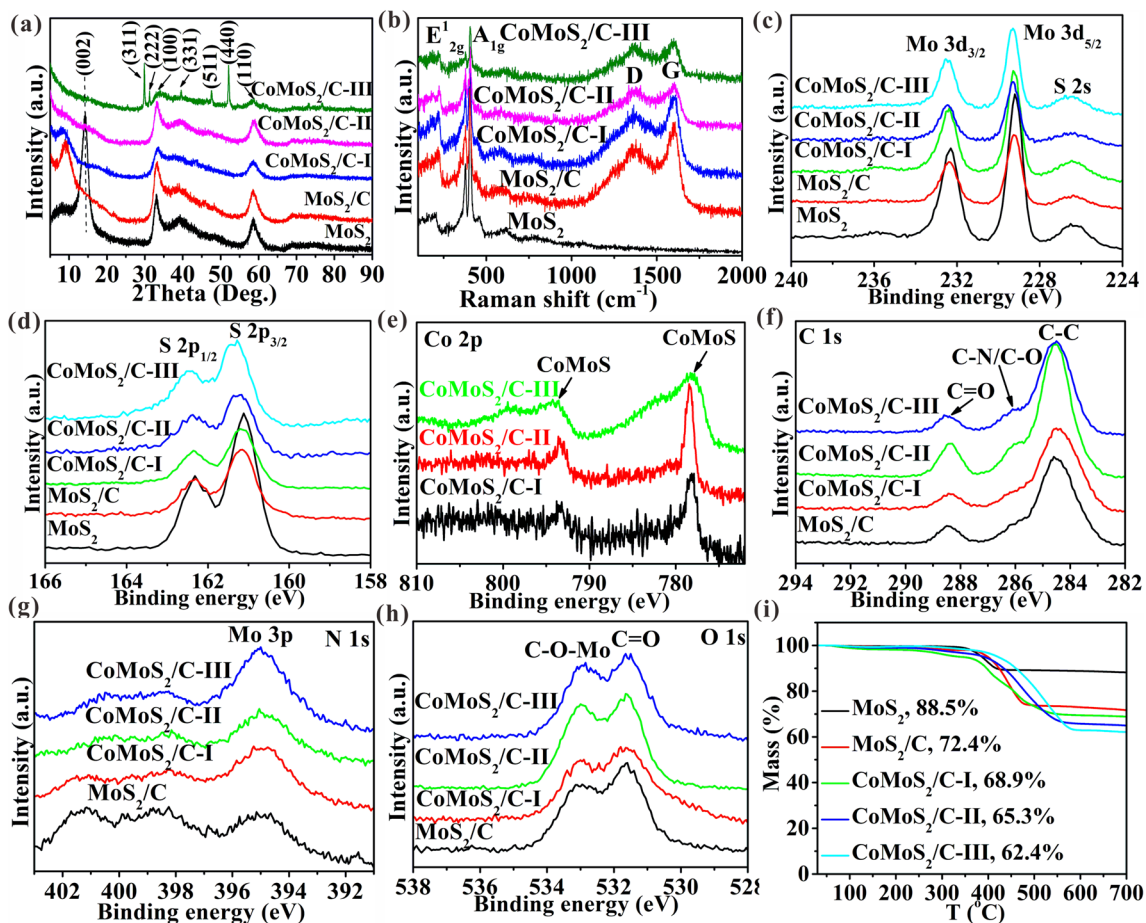


Fig. 2 Sample analysis. **a** XRD, **b** Raman, XPS spectra of **c** Mo 3d, **d** S 2p, **e** Co 2p, **f** C 1s, **g** N 1s, **h** O 1s, and **i** TGA

percentages of each element can be calculated, as shown in Table S1. The corresponding Co doping amount in the MoS₂ and the amount of N,O doping in carbon materials are also calculated and are shown in Tables S2 and S3, respectively. Apparently, the amount of Co doping in MoS₂ increases (5.80 at%, CoMoS₂/C-I; 11.52 at%, CoMoS₂/C-II; 21.69 at%, CoMoS₂/C-III) (Table S2) due to the increase in the addition amount of C₁₆H₃₀CoO₄, while the amount of N,O doping in C decreases (Table S3), which is attributed to the decrease in the addition amount of DMF. The spectra of Mo 3*d* (Fig. 2c) and S 2*p* (Fig. 2d) reveal typical 2H-MoS₂ peaks at ~232.5 (Mo 3*d*_{3/2}), ~229.3 (Mo 3*d*_{5/2}), ~162.3 (S 2*p*_{1/2}) ~161.2 (S 2*p*_{3/2}) eV [9]. The CoMoS₂/C samples show clear Co 2*p* XPS spectra (Fig. 2e) at ~793.6 and ~778.5 eV which are attributed to the presence of CoMoS [43], indicating that Co replaces Mo in the doped form. Differently, the CoMoS₂/C-III shows two peaks at 782.3 and 789.6 eV ascribed to the Co₃S₄ (Fig. S10) [44], further confirming the formation of Co₃S₄. The C 1*s* spectra shows peaks at ~284.5 (C–C), 286.1 (C–N/C–O), and 288.4 (C=O) eV (Fig. 2f), which validates the presence of N,O codoped carbon [9]. The N 1*s* spectra exhibits three peaks at ~400.8, 398.3, and 395.0 eV (Fig. 2g), in which the front two peaks can be assigned to the pyridinic nitrogen, quaternary nitrogen, and pyrrolic nitrogen (Fig. S11), suggesting the existence of N doping carbon [9, 40]. The other peak is ascribed to the Mo 3*p*. The peaks of C–O–Mo at ~533.0 eV [9], and C=O at ~531.6 eV appear in O 1*s* spectra (Fig. 2h), affirming the existence of O-doped carbon [45]. The presence of C–O–Mo bonds indicates that the monolayer MoS₂ and carbon matrix are combined by chemical bonding of C–O–Mo [9].

The contents of each element in samples are determined by EA (Table S4). Clearly, carbon mass fraction values are 18.1, 19.2, 20.4, and 21.7 wt%, corresponding to MoS₂/C, CoMoS₂/C-I, CoMoS₂/C-II, and CoMoS₂/C-III, respectively. After heating these samples in air atmosphere, Mo, Co, C, and N can be oxidated into MoO₃, Co₂O₃, CO₂, and NO₂, respectively, in which the front two result in the increase in the mass; the latter two, together with the loss of O, lead to the decrease in mass. Therefore, the final residues after heating these samples are MoO₃ and/or Co₂O₃. According to the EA results (Table S4), final residues mass for MoS₂, MoS₂/C, CoMoS₂/C-I, CoMoS₂/C-II, and CoMoS₂/C-III are 88.9, 73.4, 69.6, 66.2, and 60.1 wt%, respectively, which shows a similar trend with the results in TGA curves (Fig. 2i).

3.2 Lithium-ion Storage Performance Testing in Half Cells

Figure 3a shows the first charge/discharge curves, in which the CoMoS₂/C-II shows a higher first capacity (1512.9 mAh g⁻¹) than the others (i.e., 605.1 mAh g⁻¹ of MoS₂, 860.3 mAh g⁻¹ of MoS₂/C, 1144.3 mAh g⁻¹ of CoMoS₂/C-I, and 1272.8 mAh g⁻¹ of CoMoS₂/C-III) due to its successful construction of Co-doped monolayer MoS₂ and the absence of large-size Co₃S₄. Figure 3b shows the cycling curves, in which the CoMoS₂/C-II shows the highest capacity (1504.3 mAh g⁻¹) after 100 cycles and delivers almost 100% capacity retention similar to MoS₂/C and CoMoS₂/C-I. This is due to the integrity of electrode structure after cycling (Fig. S12) and the low volume expansion in the electrode thickness (11.8%, Fig. S13) after 100 cycles. Obviously, the pure MoS₂ shows the worst cyclability with a retention of 41.5% after 100 cycles due to its severe structural deterioration (Fig. S12a, b) and large volume expansion in the electrode thickness (116.5%, Fig. S13a, b) after 100 cycles, which is attributed to the absence of few-layered or single-layered MoS₂ and N,O codoped carbon matrix. Besides, the CoMoS₂/C-III also shows poor cyclability with a retention of 83.6% after 100 cycles due to electrode cracking (Fig. S12i, j) caused by the presence of large-sized Co₃S₄. Figure 3c shows the rate performances of these samples, in which the CoMoS₂/C-II obviously exhibits superior Li⁺ transport rate (1063.6 mAh g⁻¹ at 20 A g⁻¹) compared to other samples, which is ascribed to its lowest charge transfer resistance (*R*_{ct}, the diameter of semicircle in the high frequency 75.6 Ω, data from fitted circuit shown in Fig. S14 and Table S5) [3], the lowest ion diffusion impedance (the slope of inclined line in the low frequency, Fig. 3d and Table S5) [3], the highest specific surface area (Fig. S15 and Table S6), and the highest EC (Table S7). Lower *R*_{ct} and ion diffusion impedance can accelerate charge transfer, thus strengthening rate capability. Higher specific surface area can ensure more complete contact of active materials and electrolyte to boost ion transport and thus improve the rate performance. Besides, a higher EC can cause electrons to transfer faster, thus enhancing the rate capability.

Due to its best lithium-ion storage performance, the electrochemical behaviors of CoMoS₂/C-II are further tested. A first charge capacity of 1512.9 mAh g⁻¹ with a CE of 75.3%

is achieved (Fig. 3e), in which the 24.7% is owing to irreversible solid electrolyte interphase (SEI) film [9]. Besides the first charge/discharge curves, the other curves show a similar shape (Fig. 3e), which indicates high electrode stability upon cycling. From Nyquist plots (Fig. S16), after the first cycle, the R_{ct} increases mostly due to the formation of the SEI film, which decreases with the cycle mainly attributed to the electrochemical activation [10]. After 300 cycles, a high capacity of $1661.6 \text{ mAh g}^{-1}$ with a retention of 109.8% is achieved at 0.1 A g^{-1} . The capacity increases with increasing number of cycles may be attributed to extensive interfacial storage of Li^+ , amorphization of active materials, and change of Li^+ storage reaction [46]. Besides, high reversible capacities of 1353.1, 1261.2, and $1115.2 \text{ mAh g}^{-1}$ with retentions of 99.5%, 95.9%, and 92.0% are achieved at 1, 2, and 5 A g^{-1} after 1000, 2000, and 3000 cycles (Figs. 3g, S17 and 3 h, respectively). So high capacity retentions demonstrate the superior stability of $\text{CoMoS}_2/\text{C-II}$ electrodes under high current densities. The lithium-ion storage performances of $\text{CoMoS}_2/\text{C-II}$ are better than that of the MoS_2 -based anode

(Fig. 3i and Table S8). Note that the cycling capacity at the low current density of 0.1 A g^{-1} obviously increases with increasing cycling number (Fig. 3f), which is different from other current densities (see Figs. 3g, S17 and 3 h). The phenomena often appear in the transition metal sulfides and oxides [19, 47, 48], which may be attributed to two points: 1) the lithium-ion storage sites of the active materials can be continuously activated during cycling due to the long reaction time at low current density, thus providing a significant increase in capacity upon cycling [48]; 2) pseudocapacitance has a dominant contribution to the total capacity at high current density [48].

The kinetic analysis of the $\text{CoMoS}_2/\text{C-II}$ is performed by testing the CV curves at different rates (Fig. 4a). The equation $i = av^b$ shows the relationship between current (i) and scan rate (v) [14]. Generally, the b values of 0.5 and 1.0 indicate the diffusion-controlled and capacitance process, respectively. Clearly, the b values in the redox peaks are about 0.9 (Fig. 4b) to validate the main contribution of pseudocapacitance in Li^+ storage. In addition, the equation

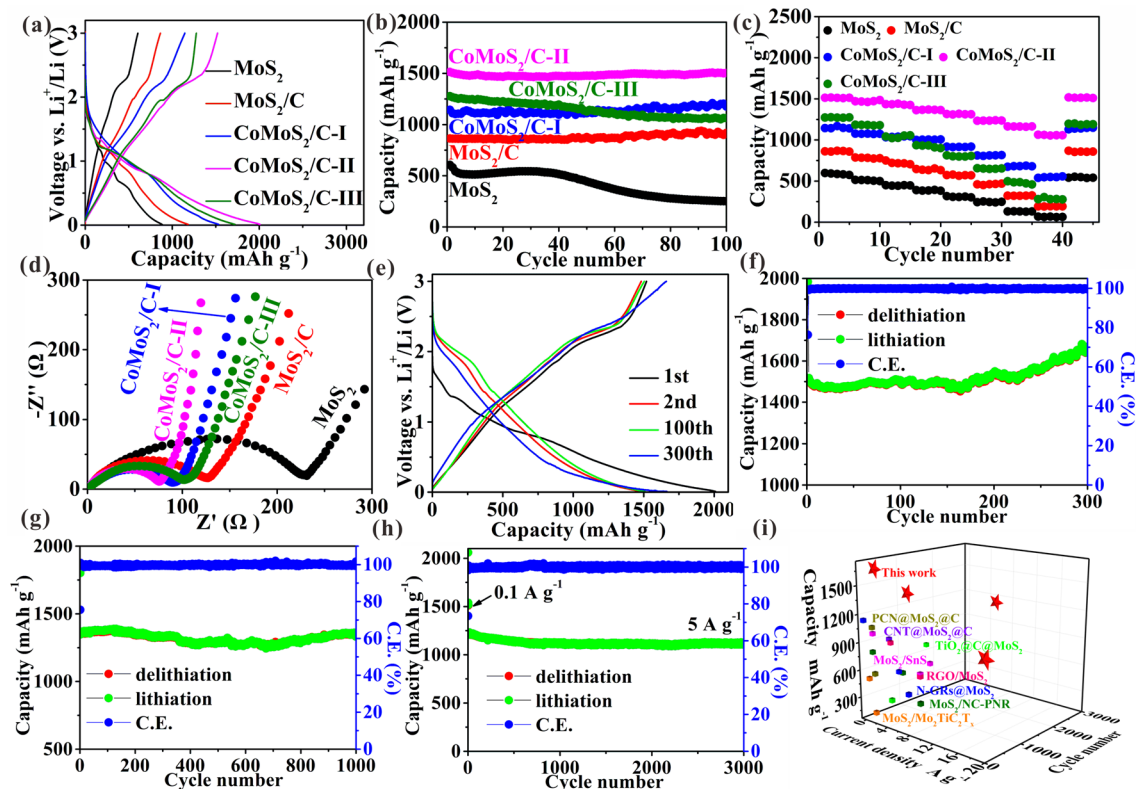


Fig. 3 Lithium-ion storage performance testing and comparison. **a** First lithiation/delithiation profiles at 0.1 A g^{-1} . **b** Cycling profiles at 0.1 A g^{-1} . **c** Rate profiles, and **d** Nyquist plots of all the prepared samples. **e** Lithiation/delithiation profiles at 0.1 A g^{-1} . Cycling profiles at **f** 0.1 A g^{-1} , **g** 1 A g^{-1} , and **h** 5 A g^{-1} of $\text{CoMoS}_2/\text{C-II}$. **i** Performance comparison curve

$i(V) = k_1v + k_2v^{1/2}$ reveals the specific contribution percentages of capacitive and diffusion-controlled behaviors [14], where $i(V)$, k_1V , and $k_2v^{1/2}$ represent the total current at a fixed voltage (V), pseudocapacitance ratio, and diffusion-controlled ratio, respectively. Obviously, the pseudocapacitance contribution increases from 55.3 to 81.3% (Fig. 4c), corresponding to the scan rate of 0.1 to 1 mV s^{-1} , respectively, higher than other samples (i.e., 3.7–14.3% of MoS_2 (Fig. S18), 28.3–50.3% of MoS_2/C (Fig. S19), 39.3–65.3% of $\text{CoMoS}_2/\text{C-I}$ (Fig. S20), and 43.2–69.0% of $\text{CoMoS}_2/\text{C-III}$ (Fig. S21). The higher pseudocapacitance ratio for $\text{CoMoS}_2/\text{C-II}$ results in faster ion transport and greater ion storage than other samples. The detailed pseudocapacitance contribution (81.3%) at 1 mV s^{-1} is depicted in red region (Fig. 4d). Note that the peak 5 at 0.01 V does not belong to the reduction peak, which is ascribed to pseudocapacity lithium-ion storage on the surface of formed superparamagnetic Mo and Co particles during conversion reaction. As confirmed in Fig. 5 below, the space charge zone is constructed on the surface of formed superparamagnetic Mo and Co particles after the electrodes discharged to 0.01 V. Due to the formation of space charge zone, rectangular CV curves representing capacitive or pseudocapacitive behavior appear in voltage range of 0.01–1.0 V. The b value for peak 5 at 0.01 V

is calculated to be approximately equal to 1, which signals that a strong capacitive response occurs in the $\text{CoMoS}_2/\text{C-II}$ electrode. The equation $i_p = 2.69 \times 10^5 n^{3/2} A D_{\text{Li}^+}^{1/2} C_{\text{Li}^+} v^{1/2}$ can be used to calculate the lithium-ion diffusion coefficient (D_{Li^+}) [7] to further reveal Li^+ diffusion kinetics, in which i_p , v , A , n , and C_{Li^+} represent peak current, scan rate, contact area of materials/electrolyte, electrons number involved in reaction, and Li^+ bulk concentration, respectively. According to linear relationship of i_p and $v^{1/2}$ (Figs. 4e and S18–S21), the calculated D_{Li^+} of $\text{CoMoS}_2/\text{C-II}$ is in the range of 7.05×10^{-10} – $1.67 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ with an average value of $1.19 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. This value is higher than 2.21×10^{-12} , 1.58×10^{-11} , 2.43×10^{-10} , and $1.72 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, corresponding to MoS_2 , MoS_2/C , $\text{CoMoS}_2/\text{C-I}$, and $\text{CoMoS}_2/\text{C-III}$, respectively. The results fully demonstrate that monolayer MoS_2 has faster lithium-ion diffusion capability than multilayered or few-layered MoS_2 . The D_{Li^+} of $\text{CoMoS}_2/\text{C-II}$ is higher than the value reported for MoS_2 -based anodes (Fig. 4f and Table S9), which is advantageous to fast Li^+ transport. The high pseudocapacitive ratio is owing to extra lithium-ion storage sites from interfaces, defects, and space charge region, which are confirmed below.

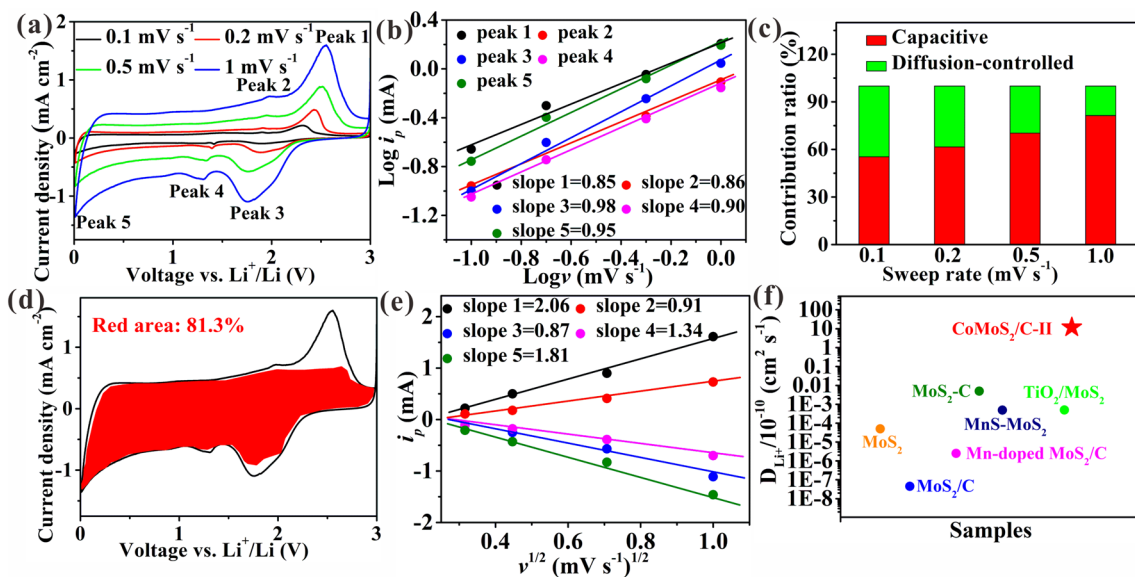


Fig. 4 Kinetic analysis of $\text{CoMoS}_2/\text{C-II}$. **a** CV curves. **b** $\text{Log } i_p$ vs $\text{Log } v$. **c** Pseudocapacitive contribution percentages. **d** Specific capacitive contribution curve. **e** i_p vs $v^{1/2}$. **f** Comparison of D_{Li^+}

3.3 Characterizations of Electrode before and after Cycling

Space charge zone is confirmed in detail. TEM images (Fig. 5a, b), SAED pattern (Fig. 5c), and EDS mapping images (Fig. S22) validate homogeneous distribution and appearance of ultrasmall Mo and Co particles (~ 2.0 nm, marked by red circles) after the electrode discharged down to 0.01 V. Vast spin-polarized electrons can enter the d orbitals of Mo and Co under an electric field to trigger spin-polarized surface capacitance, thus creating a space charge region (Fig. S23) [49]. Compared to original Mo $3d$ (229.3 eV) and Co $2p$ (778.5 eV), Mo $3d$ and Co $2p$ (Fig. 5d, e, respectively) show an apparent shift to 228.3 and 777.8 eV belonging to Mo^0 and Co^0 after the electrode discharged to 0.01 V. This validates the formed metal Mo and Co [49, 50], which further shifts to 227.8 and 777.1 eV when the electrode is charged to 3 V owing to delithiation of Mo and Co surface, respectively [49]. Additionally, compared to original electrode magnetization of ~ 0 emu g^{-1} (Fig. 5f), a magnetization of 12.3 emu g^{-1} is obtained after the electrode discharged to 0.01 V owing to the formed superparamagnetic Mo and Co particles. This continues to increase to 18.4 emu g^{-1} after

the electrode charged to 3 V due to surface delithiation of Mo and Co [49]. Detailly, vast extra electrons storing into Mo and Co partly offset spin majority bands of $4d$ (Mo) and $3d$ (Co) energy levels, thereby causing the magnetization reduction. When Li ions are removed from the surface of Mo and Co, the electrons also are transferred out from the interior of Mo and Co, thus bringing about the increase in magnetization. After charging up to 3 V, the lower binding energy of Mo^0 and Co^0 and the higher electrode magnetization are attributed to the irreversibility of Co and Mo. Generally, the first discharging process involves phase transformation reactions of $\text{MoS}_2(\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2)$, and the subsequent conversion of Li_xMoS_2 to Li_2S and Mo ($\text{Li}_x\text{MoS}_2 + (4-x)\text{Li}^+ + (4-x)e^- \rightarrow \text{Mo} + \text{Li}_2\text{S}$) [8, 9, 19, 21, 32]. During the first charging process, Li^+ is removed from Li_2S to produce S ($\text{Li}_2\text{S} \rightarrow \text{S} + 2\text{Li}^+ + 2e^-$) [8, 9, 19, 21, 32]. In subsequent cycles, the charging process follows the reaction $\text{Li}_2\text{S} \rightarrow \text{S} + 2\text{Li}^+ + 2e^-$, and the discharging process follows the reaction $\text{S} + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{S}$ [19, 21, 32]. Obviously, the formed Mo in the first charging process is irreversible. Similarly, Co is also irreversible. Clearly, in the following cycles, the electrode magnetization is basically unchanged (Fig. 5f) compared with the first charging/

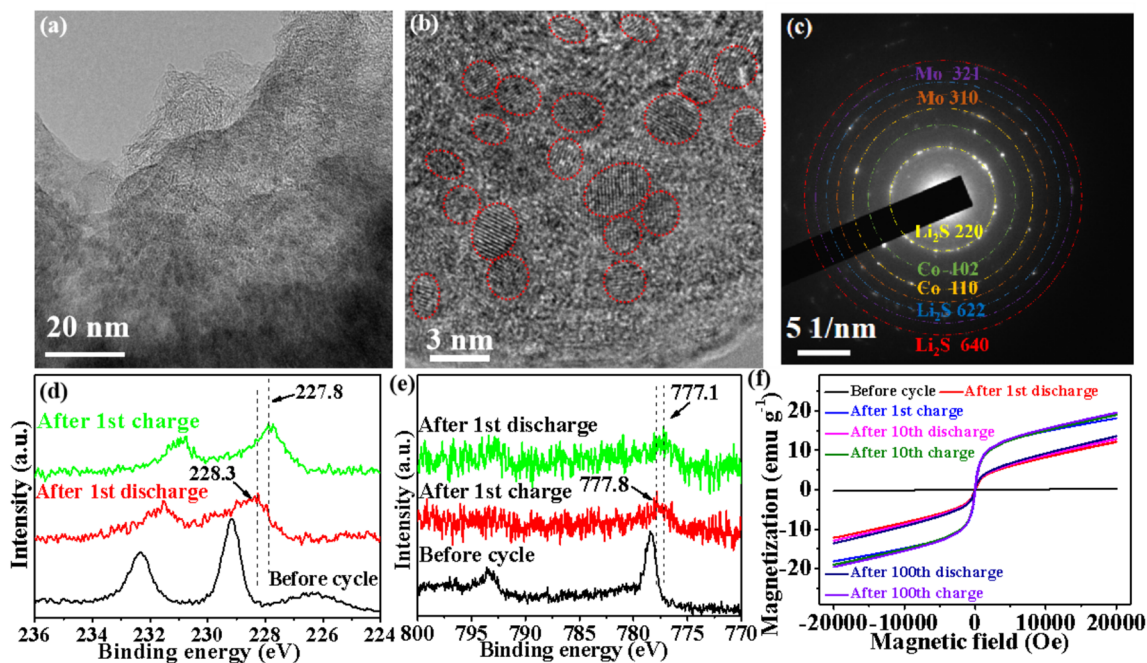


Fig. 5 *Ex situ* testing of $\text{CoMoS}_2/\text{C-II}$ electrodes. **a**, **b** TEM images after discharging to 0.01 V and **c** corresponding SAED pattern. XPS spectra of **d** Mo $3d$, **e** Co $2p$. **f** Magnetic hysteresis loops

discharging, which confirms that the space charge region has a persistent effect. These results confirm the successful creation of space charge region when Mo and Co nanoparticles are formed.

To further demonstrate the advantage of monolayer MoS₂ on lithium-ion storage, *ex situ* TEM observations are performed after discharging the MoS₂, MoS₂/C, CoMoS₂/C-I, and CoMoS₂/C-III electrodes to 0.01 V, where nanoparticles with sizes of ~5.4, 4.0, 3.0, and 3.5 nm are formed for pure MoS₂ (Fig. S24), MoS₂/C (Fig. S25), CoMoS₂/C-I (Fig. S26), and CoMoS₂/C-III (Fig. S27) electrodes, respectively. Obviously, the size (~2 nm) of nanoparticles obtained for CoMoS₂/C-II electrode after discharging to 0.01 V (Fig. 5b) is the smallest among these samples due to the limited two-dimensional transport of Mo and Co atoms in the monolayer [21] and the absence of large-sized Co₃S₄. The smaller nanoparticles have a larger specific surface area to produce more interfaces for storing Li⁺ [46, 51] and create a stronger space charge region [49, 52], thus heightening the capacity and Li⁺ transport rate.

Considering the above results, the capacity of CoMoS₂/C-II is about 2.5 times theoretical capacity of MoS₂ for the following reasons: i) enormous Co doping sites to enhance surface energy of MoS₂ to store extra Li⁺ [7, 19]; ii) extremely high capacity of monolayer MoS₂ [30, 32]; iii) vast contact interfaces of monolayer MoS₂ and C to increase Li⁺ active sites [7, 9, 46, 51]; iv) formed ultrasmall Co particles to create strong space charge region as excess Li⁺ active sites [49, 52]. Among them, creating space charge regions during conversion reaction due to the formation of ultrasmall Co has changed Li⁺ storage mechanism of traditional MoS₂ materials.

3.4 Lithium-Ion storage Performances in Full Cells

Full cells assembled with a commercial LiFePO₄ cathode are tested to evaluate the application potential of CoMoS₂/C-II anode. The charge/discharge profiles of cycles 1 and 100 (Fig. 6a) show a similar shape, indicating excellent stability of the electrode in cycles, in which a nominal voltage of ~2.2 V and a high capacity of 164.4 mAh g⁻¹ with 95.1% retention are achieved at 0.1 C after cycling (Fig. 6b). Moreover, a high capacity of 133.9 mAh g⁻¹ is obtained after cycling at 1 C with a high retention of 90.2% (Fig. 6c). Figure 6d, e exhibits rate curves where high capacities of

164.3, 159.9, 153.9, 148.4, 142.3, and 131.8 mAh g⁻¹ are obtained at 0.1, 0.2, 0.5, 1, 2, and 4 C, respectively. Equation ($E_G, \text{Wh kg}^{-1}$) = ($C_c \times V$) / ($m_{\text{active}} + m_{\text{inactive}}$) [10] can be used to calculate the gravimetric energy density (E_G), where C_c , V , m_{active} , and m_{inactive} denote the cell capacity (2.7 mAh), nominal voltage, active mass of cathode and anode (17.8 mg), and inactive mass (15.6 mg), respectively. The E_G at 0.1 C can be calculated as 177.8 Wh kg⁻¹ and remains 136.2 Wh kg⁻¹ (76.6% retention relative to 177.8 Wh kg⁻¹) at 4 C within a charging time of 11.5 min (Fig. 6f). After activation at 0.1 C, the full cell retains a high retention of 80.2% after 500 cycles at 4 C (Fig. 6g). The above results fully imply excellent rate performances and cycling stability of the cell, which are superior to previously reported cells of MoS₂-based anode materials (Table S10). Clearly, a light-emitting-diode array with 59 unit elements is cushily lighted by a single full cell (Fig. 6h) and the lighting time is about 2 h. The above results fully imply that the CoMoS₂/C-II materials have potential practicality for fast-charging LIBs with high energy density.

3.5 Effect of Co on Monolayer MoS₂ Revealed by DFT

To investigate the role of Co doping on energy barriers of lithium-ion diffusion in the monolayer MoS₂ plane of CoMoS₂/C-II, the DFT calculations are performed, where the amount of Co doping follows the XPS results (Table S2). Figure 7a, b is configurations of Li⁺ migration paths in monolayer MoS₂ and Co-doped monolayer MoS₂, respectively. It can be seen that the Li-ion diffusion energy barrier (0.19 eV) of Co-doped monolayer MoS₂ is lower than 0.28 eV of monolayer MoS₂. This implies that Co doping can greatly improve the Li-ion diffusion kinetics, thus causing fast Li⁺ transport. Besides, the doped Co atoms can significantly reduce the bandgap of monolayer MoS₂ to enable high carrier transport, as validated by calculated density of states (DOS) (Fig. 7d). Monolayer MoS₂ shows a semiconductor attribute with a bandgap of 1.30 eV, while the Co-doped monolayer MoS₂ exhibits a metallic characteristic with a bandgap of 0 eV to improve carrier transport due to the lattice distortion of MoS₂ triggered by Co doping, thereby adjusting the electronic structure of MoS₂ [53, 54].

Besides, the fully exposed basal plane for Co-doped monolayer MoS₂ can make lithium ions have isotropic transport behavior (Fig. 7e). Evidently, the multilayered MoS₂

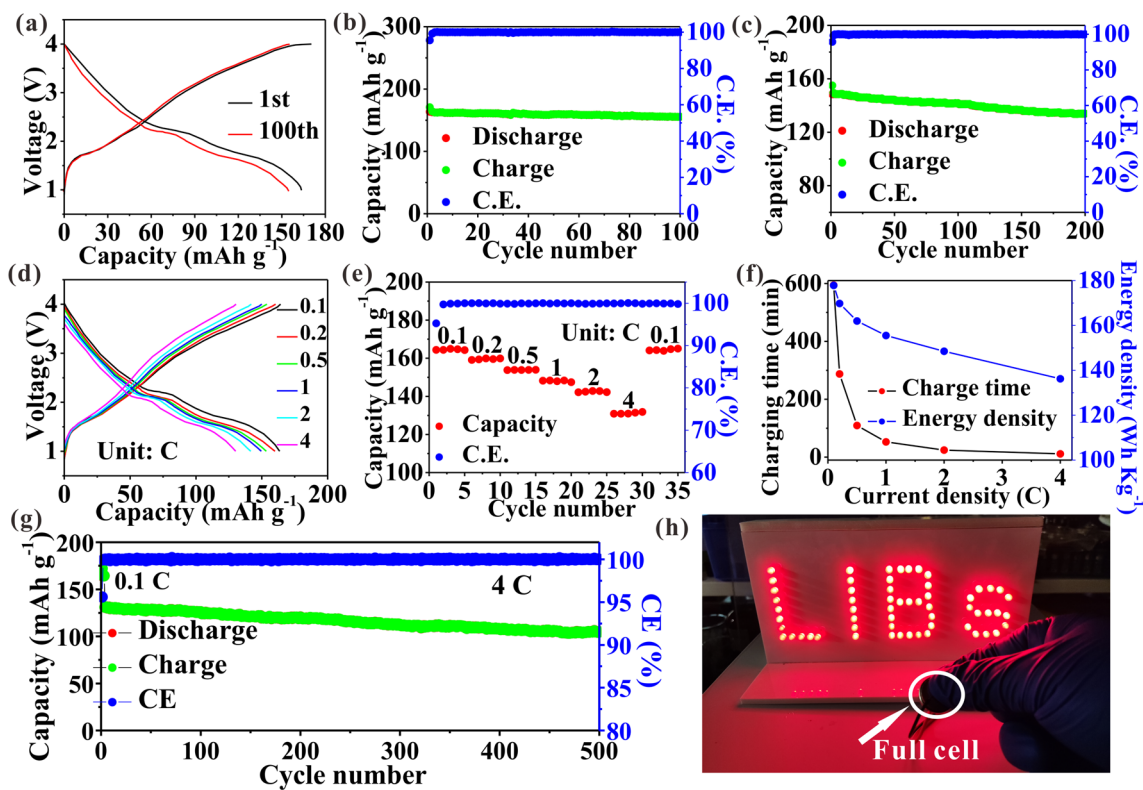


Fig. 6 Full cells testing. **a** Voltage profiles at 0.1 C. **b** Cycling curves at 0.1 C. **c** Cycling curves at 1 C. **d, e** Rate curves. **f** Charging time and corresponding E_G . **g** Cycling curves at 4 C. **h** Lighting LED

has anisotropic transport behavior (Fig. 7f). To support this view, the corresponding DFT calculations are executed. Lithium ions transport to react with multilayered structure including A, B, and C layers shown in Fig. S28. Li^+ diffuses to react with B and C layers, which involves two diffusion paths: path I is completely through layer A (Fig. S28a); path II is to bypass layer A and diffuse to the interlayer to react with layers B and C (Fig. S28b). Through DFT calculation, it is found that path I is impossible because forcing lithium-ion diffusion through layer A makes the model collapse. In other words, the diffusion energy barrier that lithium ion in path I needs to overcome is extremely high. Path II is feasible, and DFT calculation results show that the diffusion energy barrier of lithium ion between layers is only 0.23 eV (Figs. 7g and S29). This indicates that lithium ions preferentially choose interlayer transport to confirm anisotropic Li^+ transport characteristics of multilayered structure. Once multiple layers are reduced to single layer, which can cause the disappearance of interlayer structure, thereby transforming anisotropic Li-ion storage into isotropic Li-ion storage.

In view of the above results, the $\text{CoMoS}_2/\text{C-II}$ shows outstanding electrochemical performances, especially fast-charging performances, which are mainly attributed to its unique nanostructure. First, the Co-doped monolayer MoS_2 with fully exposed basal planes can maximize the contact area with the amorphous carbon matrix, which not only transforms lithium-ion transport path from anisotropy to isotropy, but also substantially improves the EC of monolayer MoS_2 , thus enhancing lithium-ion transport (Fig. 7e). Second, monolayer MoS_2 , together with the carbon matrix, can fully limit the growth of Co and Mo to obtain very small nanoparticles (~ 2 nm) during conversion reaction, thus creating strong surface-capacitance effects to accelerate lithium-ion transport (Fig. 7f).

4 Conclusions

An original nanocomposite consisting of Co-doped monolayer MoS_2 and N,O codoped carbon substrate is successfully fabricated via in situ construction of electrostatic repulsion in the

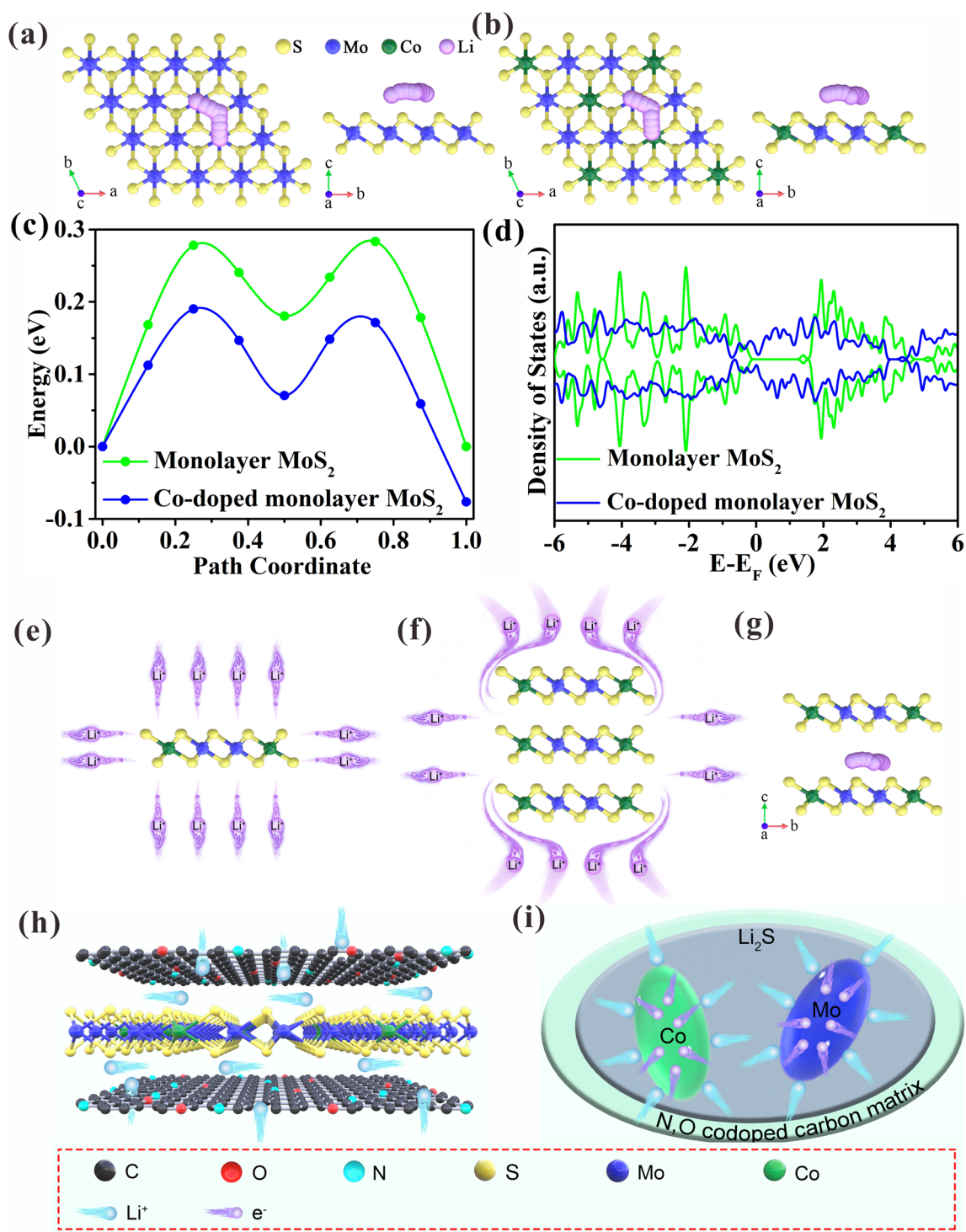


Fig. 7 Configurations of Li^+ migration paths in **a** monolayer MoS_2 , **b** Co-doped monolayer MoS_2 , **c** Li^+ diffusion energy barrier. **d** Calculated DOS. Schematic diagram of lithium ion **e** isotropic transport in monolayer MoS_2 , and **f** anisotropic transport in multilayered MoS_2 , **g** Configurations of Li^+ migration paths in multilayered MoS_2 . **h**, **i** Diagrammatic sketch of Li^+ storage mechanism in $\text{CoMoS}_2/\text{C-II}$

MoS₂ interlayer under high-pressure vapor phase. DFT calculation results demonstrate the formation mechanism of monolayer MoS₂ and confirm that the bandgap and lithium-ion diffusion energy barrier of monolayer MoS₂ can be reduced by Co doping, thus boosting the charge transfer. Besides, monolayer MoS₂ possesses an open lithium-ion transport path and a maximum contact area with the carbon matrix to achieve high D_{Li+}. In addition, the doped Co atoms can create a space charge region during the conversion reaction, thus accelerating the ion transport rate. In view of these advantages, the nanocomposite exhibits an ultrahigh capacity of 1661.6 mAh g⁻¹ and an ultrafast ion transport capability of 1063.3 mAh g⁻¹ at 20 A g⁻¹. Besides, a high energy density of 136.2 Wh kg⁻¹ is obtained at 4 C in a charging time of 11.5 min in full cells, indicating that the fabricated nanocomposite is a promising fast-charging anode in LIBs.

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References

- H. Liu, Z. Zhu, Q. Yan, S. Yu, X. He et al., A disordered rock salt anode for fast-charging lithium-ion batteries. *Nature* **585**, 63–67 (2020). <https://doi.org/10.1038/s41586-020-2637-6>
- G. Li, Regulating mass transport behavior for high-performance lithium metal batteries and fast-charging lithium-ion batteries. *Adv. Energy Mater.* **11**, 2002891 (2021). <https://doi.org/10.1002/aenm.202002891>
- Y. Mu, M. Han, J. Li, J. Liang, J. Yu, Growing vertical graphene sheets on natural graphite for fast charging lithium-ion batteries. *Carbon* **173**, 477–484 (2021). <https://doi.org/10.1016/j.carbon.2020.11.027>
- J. Li, Z. Li, M. Han, Ge Nanocrystals tightly and uniformly distributed in carbon matrix through nitrogen and oxygen bridging bonds for fast-charging high-energy-density lithium-ion batteries. *Mater. Adv.* **2**, 2068–2074 (2021). <https://doi.org/10.1039/D1MA00021G>
- J. Ru, T. He, B. Chen, Y. Feng, L. Zu et al., Covalent assembly of MoS₂ nanosheets with SnS nanodots as linkages for lithium/sodium-ion batteries. *Angew. Chem. Int. Ed.* **59**, 14729–14735 (2020). <https://doi.org/10.1002/anie.202005840>
- C. Wu, J.Z. Ou, F. He, J. Ding, W. Luo et al., Three-dimensional MoS₂/carbon sandwiched architecture for boosted lithium storage capability. *Nano Energy* **65**, 104061 (2019). <https://doi.org/10.1016/j.nanoen.2019.104061>
- Z. Li, F. Yuan, M. Han, J. Yu, Atomic-scale laminated structure of O-doped WS₂ and carbon layers with highly enhanced ion transfer for fast-charging lithium-ion batteries. *Small* **18**, 2202495 (2022). <https://doi.org/10.1002/sml.202202495>
- Y. Liu, X. He, D. Hanlon, A. Harvey, U. Khan et al., Electrical, mechanical, and capacity percolation leads to high-performance MoS₂/nanotube composite lithium ion battery electrodes. *ACS Nano* **10**, 5980–5990 (2016). <https://doi.org/10.1021/acsnano.6b01505>
- M. Han, Z. Lin, J. Yu, Ultrathin MoS₂ nanosheets homogeneously embedded in a N, O-codoped carbon matrix for high-performance lithium and sodium storage. *J. Mater. Chem. A* **7**, 4804–4812 (2019). <https://doi.org/10.1039/C8TA10880C>
- M. Han, J. Li, J. Yu, Microspheres integrating Ti₂O₃ nanocrystals, carbon matrix, and vertical graphene enable fast ion transport for fast-charging lithium-ion batteries. *J. Energy Stor.* **43**, 103179 (2021). <https://doi.org/10.1016/j.est.2021.103179>
- G. Zhang, X. Li, D. Wei, H. Yu, J. Ye et al., Synergistic engineering of structural and electronic regulation of In₂Se₃ for ultrastable Li-ion battery. *Chem. Eng. J.* **453**, 139841 (2023). <https://doi.org/10.1016/j.cej.2022.139841>
- J. Zhong, T. Wang, L. Wang, L. Peng, S. Fu et al., A silicon monoxide lithium ion battery anode with ultrahigh areal capacity. *Nano-Micro Lett.* **14**, 50 (2022). <https://doi.org/10.1007/s40820-022-00790-z>
- M. Jiang, P. Mu, H. Zhang, T. Dong, B. Tang et al., An endotenon sheath-inspired double-network binder enables superior cycling performance of silicon electrodes. *Nano-Micro Lett.* **14**, 87 (2022). <https://doi.org/10.1007/s40820-022-00833-5>
- M. Han, Y. Mu, F. Yuan, J. Liang, T. Jiang et al., Vertical graphene growth on uniformly dispersed sub-nanoscale SiO_x/N-doped carbon composite microspheres with a 3D conductive network and an ultra-low volume deformation for fast and stable lithium-ion storage. *J. Mater. Chem. A* **8**, 3822–3833 (2020). <https://doi.org/10.1039/C9TA12554J>



15. C. Zhang, N. Mahmood, H. Yin, F. Liu, Y. Hou, Synthesis of phosphorus-doped graphene and its multifunctional applications for oxygen reduction reaction and lithium ion batteries. *Adv. Mater.* **25**, 4932–4937 (2013). <https://doi.org/10.1002/adma.201301870>
16. Y. Jiao, A. Mukhopadhyay, Y. Ma, L. Yang, A.M. Hafez et al., Ion transport nanotube assembled with vertically aligned metallic MoS₂ for high rate lithium-ion batteries. *Adv. Energy Mater.* **8**, 1702779 (2018). <https://doi.org/10.1002/aenm.201702779>
17. J.B. Cook, H.S. Kim, Y. Yan, J.S. Ko, S. Robbenolt et al., Mesoporous MoS₂ as a transition metal dichalcogenide exhibiting pseudocapacitive Li and Na-ion charge storage. *Adv. Energy Mater.* **6**, 1501937 (2016). <https://doi.org/10.1002/aenm.201501937>
18. H. Liu, D. Su, R. Zhou, B. Sun, G. Wang et al., Highly ordered mesoporous MoS₂ with expanded spacing of the (002) crystal plane for ultrafast lithium ion storage. *Adv. Energy Mater.* **2**, 970–975 (2012). <https://doi.org/10.1002/aenm.201200087>
19. M. Han, J. Chen, Y. Cai, L. Wei, T. Zhao, Magnetic-atom strategy enables unilamellar MoS₂-C interoverlapped superstructure with ultrahigh capacity and ultrafast ion transfer capability in Li/Na/K-ion batteries. *Chem. Eng. J.* **454**, 140137 (2023). <https://doi.org/10.1016/j.cej.2022.140137>
20. B. Zhao, Z. Wang, Y. Gao, L. Chen, M. Lu et al., Hydrothermal synthesis of layer-controlled MoS₂/graphene composite aerogels for lithium-ion battery anode materials. *Appl. Surf. Sci.* **390**, 209–215 (2016). <https://doi.org/10.1016/j.apsusc.2016.08.078>
21. S.H. Yu, M.J. Zachman, K. Kang, H. Gao, X. Huang et al., Atomic-scale visualization of electrochemical lithiation processes in monolayer MoS₂ by cryogenic electron microscopy. *Adv. Energy Mater.* **9**, 1902773 (2019). <https://doi.org/10.1002/aenm.201902773>
22. A. Aljarb, J. Fu, C. Hsu, C. Chu, Y. Wan et al., Ledge-directed epitaxy of continuously self-aligned single-crystalline nanoribbons of transition metal dichalcogenides. *Nat. Mater.* **19**, 1300–1306 (2020). <https://doi.org/10.1038/s41563-020-0795-4>
23. J. Tao, J. Chai, X. Lu, L.M. Wong, T.I. Wong et al., Growth of wafer-scale MoS₂ monolayer by magnetron sputtering. *Nanoscale* **7**, 2497–2503 (2015). <https://doi.org/10.1039/C4NR06411A>
24. Y. Wang, S. Gali, A. Slassi, D. Beljonne, P. Samori, Collective dipole-dominated doping of monolayer MoS₂: orientation and magnitude control via the supramolecular approach. *Adv. Funct. Mater.* **30**, 2002846 (2020). <https://doi.org/10.1002/adfm.202002846>
25. J. Coleman, M. Lotya, A. O'Neill, S. Bergin, P. King et al., Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **331**, 568–571 (2011). <https://doi.org/10.1126/science.1194975>
26. G. Liu, A.W. Robertson, M.J. Li, W.C. Kuo, M.T. Darby et al., MoS₂ monolayer catalyst doped with isolated Co atoms for the hydrodeoxygenation reaction. *Nat. Chem.* **9**, 810–816 (2017). <https://doi.org/10.1038/nchem.2740>
27. Z.T. Shi, W. Kang, J. Xu, Y.W. Sun, M. Jiang et al., Hierarchical nanotubes assembled from MoS₂-carbon monolayer sandwiched superstructure nanosheets for high-performance sodium ion batteries. *Nano Energy* **22**, 27 (2016). <https://doi.org/10.1016/j.nanoen.2016.02.009>
28. L. Wang, H. Zhang, Y. Wang, C. Qian, Q. Dong et al., Unleashing ultra-fast sodium ion storage mechanisms in interface-engineered monolayer MoS₂/C interoverlapped superstructure with robust charge transfer networks. *J. Mater. Chem. A* **8**, 15002 (2020). <https://doi.org/10.1039/D0TA04916F>
29. Z. Wang, T. Chen, W. Chen, K. Chang, L. Ma et al., CTAB-assisted synthesis of single-layer MoS₂-graphene composites as anode materials of Li-ion batteries. *J. Mater. Chem. A* **1**, 2202 (2013). <https://doi.org/10.1039/C2TA00598K>
30. C. Zhu, X. Mu, P.A. van Aken, Y. Yu, J. Maier, Single-layered ultrasmall nanoplates of MoS₂ embedded in carbon nanofibers with excellent electrochemical performance for lithium and sodium storage. *Angew. Chem. Int. Ed.* **126**, 2184 (2014). <https://doi.org/10.1002/ange.201308354>
31. X. Zhang, W. Weng, H. Gu, Z. Hong, W. Xiao et al., Versatile preparation of mesoporous single-layered transition-metal sulfide/carbon composites for enhanced sodium storage. *Adv. Mater.* **34**, 2104427 (2022). <https://doi.org/10.1002/adma.202104427>
32. B. Jia, Y. Zhao, M. Qin, W. Wang, Z. Liu et al., Multi-role organic-induced scalable synthesis of a mesoporous MoS₂-monolayer/carbon composite for high-performance lithium and potassium storage. *J. Mater. Chem. A* **6**, 11147 (2018). <https://doi.org/10.1039/C8TA03166E>
33. M. Han, J. Yu, Pressure-induced vapor synthesis, formation mechanism, and thermal stability of well-dispersed boron nitride spheres. *Diam. Relat. Mater.* **87**, 10–17 (2018). <https://doi.org/10.1016/j.diamond.2018.04.029>
34. J. Sun, Z. Cheng, Q. Huang, H. He, J.S. Francisco et al., Universal principle for large-scale production of a high-quality two-dimensional monolayer via positive charge-driven exfoliation. *J. Phys. Chem. Lett.* **13**, 6597 (2022). <https://doi.org/10.1021/acs.jpcclett.2c01403>
35. B. Chen, H. Lu, J. Zhou, C. Ye, C. Shi et al., Porous MoS₂/carbon spheres anchored on 3D interconnected multiwall carbon nanotube networks for ultrafast Na storage. *Adv. Energy Mater.* **8**, 1702909 (2018). <https://doi.org/10.1002/aenm.201702909>
36. Y. Yu, S. Huang, Y. Li, S.N. Steinmann, W. Yang et al., Layer-dependent electrocatalysis of MoS₂ for hydrogen evolution. *Nano Lett.* **14**, 553–558 (2014). <https://doi.org/10.1021/nl403620g>
37. Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang et al., Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS₂ films. *Sci. Rep.* **3**, 1866 (2013). <https://doi.org/10.1038/srep01866>
38. C. Lee, H. Yan, L.E. Brus, T.F. Heinz, J. Hone et al., Anomalous lattice vibrations of single- and few-layer MoS₂. *ACS Nano* **4**, 2695–2700 (2010). <https://doi.org/10.1021/nn1003937>

39. M. Han, Y. Mu, Y. Cai, L. Wei, L. Zeng et al., Atomic-interface strategy and N, O Co-doping enable W_52 electrodes with ultrafast ion transport rate in sodium-ion batteries. *J. Mater. Chem. A* **10**(38), 20283–20293 (2022). <https://doi.org/10.1039/D2TA04984H>
40. H. Luo, M. Chen, J. Cao, M. Zhang, S. Tan et al., Cocoon silk-derived, hierarchically porous carbon as anode for highly robust potassium-ion hybrid capacitors. *Nano-Micro Lett.* **12**, 113 (2020). <https://doi.org/10.1007/s40820-020-00454-w>
41. S. Li, Y. Liu, X. Zhao, K. Cui, Q. Shen et al., Molecular engineering on MoS_2 enables large interlayers and unlocked basal planes for high-performance aqueous Zn-ion storage. *Angew. Chem. Int. Ed.* **60**, 20286–20293 (2021). <https://doi.org/10.1002/ange.202108317>
42. Z. Hui, Y. Dong, P. Jiang, H. Miao, J. Zhang, In situ light-assisted preparation of MoS_2 on graphitic C_3N_4 nanosheet for enhanced photocatalytic H_2 production from water. *J. Mater. Chem. A* **3**, 7375–7381 (2015). <https://doi.org/10.1039/C5TA00402K>
43. X. Dai, K. Du, Z. Li, M. Liu, Y. Ma et al., Co-doped MoS_2 nanosheets with the dominant $CoMoS$ phase coated on carbon as an excellent electrocatalyst for hydrogen evolution. *ACS Appl. Mater. Interfaces* **7**, 27242–27253 (2015). <https://doi.org/10.1021/acsami.5b08420>
44. C. Dong, L. Guo, H. Li, B. Zhang, X. Gao et al., Rational fabrication of $CoS_2/Co_4S_3@N$ -doped carbon microspheres as excellent cycling performance anode for half/full sodium ion batteries. *Energy Stor. Mater.* **25**, 679–686 (2020). <https://doi.org/10.1016/j.ensm.2019.09.019>
45. K. Lv, W. Suo, M. Shao, Y. Zhu, X. Wang et al., Nitrogen doped MoS_2 and nitrogen doped carbon dots composite catalyst for electroreduction CO_2 to CO with high faradaic efficiency. *Nano Energy* **63**, 103834 (2019). <https://doi.org/10.1016/j.nanoen.2019.06.030>
46. T. He, J. Feng, J. Ru, Y. Feng, R.J. Yang et al., Constructing heterointerface of metal atomic layer and amorphous anode material for high-capacity and fast lithium storage. *ACS Nano* **13**, 830–838 (2019). <https://doi.org/10.1021/acsnano.8b08344>
47. J. Luo, J. Liu, Z. Zeng, C.F. Ng, L. Ma et al., Three-dimensional graphene foam supported Fe_3O_4 lithium battery anodes with long cycle life and high rate capability. *Nano Lett.* **13**, 6136–6143 (2013). <https://doi.org/10.1021/nl403461n>
48. M. Han, Y. Mu, F. Yuan, X. Bai, J. Yu, Vapor pressure-assisted synthesis of chemically bonded TiO_2/C nanocomposites with highly mesoporous structure for lithium-ion battery anode with high capacity, ultralong cycling lifetime, and superior rate capability. *J. Power Sources* **465**, 228206 (2020). <https://doi.org/10.1016/j.jpowsour.2020.228206>
49. Q. Li, H. Li, Q. Xia, Z. Hu, Y. Zhu et al., Extra storage capacity in transition metal oxide lithium-ion batteries revealed by in situ magnetometry. *Nat. Mater.* **20**, 76–83 (2021). <https://doi.org/10.1038/s41563-020-0756-y>
50. A. Santoni, F. Rondino, C. Malerba, M. Valentini, A. Mittiga, Electronic structure of Ar^+ ion-sputtered thin-film MoS_2 : A XPS and IPES study. *Appl. Surf. Sci.* **392**, 795–800 (2017). <https://doi.org/10.1016/j.apsusc.2016.09.007>
51. B. Hou, Y. Wang, J. Guo, Y. Zhang, Q. Ning et al., A scalable strategy to develop advanced anode for sodium-ion batteries: Commercial Fe_3O_4 -derived $Fe_3O_4@FeS$ with superior full-cell performance. *ACS Appl. Mater. Interfaces* **10**, 3581–3589 (2018). <https://doi.org/10.1021/acsami.7b16580>
52. H. Nguyen, R.J. Clement, Rechargeable batteries from the perspective of the electron spin. *ACS Energy Lett.* **5**, 3848–3859 (2020). <https://doi.org/10.1021/acscenergylett.0c02074>
53. Y. Zhang, L. Tao, C. Xie, D. Wang, Y. Zou et al., Defect engineering on electrode materials for rechargeable batteries. *Adv. Mater.* **32**, 1905923 (2020). <https://doi.org/10.1002/adma.201905923>
54. J. Paier, C. Penschke, J. Sauer, Oxygen defects and surface chemistry of ceria: Quantum chemical studies compared to experiment. *Chem. Rev.* **113**, 3949 (2013). <https://doi.org/10.1021/cr3004949>

