Electrochemical and Pseudocapacitive Analysis of Rod-Like MoO₂@MoSe₂@NC Heterostructures for High-Performance Lithium Ion Batteries

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Received: 24 November 2020 / Revised: 27 December 2020 / Accepted: 8 January 2021 / Published online: 23 February 2021
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Abstract

A micro-scale rod-like heterostructure derived from molybdenum-based metal organic framework (Mo-MOF) has been successfully prepared via subsequent annealing treatment, which assembled from N-doped carbon encapsulated MoSe₂ nanosheets grown on the surface of MoO₂ microrod (named as MoO₂@MoSe₂@NC). For this novel heterostructure, the MoO₂ nanoparticles assembled into rod core not only serve as supporting substrate for facilitating the fast kinetics of Li⁺ cations inside the electrode but also protect the MoSe₂ structure from restacking in the charge/discharge process. Moreover, the outer-layered MoSe₂ nanosheets enable the fast lithium ion movement owing to its large interlayer spacing. Moreover, this unique rod-like core-shell structure composite could further effectively alleviate the structural strains caused by large volume expansion during charge/discharge process, thus leading to stable electrochemical performance when evaluated as anode material for lithium ion batteries. Electrochemical testing exhibits that the MoO₂@MoSe₂@NC heterostructure presents highly reversible capacity of 468 mAh g⁻¹ at 0.5 A g⁻¹ and superior rate capability (318 mAh g⁻¹ even at 5.0 A g⁻¹), which is attributed to the synergistic effect of N-doped carbon encapsulated MoSe₂ nanosheets and MoO₂ nanoparticles.

Keywords Mo-MOF · MoO₂@MoSe₂@NC · MoSe₂ nanosheet · Heterostructure · Lithium ion batteries (LIBs)

1 Introduction

Lithium ion batteries (LIBs) have been widely applied as indispensable rechargeable energy storage device in portable electronic products and hybrid electric vehicles due to its long-life cycling capability, high energy density and safety in the past decades. Nevertheless, the battery performances of LIBs are limited for various applications

such as electric vehicles and portable devices with high energy density and fast charging capability based on commercial graphite anode. Generally, the relatively low theoretical specific capacity (372 mAh g⁻¹) of graphite and the sluggish lithium ion kinetics hinder the intercalation and deintercalation of Li ions, thus deteriorating the rate performances. Furthermore, the structure pulverization caused by the large volume change and the formed lithium dendrites on the electrode surface together result in poor cycling stability. Considering the urgent market demands, exploring high performance anode materials becomes crucial challenge of the research. Noticeably, inspired by their large theoretical capacity, low cost and abundant natural resource, transitional oxides (TMOs) have been extensively researched [1–4]. Molybdenum dioxide (MoO₂), as one of frequently researched TMOs, shows good capability as a promising anode candidate material for LIBs. It also possesses high theoretical specific capacity of 838 mAh g⁻¹ [3]. Moreover, the high electrical conductivity (~190 S cm⁻¹) enabling faster electron kinetics during charge and discharge processes, makes it more appealing than its counterparts [5]. However, the uncontrollable

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Available online at <http://link.springer.com/journal/40195>.

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volume changes of bare MoO_2 can cause severe capacity decay, making it unsuitable for direct use as anode in LIBs. Recently, transitional metal chalcogenides (TMCs) [6–9] have displayed remarkably different electrochemical performance in rechargeable batteries because of the lower electronegativity compared with TMOs [10].

Among all, molybdenum diselenide (MoSe_2) has attracted considerable attentions in LIBs, which shows two-dimensional layered structure stacked with a lamellar crystal unit of Se-Mo-Se bonded by weak van der Waals forces along the axis [11]. It has large interlayer spacing of 0.64 nm larger than that of graphite (0.34 nm), providing large surface contact areas and lower lithium ion transport resistance [12, 13]. Although MoSe_2 presents intriguing advantages, few issues still remain for MoSe_2 , which hampers its further development as LIBs anode. Firstly, theoretical calculation results reveal that the short-range Li^+ diffusion rate is slow, which may cause fast capacity recession. On the other hand, experiment investigation shows that the long-range Li diffusion behavior stays unclear [9, 14, 15]. Secondly, 2D sheet-like materials tend to restack during lithium ion insertion/extraction process [2, 16]. As a result, it greatly reduces the active surface sites for Li cation insertions. To solve these problems, designing novel structured MoSe_2 anode materials becomes the focus of this study. In electrode design, compositing with other materials is widely conducted since it is reported that the interface effects provided by heterostructure may productively tackle those problems [17]. Given the aforementioned merits of MoO_2 , coupling with layered MoSe_2 presents fascinating prospects for high-performance electrode. Furthermore, the incorporation of carbon materials has proven to be an effective method for improving electronic conductivity and cycling life-span in electrochemical devices [2–4, 6, 7, 18–22]. Benefiting from the synergistic effects offered by compositing with layered materials and N-doped carbon, the $\text{MoO}_2@/\text{MoSe}_2@/\text{NC}$ composite could further attain enhanced surface interaction kinetics, low surface resistances and fast charge transport [21].

Metal organic frameworks (MOFs) have been widely used as self-sacrificed template to synthesize battery/catalysis-based materials owing to their diversity in metal, resource and controllable morphology [22, 23]. Herein, with the aim of synergistically boosting electrochemical performance, we proposed a low-cost and simple method to fabricate rod-like $\text{MoO}_2@/\text{MoSe}_2@/\text{NC}$ heterostructure derived from molybdenum MOFs by two-step annealing. The hierarchical composite where MoSe_2 were well dispersed on the MoO_2 rods effectively circumvent the restacking of MoSe_2 nanosheet and as well fast capacity fading. The N-doped carbon contribution profoundly elevated the conductivity of active materials, leading to excellent rate performances and cycling capacity.

2 Experimental

2.1 Synthesis of Mo-MOFs

In a typical synthesis, 3.5 g MoO_3 powder and 1.66 g imidazole were mixed into 250 mL deionized (DI) water to form homogeneous solution [24]. After refluxing overnight, the sediment was collected by vacuum filtration, washed with DI water for several times and vacuum-dried at 50 °C overnight. Finally, the Mo-MOFs were obtained.

2.2 Synthesis of $\text{MoO}_2@/\text{MoSe}_2@/\text{NC}$ Heterostructure

0.1 g synthesized Mo-MOFs were placed into a corundum crucible and calcined at 600 °C for 2 h under N_2 atmosphere with a heating ramp of 2 °C to yield $\text{MoSe}_2@/\text{NC}$. For the synthesis of $\text{MoO}_2@/\text{MoSe}_2@/\text{NC}$, the above prepared $\text{MoSe}_2@/\text{NC}$ black powder was mixed with Se powder and grinded in a mortar with the weight ratio of 1: 2. The mixture was then calcined at 600 °C under N_2 atmosphere with a heating ramp of 2 °C to obtain the product. For comparison, the sample was also calcined at different temperatures of 500 and 700 °C, respectively.

2.3 Characterizations

The morphology and crystalline structure of the prepared sample were characterized by field emission scanning electron microscopy (FESEM, JEOL JSE-7001F), X-ray diffraction patterns (XRD, D8 Rigaku9000 with CuK_α radiation) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, AlK_α radiation). The working electrode was prepared by mixing active materials, acetylene black and polyacrylic acid (PAA) with a weight ratio of 7: 2: 1 and evenly pasted on Cu foil. The electrolyte was 1 M LiPF_6 in mixed solution of ethylene carbonate/diethyl carbonate (EC/DEC, 1:1, v/v). The electrochemical measurements were carried out by using CR-2032 coin-cell assembled in a highly argon filled glove box. Cyclic voltammetry (CV) was tested on an IviumStat working station in a potential range of 0.01–3.0 V and at a scan rate from 0.1 to 1.0 mV s^{-1} . Galvanostatic charge/discharge (GCD) performances were measured on NEWARE battery tester at different currents densities.

3 Results and Discussion

A schematic diagram in Fig. 1 illustrates the fabrication route of $\text{MoO}_2@/\text{MoSe}_2@/\text{NC}$ micro-architectures. In general, the nitrogen-doped molybdenum-based heterostructures are prepared by using two-step of annealing. The Mo-based

Fig. 1 Schematic illustration of the preparation of $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ heterostructures

MOFs are firstly fabricated by the polymerization of imidazole with MoO_3 through coordinative bonds and hydrogen bonds. After overnight refluxing under vigorous stirring, micro-sized rod-like Mo based MOFs were formed with uniform morphology. After, annealed in nitrogen atmosphere, the organic components of Mo-MOF gradually decomposed and transferred to amorphous carbon, leading to the generation of $\text{MoO}_2\text{@NC}$ rod-like microstructure. Interestingly, the formed mesoporous $\text{MoO}_2\text{@NC}$ microrods are assembled from numerous aggregated nanoparticles. In the following annealing procedure, the selenide power reacts with MoO_2 to finally yield $\text{MoO}_2\text{@MoSe}_2\text{@NC}$. Through the subsequent annealing processes, MoSe_2 are successfully grown on the rod-liked $\text{MoSe}_2\text{@NC}$ composite, resulting in the formation of $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ heterostructure. This unique morphology will not only improve the electric conductivity of electrode, but also avoid the severe aggregation/restacking during lithiation and delithiation processes, which is conducive to realizing good electrochemical performances with long-life cycling and rate capability than that of pure molybdenum dioxide.

Scanning electron microscopy (SEM) was used to analyze the morphologies of as-prepared samples shown in Fig. 2a–c. From the SEM image (Fig. 2a), the micro-scaled rod-liked Mo-MOF precursors were uniformly generated by the reaction between molybdenum trioxide and imidazole. It predominantly has sizes with width of 2–4 μm and length of 25–40 μm . After the precursors were calcined in nitrogen atmosphere (Fig. 2b, c), the structure remains structurally integrative with MoO_2 nanoparticles align together homogeneously dispersed on the microrods. The reservation of the N-doped carbon can not only reduce MoO_3 into

MoO_2 but also retain the rod structure by connecting MoO_2 nanoparticles.

The crystal structure of as prepared samples was characterized by XRD in the 2θ range from 5° to 80° . Figure 2d shows the XRD patterns of $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ and pure $\text{MoO}_2\text{@NC}$. All the diffraction peaks at $2\theta = 26.03^\circ, 37.02^\circ, 53.51^\circ, 60.19^\circ, 66.66^\circ$ in pure $\text{MoO}_2\text{@NC}$ can be well indexed to (111), (211), (312), (031), (402) planes (JCPDS Card 32–0671, space group $P21/n$), respectively. The sharp and intense peaks show good crystallinity and impurity of as-prepared MoSe_2 . From the diffraction peaks of $\text{MoO}_2\text{@MoSe}_2\text{@NC}$, major peaks at $13.70^\circ, 31.70^\circ, 41.78^\circ, 56.97^\circ$ ascribed to (003) (101), (009), (0012) planes respectively, can be fit to JCPDS Card 20–0757. The broadened (003), (101) and (0012) peaks indicate its few-layered MoSe_2 nanosheet according to Debye–Scherrer equation. It is noted that broad peaks on XRD result are the typical epitome of 2D layered nanosheet materials, which can be inferred that as-synthesized MoSe_2 nanosheets are likely few atomic layered structures uniformly dispersed on MoO_2 supporting substrates [25, 26]. The XRD patterns of rod-liked $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ composite at different annealing temperatures are also displayed. The intensity of typical strong peaks in pure MoO_2 decreases with increasing annealing temperature due to the conversion of MoO_2 into MoSe_2 . While for the strong (003) peak of MoSe_2 , the intensity achieves the highest at 600 $^\circ\text{C}$, indicating better crystallinity. The XRD patterns analysis suggests that $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ heterostructures have been efficiently prepared.

Figure 3 depicts $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ composites annealed under different temperatures. From Fig. 3a–c (500 $^\circ\text{C}$), the micro-rods were broken down into shorter

Fig. 2 SEM images of Mo-MOF **a**, and pure MoO₂@NC composite **b**, **c**; **d** XRD patterns of MoO₂@MoSe₂@NC composite annealed at different temperatures

ones along axial directions after subsequent annealing procedure. According to magnification pictures shown in Fig. 3c, the final black products appeared to have some rough and creased surfaces, which indicates that MoSe₂ nanosheets were in-situ grown on MoO₂ nanoparticles to form the heterostructure. Apparently, synthesis temperature barely has impacts on the morphology and all three temperatures can homogeneously prepare this hierarchical composite. However, higher temperature such as 700 °C probably restrains the formation of MoSe₂ nanosheet as selenide power evaporates much quickly before a deeper transformation, corresponding to XRD result. Based on the analysis of XRD patterns, it can be concluded that reaction temperature at 600 °C results in best MoO₂@MoSe₂@NC sample with excellent crystallinity and structural composition.

X-ray photoelectron spectroscopy (XPS) was conducted to detect valences state corresponding compositional element in MoO₂@MoSe₂@NC. As shown in the high-resolution Mo 3d spectrum (Fig. 4a), peaks at 232.3 eV and 229.2 eV may correspond to Mo 3d_{3/2} and Mo 3d_{5/2} for Mo-Se bond of MoSe₂ [27–29]. The remaining two peaks at 232.9 eV and 229.9 eV are assigned to Mo 3d_{3/2} and Mo 3d_{5/2} of Mo⁴⁺ in MoO₂, respectively [30]. Both characteristic peaks of MoSe₂ and MoO₂ have spin–orbit splitting

energy of 3.1 eV and 3.0 eV, respectively [31, 32]. No Mo⁶⁺ peaks with higher binding energy in the spectrum could be detected, revealing no surface oxidation of MoO₂@MoSe₂@NC heterostructures according to previous reports [33–35]. The Se 3d spectrum (Fig. 4b) with two peaks located in 55.7 eV and 54.9 eV are attributed to Se 3d_{3/2} and Se 3d_{5/2}, respectively, consistent well with that of Se(II) [36, 37]. The O 1s (Fig. 4c) with a broad peak at 530.3 eV corresponds to Mo(IV)-O bond in MoO₂, which further proves the presence of MoO₂ in the composite [34]. One peak detected with binding energy of 532.3 eV can be ascribed to absorbed trace water [38]. The C 1s spectrum is exhibited in Fig. 4d. The two main broad peaks at 283.9 eV and 284.9 eV belong to C–C/C=C and C–N, while peaks at 286.4 eV and 287.8 eV can be directed to C–O and C=O, respectively [39, 40].

Cyclic voltammetry (CV) curves of the MoO₂@MoSe₂@NC recorded at a scan rate of 0.1 mV s^{−1} are shown in Fig. 5a. A broad reduction peak could be observed at around 0.40 V due to the irreversible formation of solid electrolyte interface (SEI) layer on the surface of MoO₂@MoSe₂@NC [4, 41]. The cathodic peak at around 1.57 V and anodic peak at around 1.38 V are ascribed to MoO₂ [42]. These redox peaks could represent the crystal transformation from monoclinic MoO₂ into orthorhombic Li_xMoO₂ during

Fig. 3 SEM images of $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ composite annealed at different selenization temperatures: **a–c** 500 °C, **d–f** 600 °C, **g–i** 700 °C, respectively

lithiation process [42]. The intensity of redox peak gradually increased during subsequent curves, which is likely the lithiation extent of MoO_2 nanoparticles deepen with incremental testing cycles [43]. When discharged below 1.0 V, the as-formed Li_xMoO_2 would be converted into metallic Mo and Li_2O . The cathodic peaks at about 1.29 V, 1.84 V and anodic peaks at 1.71 V, 2.17 V are similar to typical CV curves of MoSe_2 [8]. The cathodic peak observed at 1.29 V could be considered to be Li inserted into the interlayer of MoSe_2 nanosheets to form Li_xMoSe_2 . For the third cycle, a small reduction peak appeared at about 0.25 V, possibly indicating a further conversion reaction from Li_xMoO_2 and Li_xMoSe_2 to Mo and Li_2O , Li_2Se , respectively [9, 44]. In addition, the anodic curves from first to fifth cycle and the cathodic peaks from second to fifth cycle nearly overlap, implying excellent insertion/extraction reversibility of the $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ electrode.

Figure 5b–d presents the galvanostatic charge/discharge curves of the $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ composite annealed under various temperatures at a current density of 0.2 A g^{-1} from 1st, 3th, 5th, 20th, 50th cycle, respectively. During the first cycle, the $\text{MoO}_2\text{@MoSe}_2\text{@NC}$ delivers high discharge/charge capacities of 635/448, 651/587, 542/521 mAh g^{-1} at selenization temperature of 500, 600, 700 °C, giving a columbic efficiency of 70.6%, 90.2%, 96.1%, respectively. The formation of SEI film and trapping of intercalated lithium ions in the lattices are primary reason to cause capacity loss [44, 45]. It can be observed that after 50th cycling, the discharge/charge curves nearly overlap indicating excellent reversible specific capacity and high capacity retention. The charge curves in three electrodes under different temperatures all show three plateaus at about ~ 1.39 , 1.68 and 2.16 V (vs. Li/Li^+), which are consistent with the CV result observed at around ~ 1.38 , 1.71, 2.17 V (vs. Li/Li^+). While

Fig. 4 High resolution XPS spectra: **a** Mo 3d; **b** Se 3d; **c** O 1s; **d** C 1s peaks of MoO₂@MoSe₂@NC heterostructures

discharge curves at about ~1.30, 1.91 V can also be clearly detected. This test result demonstrates that the as-prepared products of MoO₂@MoSe₂@NC composite possess good crystallinity with low polarization.

The rate capability of as-synthesized MoO₂@MoSe₂@NC composite was evaluated and shown in Fig. 6a. The assembled half-cell was first tested at a current density of 0.1 A g⁻¹, then increased to 0.2 to 5.0 A g⁻¹, and finally taken back to 0.1 A g⁻¹. The average discharge capacity of MoO₂@MoSe₂@NC electrode annealed at 600 °C can reach 608, 564, 514, 412, 311 mAh g⁻¹ at 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 A g⁻¹, respectively. When the current density returned to 0.1 A g⁻¹, it is noted that discharge capacity surpasses the initial one with around 730 mAh g⁻¹, indicating superior rate capability. It is clear that better electrochemical results are attained at annealing temperature of 600 °C. The superior electrochemical properties of MoO₂@MoSe₂@NC heterostructure could be attributed to the improved Li transport kinetic boosted by MoSe₂ as well as N-doped carbon, and the protection of rod structure by MoO₂ derived from MOF template. Figure 6b–d presents the galvanostatic charge/discharge curves of MoO₂@MoSe₂@NC anode at different current densities. At corresponding current density, MoO₂@MoSe₂@NC-600 shows higher discharge capacity than other

temperatures. All curves display clear charge/discharge plateaus even at a high current density of 2.0 A g⁻¹. However, as current density increased as high as 5.0 A g⁻¹, the discharge platforms at 1.38 and 1.71 V observed from CV curve (Fig. 5a) become inconspicuous, because the faster electron transportation rate than lithium ion (polarization) reduces redox reaction, thus generating low discharge capacity.

Long-term cycling performance of MoO₂@MoSe₂@NC anode was assessed at a higher current density of 0.5 A g⁻¹ (Fig. 6e). At first sixth cycles, it was tested under a small current density of 0.1 A g⁻¹ to undertake an activation process (forming stable SEI film). Then the discharge capacity shows a small decreasing tendency, which is possibly owing to the SEI layer generation and electrolyte decomposition [46]. The MoO₂@MoSe₂@NC-600 anode presents a high discharge capacity of 468 mAh g⁻¹ when recorded at 0.5 A g⁻¹ with columbic efficiency nearly around 100% after 80 cycles. In contrast, MoO₂@MoSe₂@NC at 500 and 700 °C only attained 360 and 350 mAh g⁻¹ after cycling. The obtained discharge capacity of 468 mAh g⁻¹ upon MoO₂@MoSe₂@NC anode is higher than the theoretical specific capacity of MoSe₂ (442 mAh g⁻¹) but lower than that of MoO₂ (838 mAh g⁻¹), which demonstrates the synergistic effects of MoO₂ and MoSe₂. The above electrochemical

Fig. 5 **a** CV curves of MoO₂@MoSe₂@NC in the three cycles at a scan rate of 0.1 mV s⁻¹; **b–d** Charge and discharge profiles of MoO₂@MoSe₂@NC in the first 50 cycles at the current density of 0.2 A g⁻¹ at 500, 600, 700 °C, respectively

performances show a high reversibility and structural stability of MoO₂@MoSe₂@NC anode.

To gain further understanding of remarkable electrochemical kinetic properties of MoO₂@MoSe₂@NC electrode, CV profiles were recorded at various sweep rates from 0.1 to 1.0 mV s⁻¹ as shown in Fig. 7a. Generally, many materials can exhibit pseudocapacitive behavior, which usually takes place at or near the surface of material in contact with electrolyte during reversible redox reaction [47, 48]. Therefore, the charge storage mechanism consists of pseudocapacitive contribution (k_1v) and diffusion-controlled contribution ($k_2v^{1/2}$), as defined in the equation: $i(V) = k_1v + k_2v^{1/2}$. While the relation between i (peak current) and v (scan rate) can be expressed as $i = av^b$, where b value is from 0.5 to 1.0. According to Dunn et al. [49], b value of 0.5 represents a total battery diffusion-controlled behavior and b value of 1.0 suggests an ideal capacitive behavior. Figure 7b shows the b values of 0.77, 0.79, 0.81, 0.82, 0.96 obtained by linear fitting. Pseudocapacitive contributions at different scan rates presented in Fig. 7c are 69.02%, 74.08%, 75.58%, 80.92%, 83.33% of 0.2, 0.4, 0.6, 0.8, 1.0 mV s⁻¹, respectively. Since the capacitive process has large contribution, capacitive behavior dominates battery capacities storage. Such capacitive contribution may benefit from MoSe₂ nanosheet grown

on rod-like heterostructure, providing more highly accessible surface areas, which strengthens the contact between Li⁺ and electrode materials. Figure 7d shows an example of pseudo-capacitive fraction (the pink region) at a scan rate of 0.6 mV s⁻¹. Above analysis suggests that capacitive process plays a vital part in Li⁺ storage of MoO₂@MoSe₂@NC.

4 Conclusion

Derived from Mo-MOF, the rod-like MoO₂@MoSe₂@NC composites with MoSe₂ nanosheet grown on the surface of MoO₂ nanoparticles have been synthesized via two-step annealing processes. In such heterostructure, uniform MoSe₂ nanosheet with good electronic conductivity can not only provide more active surface area for full contact between electrode and electrolyte but also avoid aggregation of both MoSe₂ nanosheet and MoO₂ nanoparticles, leading to structural integrity and stabilization. Besides, MoSe₂ nanosheet was homogeneously distributed on the MoO₂ nanoparticles, which can further prevent MoSe₂ from restacking during extensive lithiation/delithiation. Such unique heterostructure favors for relatively high reversible capacity and rate performance in contrasting to other MoO₂-based anode materials.

Fig. 6 **a** Rate performance of $\text{MoO}_2@ \text{MoSe}_2@ \text{NC}$ at different annealing temperatures; **b–d** Charge and discharge profiles of $\text{MoO}_2@ \text{MoSe}_2@ \text{NC}$ under various current densities at 500, 600, 700 °C, respectively; **e** Cycling performance of $\text{MoO}_2@ \text{MoSe}_2@ \text{NC}$ electrodes at a current density of 0.5 A g^{-1}

When tested in LIBs, the $\text{MoO}_2@ \text{MoSe}_2@ \text{NC}$ -600 delivers a high discharge capacity of 468 mAh g^{-1} at 0.5 A g^{-1} after 80 cycles and it still remains 318 mAh g^{-1} even at a high current density of 5 A g^{-1} in rate performance. Based on above analysis, the enhanced electrochemical properties

demonstrate the synergistic effects of well-distributed MoSe_2 nanosheet and MoO_2 nanoparticles, indicating that this heterostructure in this study can be used as promising anode material in LIBs for further application.

Fig. 7 Kinetics investigation of MoO₂@MoSe₂@NC: **a** CV curves at different scan rates; **b** Corresponding ln (peak current) versus ln (scan rate) plots at different redox states; **c** Bar chart of the percent of pseudocapacitive contribution at different scan rates; **d** CV curve of the pseudocapacitive fraction shown by the purple region at a scan rate of 0.6 mV s⁻¹

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