



Carbon-encapsulated MoSe₂/C nanorods derived from organic-inorganic hybrid enabling superior lithium/sodium storage performances

Qiong Su^a, Xinxin Cao^a, Xiangzhong Kong^a, Yaping Wang^a, Cheng Peng^{b, **}, Jing Chen^a, Bo Yin^a, Junrong Shi^a, Shuquan Liang^a, Anqiang Pan^{a, *}

^a School of Materials Science and Engineering, Central South University, Changsha 410083, Hunan, China

^b Department of Plastic Surgery, The 3rd Xiangya Hospital of Central South University, Changsha 410083, Hunan, China

ARTICLE INFO

Article history:

Received 19 August 2018
Received in revised form
18 September 2018
Accepted 23 September 2018
Available online 25 September 2018

Keywords:

MoSe₂/C nanorods
Carbon coating
Bicontinuous electron/ion pathways
Lithium-ion batteries
Sodium-ion batteries

ABSTRACT

Transition metal dichalcogenides (TMDs) have attracted increasing attention for rechargeable batteries because of its high theoretical capacity. However, its real application is limited by the intrinsic low electron conductivity and inferior structural stability. Herein, we report the fabrication of one-dimensional (1D) MoSe₂/C nanorods composite from organic-inorganic hybrid Mo₃O₁₀(C₂H₁₀N₂) (named as MoO_x-EDA) with subsequent selenization and carbon coating process. As anode materials for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), the carbon-encapsulated composite exhibited enhanced Li⁺/Na⁺ storage properties compared to MoSe₂ nanorods, including good cycling stability and high rate capability. A specific capacity of 835 mA h g⁻¹ can be obtained at a current density of 200 mA g⁻¹ for the MoSe₂/C electrode in LIBs, which retained 755 mA h g⁻¹ after 200 cycles. Moreover, a reversible Na⁺ storage capacity of 404 mA h g⁻¹ can be remained after 100 cycles at a current density of 200 mA g⁻¹. The good electrochemical performances of the MoSe₂/C nanorod composites can be attributed to the bicontinuous electron/ion pathways, low charge transfer resistance, and robust structure stability.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Rechargeable batteries have widely explored as clean environmental benign electrochemical energy storage devices and attracted great attention to meet the challenges of the fossil energy crisis and environmental pollution problems [1,2]. LIBs have dominated the power market for high-tech electronic devices and become the main power system for electrical vehicles because of their high energy density and power capability [3–5]. However, graphite as the state-of-the-art anode material for LIBs has a low theoretical specific capacity (372 mA h g⁻¹) [6–8]. Recently, SIBs as an alternative power system are also extensively studied due to their abundant sodium resources. However, the larger ionic radius of Na⁺ (1.06 Å) compared with Li⁺ (0.76 Å) will result in the sluggish Na⁺

diffusion and large volume variations during the de/intercalation process [9–12]. Many anode materials from LIBs can not work well for SIBs. Therefore, it is urgent to explore alternative anode materials with larger capacity to meet the demands for consumer electronics and the electrification of transportation [3,13–15].

More recently, TMDs with lamellar structures have attracted increasing attention because of their high theoretical capacity and good rate capability [7,16–18]. As a typical TMDs type, MoSe₂ has a sandwich-like structure, and the individual layers are held together by weak van der Waals forces [19,20]. The interlayer spacing of MoSe₂ is 0.65 nm, remarkably larger than that of graphite (0.34 nm), and can ensure efficient Li⁺/Na⁺ insertion/extraction, which may be an important characteristic in demonstrating excellent electrochemical behaviors in LIBs/SIBs [21]. Besides, MoSe₂ possesses a high theoretical capacity of 422 mA h g⁻¹, which is another advantage for battery configuration [22,23]. However, the electrochemical performances of MoSe₂ are limited by the large volume expansion and low electronic conductivity [24]. Great efforts have been endeavored to make MoSe₂ and conductive

* Corresponding author.

** Corresponding author.

E-mail addresses: pcheng83@csu.edu.cn (C. Peng), pananqiang@csu.edu.cn (A. Pan).

material composites to improve the electrochemical properties [25]. Liu et al. reported sheet-like MoSe_2/C composites with a reversible capacity of $576.7 \text{ mA h g}^{-1}$ at 100 mA g^{-1} after 50 cycles in LIBs [26]. MoSe_2 was grown on carbon fibers to form nanocomposites, which delivered reversible capacities of 610.8 and $347.1 \text{ mA h g}^{-1}$ as anode material for LIBs and SIBs after 100 cycles at a current density of 100 mA g^{-1} , respectively [21]. The results demonstrate the electrochemical performances can be greatly improved by making the nanocomposites. However, the packing density of these electrodes may be quite low because of their high surface area and large carbon weight percentages.

Herein, we report a facile synthesis of MoSe_2/C nanorods with low surface area. As shown in Fig. 1a, it is different from most of other MoSe_2 nanosheets which are obtained by hydrothermal and solvothermal methods with the reaction of Na_2MoO_4 , hydrazine hydrate and Se [21–24,26–29], the MoSe_2/C nanorods were fabricated via a successive selenization with Se powders (Step II) and *in situ* carbonization with oleic acid as carbon sources (Step III) by using organic-inorganic hybrid $\text{MoO}_x\text{-EDA}$ nanorods as sacrificial template, which was obtained by a co-precipitation method (Step I) in oil bath. During the selenization process (Step II), the as-prepared nanorod precursor was annealed to crystallize the MoSe_2 with the release of organic compounds, along with the generation of a large number of pores. In the process of carbon coating (Step III), the oleic acid on the surface infiltrated into the pores and underwent a process of *in situ* carbonization to form a robust conductive carbon skeleton [30]. As illustrated in Fig. 1b, the conductive carbon scaffolds can provide rapid ion/electron transport and excellent structure stability, resulting in splendid lithium and sodium storage performance.

2. Experimental section

2.1. Materials synthesis

2.1.1. Synthesis of organic-inorganic hybrid material of $\text{MoO}_x\text{-EDA}$ nanorods

All chemicals and reagents were used as received without further purification. The organic-inorganic hybrid material $\text{MoO}_x\text{-EDA}$ nanorod were similarly prepared according to previous reports [31–34]. In a typical synthesis, ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) (1.24 g, 1 mmol) and ethylenediamine (EDA)

(0.93 mL, 14 mmol) were dissolved in deionized water (20 mL) in a round-bottom flask. Afterwards, 1 M HCl aqueous solution was slowly dripped to the mixture with magnetic stirring at room temperature until a white precipitate formed (PH 4–5). The temperature was raised to 50°C in an oil bath for 4 h. The obtained product was filtered and washed several times with deionized water and then dried at 50°C for 24 h.

2.1.2. Synthesis of MoSe_2 nanorods

The as-obtained organic-inorganic hybrid material of $\text{MoO}_x\text{-EDA}$ nanorod (200 mg, 0.39 mmol) and Se powder (280 mg, 3.55 mmol) were placed in a quartz boat in a tube furnace. After that, the temperature was raised to 600°C and kept at this temperature for 2 h to finish the reaction under H_2/Ar flow (5% of H_2). The heating ramping rate was set of 3°C min^{-1} .

2.1.3. Synthesis of MoSe_2/C nanorods composite

The above mentioned MoSe_2 nanorods (200 mg, 0.79 mmol) and oleic acid (444 mg, 1.57 mmol) were mixed in a 3 mL corundum crucible and stirred at room temperature until the formation of homogenous mixture. Then, the mixture was transferred into a tube furnace and calcinated at 500°C for 2 h under the flow of Ar atmosphere to get MoSe_2/C composite. The temperature ramping rate was set of 3°C min^{-1} .

2.2. Material characterization

The phases and crystallinity of the samples were recorded by X-ray diffraction (XRD) measurements on a Rigaku D/max 2500 X-ray diffractometer ($\text{Cu-K}\alpha$, $\lambda = 1.54178 \text{ \AA}$). The properties of the carbon coating were analyzed by Raman spectrometer (LabRAM HR800). The weight percentages of carbon in the composite were measured by thermogravimetric (TG) (Netzsch, STA 449C), which were performed in air from 25 to 700°C at a temperature ramping rate of $10^\circ\text{C min}^{-1}$. A field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM 230) and a high-resolution transmission electron microscope (HRTEM, FEI Tecnai F20) were used to characterize the morphologies and microstructures of the samples. X-ray photoelectron spectroscopy (XPS) spectrum of the composite was recorded on the ESCALAB 250Xi.

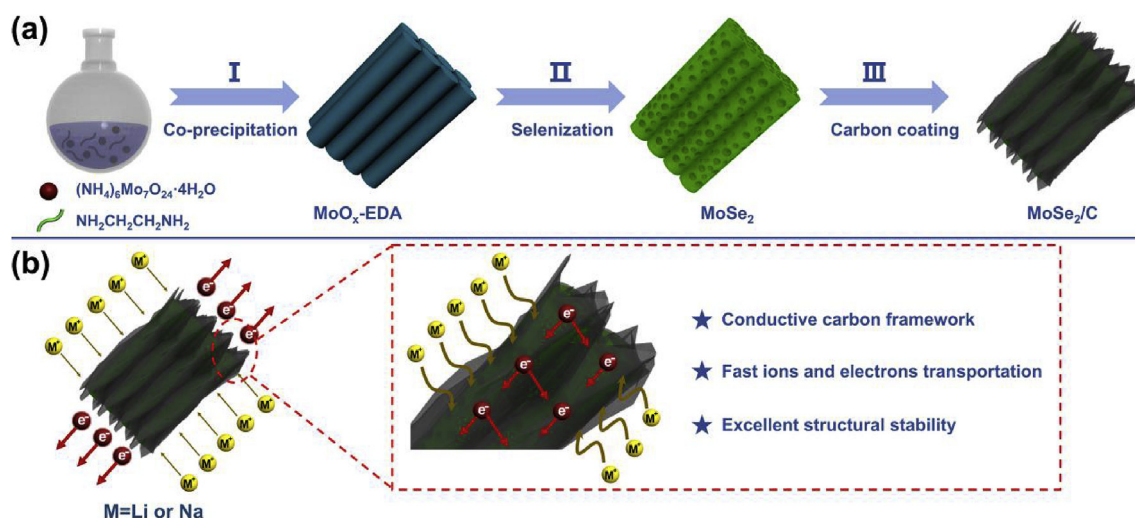


Fig. 1. Schematic illustrations for the fabrication process of MoSe_2/C composite as well as the MoSe_2/C nanorods with stable framework, fast ion diffusion and high electronic conductivity.

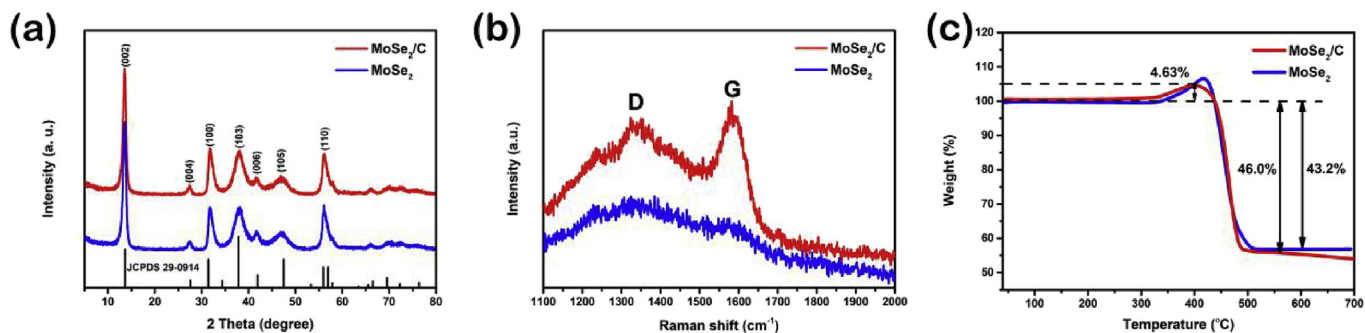


Fig. 2. (a) XRD patterns; (b) Raman scattering spectrum; (c) TG analysis of MoSe₂/C and MoSe₂ nanorods from room temperature to 700 °C at a heating rate of 10 °C min⁻¹.

2.3. Electrode fabrication and electrochemical measurements

The anode materials, super P and Carboxy Methyl Cellulose (CMC) in a mass ratio of 7: 2: 1 were grinded and dispersed in deionized water to get a slurry, which were later spread on Cu foil and dried in vacuum at 80 °C for 12 h. The diameter of the electrode is 12 mm and the loading density of the active material is around 0.8 mg cm⁻². All batteries were assembled in a glove box (Shanghai MIKROUNA) filled with ultra-high pure argon. For LIBs assembly, polypropylene membranes and 1 M LiPF₆ in ethylene carbonate (EC) – dimethyl carbonate (DMC) – diethyl carbonate (DEC) (1: 1: 1 in volume) were used as a separator and electrolyte, respectively. For SIBs, glass microfiber filters (Whatman GF/D) and 1 M NaClO₄ in propylene carbonate (PC) and fluoroethylene carbonate (FEC) mixture solution (95: 5 in volume) were employed as separator and

electrolyte, respectively. Cyclic voltammetry (CV) was conducted on a CHI660E (Shanghai Chenhua Instrument Co., China) electrochemical workstation between 0.01 and 3.0 V at a scanning rate of 0.1 mV s⁻¹. All the electrochemical measurements of the assembled batteries were tested on a Land Battery Tester (Land CT2001A). The electrochemical impedance spectroscopy (EIS) were recorded on a ZAHNER-IM6ex electrochemical workstation (ZAHNER Co., Germany) in the frequency range of 10⁵ Hz–0.01 Hz.

3. Results and discussion

3.1. Structure and morphology characterization

The structures of the obtained materials were characterized and the results are shown in Fig. 2. Fig. 2a presents the XRD patterns of

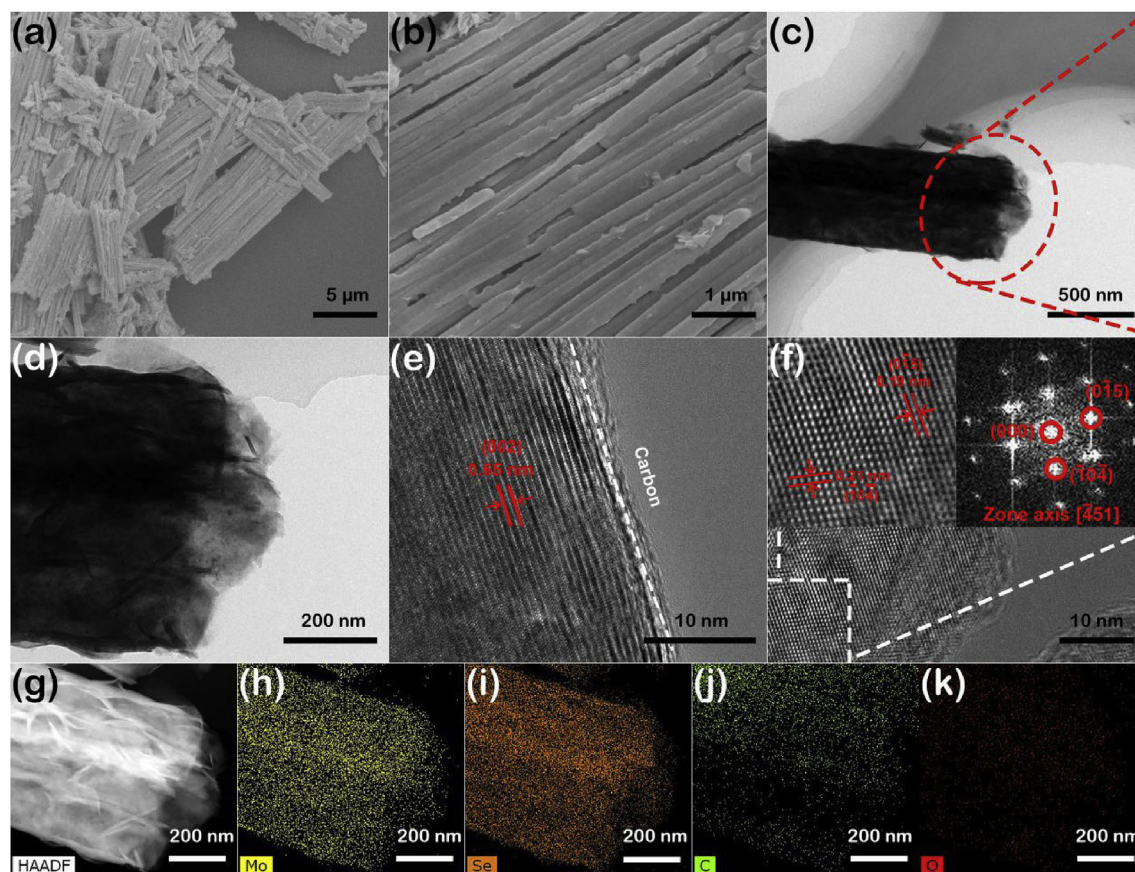


Fig. 3. (a, b) SEM images of MoSe₂/C; (c, d) TEM images; (e, f) HRTEM images, the left and the right insets of panel (f) are the magnified pattern and SAED pattern of the selected regions, respectively; (g–k) HAADF-STEM images (C, O, Mo and Se) of MoSe₂/C.

MoSe₂/C composite and the MoSe₂ nanorods. Apparently, all the peaks of MoSe₂/C composite and MoSe₂ nanorods are matched well with the hexagonal structure of crystalline MoSe₂ (JCPDS No. 29–0914). The result indicates organic-inorganic MoO_x-EDA (Fig. S1) has been fully converted into MoSe₂ after reaction with Se. According to the primary (002) diffraction peak located at 13.7°, the layer space of MoSe₂ is calculated to be 0.65 nm [26,35]. The peak intensity and broadness of the composite are quite similar for both MoSe₂ and MoSe₂/C composite, indicating the crystallinity and the crystal size do not change much during the followed carbon coating process. Raman spectroscopy of the obtained MoSe₂/C composite was shown in Fig. 2b. The peaks at 1339 cm⁻¹ and 1582 cm⁻¹ can be designated to D-band (the disorder-induce phonon mode) and the G-band (graphite band) for MoSe₂/C composite, respectively. D-band and G-band can also be observed but much weaker for MoSe₂ at 1337 cm⁻¹ and 1588 cm⁻¹, respectively. The MoSe₂ nanorods was obtained by annealing the organic-inorganic hybrid material of MoO_x-EDA nanorod and Se powder in H₂/Ar flow, whereas trace carbonization of the organic part happened at the same time. In this work, the I_D/I_G value of MoSe₂/C composite is 0.94, which is smaller than that of MoSe₂ (1.08), indicating higher graphitization degree for the MoSe₂/C composite [10,11,30]. The higher degree of graphitization is beneficial to the better electronic conductivity [36,37]. The content of MoSe₂ in MoSe₂/C composite was calculated by the TG analysis in Fig. 2c. According to the TG curve for MoSe₂/C composite, the weight increases by 4.63% in the temperature range from 300 to 400 °C was attributed to the oxidation of MoSe₂ into solid MoO₃ and SeO₂ in the air [21,22]. Subsequently, carbon was

oxidized into carbon dioxide accompanied with sublimation of SeO₂ at about 550 °C, resulting in the followed weight loss. Finally, the TG curve tends to be stable when the mass fraction is about 54.0%, and the remainder is MoO₃. In the case of MoSe₂ nanorods, 43.2% of weight is lost. Based on these considerations, the weight percentage of carbon in the MoSe₂/C composite is estimated to be 4.8%.

As shown in Fig. 3 and Fig. S3, the morphologies and microstructures of MoSe₂/C composite and MoSe₂ nanorods were investigated by SEM and TEM. The 1D nanorod morphology of organic-inorganic hybrid MoO_x-EDA (Fig. S2) can be retained after selenization (Figs. S3a–S3b). A bundle of MoSe₂ nanorods were pictured in Fig. S3c and Fig. S3d, and many pores were observed for nanocrystals (Fig. S3d), which were probably produced by the release of organic compounds during selenization process. The HRTEM images (Fig. S3e and Fig. S3f) clearly shows the distances between two adjacent layers (0.65 nm) for the (002) plane and the interplanar distance (0.24 nm) for the (103) plane of MoSe₂, respectively. The different magnification SEM images (Fig. 3a and b) of MoSe₂/C composite disclose that the nanorods are arrayed in parallel with a diameter ranging from 200 nm to 600 nm. A TEM image in Fig. 3c shows one individual nanorod decorated with carbon with a diameter about 600 nm, which is well consistent with the SEM images. The nanorod marked in Fig. 3c is magnified and displayed in Fig. 3d. The texture of the nanorod can be seen more explicitly and it seemed that the nanorod is composed of flakes. Oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇COOH), a mono-unsaturated fatty acid with a high-polarity carboxyl group and a

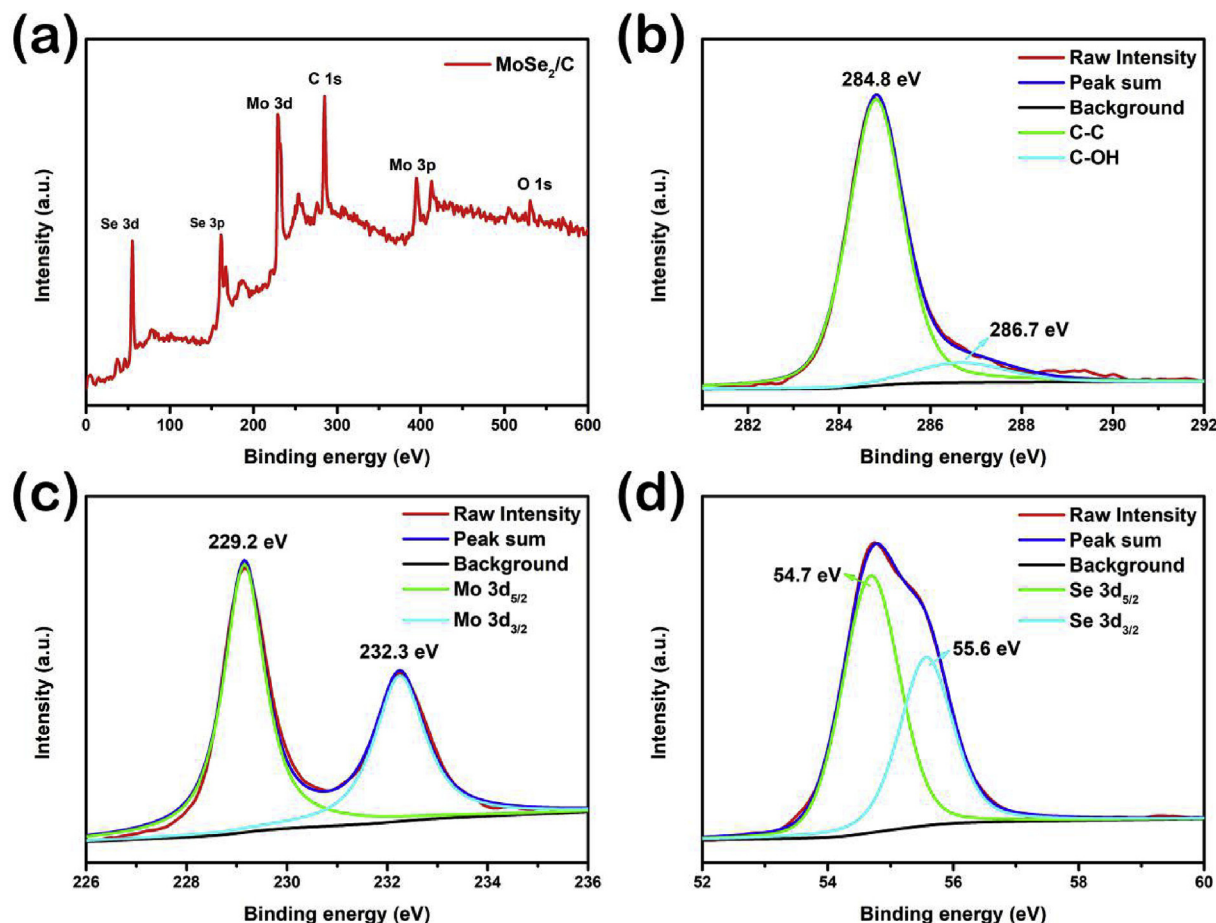


Fig. 4. (a) Survey spectrum; (b) C 1s; (c) Mo 3d; and (d) Se 3d high-resolution XPS spectra of MoSe₂/C.

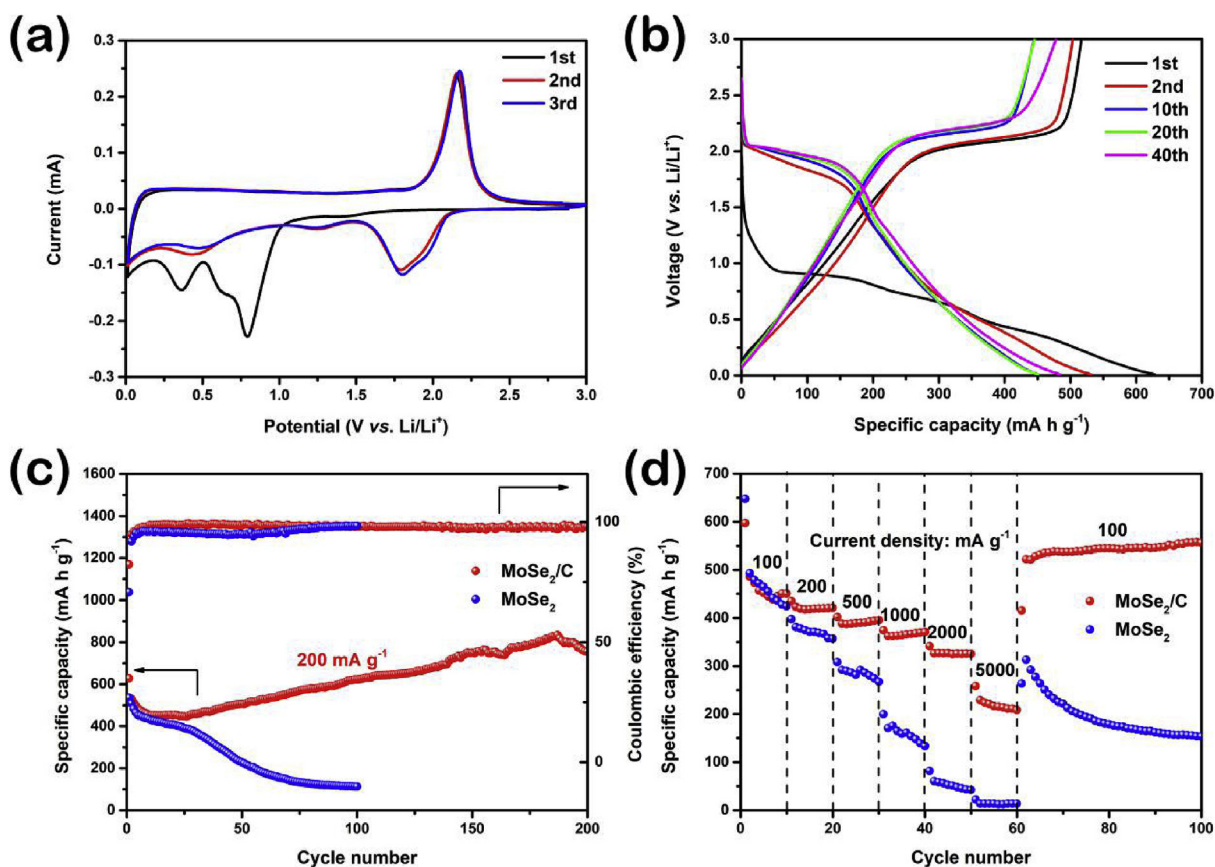


Fig. 5. Electrochemical performances for LIBs: (a) The initial three consecutive CV curves of MoSe₂/C at a scanning rate of 0.1 mV s⁻¹ between 0.01 and 3 V vs Li/Li⁺; (b) GCD profiles of the 1st, 2nd, 10th, 20th and 40th cycle at 200 mA g⁻¹; (c) cycling performances at 200 mA g⁻¹; (d) rate performances at the current densities of 100, 200, 500, 1000, 2000, 5000 mA g⁻¹.

long alkyl chain, plays an important role as a surfactant that can assemble nanocrystals to nanoflakes [10,38]. Fig. 3e–f displays the HRTEM images of the MoSe₂/C composite. From Fig. 3e, the inter-layer distance is 0.65 nm, which coincides with the (002) plane of the 2H-MoSe₂ phase (JCPDS No. 29–0914). A coated carbon layer can also be observed on the surface of the MoSe₂. Fig. 3f clearly exhibits the lattice fringes with *d*-spacings of 0.19 and 0.21 nm (the left inset of Fig. 3f), which are consistent with the interplanar distance of the (01(–)5) and (1(–)04(–)) planes of hexagonal MoSe₂ crystal, respectively. The selected area electron diffraction (SAED) pattern (the right inset of Fig. 3f) further reveals the single-crystalline nature of MoSe₂ and can be indexed to the [4(–)51] zone axis. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images in Fig. 3g–k exhibit the homogenous distribution of elements Mo, Se, C and O in nanorod, confirming that MoSe₂ is uniformly coated by carbon. It should be noted that element O are originated from the oxygen-containing functional groups on the surface-coated carbon.

Fig. 4 shows XPS result of the as-prepared MoSe₂/C composite. The survey spectrum in Fig. 4a presents the coexistence of four elements, covering Mo, Se, C and a small amount of O. The C 1s profile in Fig. 4b can be deconvoluted into two individual peaks at 284.8 (C–C) and 286.7 eV (C–OH) [39], respectively. As observed from Fig. 4c, the Mo 3d spectrum is fitted by two peaks at 229.2 and 232.3 eV, which correspond to the spin orbit peaks of Mo 3d_{5/2} and Mo 3d_{3/2} in MoSe₂/C composite, respectively, suggesting Mo IV state in the sample. Additionally, the Se 3d peak can be divided into two characteristic peaks at 54.7 and 55.6 eV, which belong to Se

3d_{5/2} and Se 3d_{3/2} peaks, respectively, revealing the –2 oxidation state for Se [26].

The electrode materials are assembled into coin cells to investigate their electrochemical performances as anode materials for LIBs and the result are shown in Fig. 5. The CV curves of MoSe₂/C composite in the initial three cycles are presented in Fig. 5a. In the first cycle, two reduction peaks at around 0.79 V and 0.36 V, and an oxidation peak at 2.2 V can be observed. The first reduction peak at 0.79 V which is shifted to 1.8 V in the following cycles is ascribed to the insertion of Li⁺ into the MoSe₂ layers to form Li_xMoSe₂ [22,26]. The second reduction peak at 0.36 V is attributed to the phase conversion from Li_xMoSe₂ to Mo and Li₂Se and the formation of solid electrolyte interface (SEI) film [40,41]. The oxidation peak at 2.2 V is assigned to the oxidation from Mo to MoSe₂. The CV curves overlapped well in the following cycles, demonstrating the excellent stability and reversibility.

Fig. 5b displays the galvanostatic charge-discharge (GCD) profiles of selected cycles of the 1st, 2nd, 10th, 20th, and 40th cycles for LIBs at 200 mA g⁻¹. The discharge and charge plateaus are around 0.79 and 0.36 V in the initial cycle and charge plateau located around 2.2 V, which are in good accordance with CV results. The cycling performances of the MoSe₂/C composite and MoSe₂ nanorods at 200 mA g⁻¹ are demonstrated in Fig. 5c. The specific capacity of the MoSe₂ nanorods decreases from 536 mA h g⁻¹ for the first cycle to 113 mA h g⁻¹ after 100 cycles, possessing the inferior cycling stability. Interestingly, the specific capacity of the MoSe₂/C composite decreases slowly in the first 26 cycles, then increases steadily and retains 755 mA h g⁻¹ after 200 cycles, which is higher than the

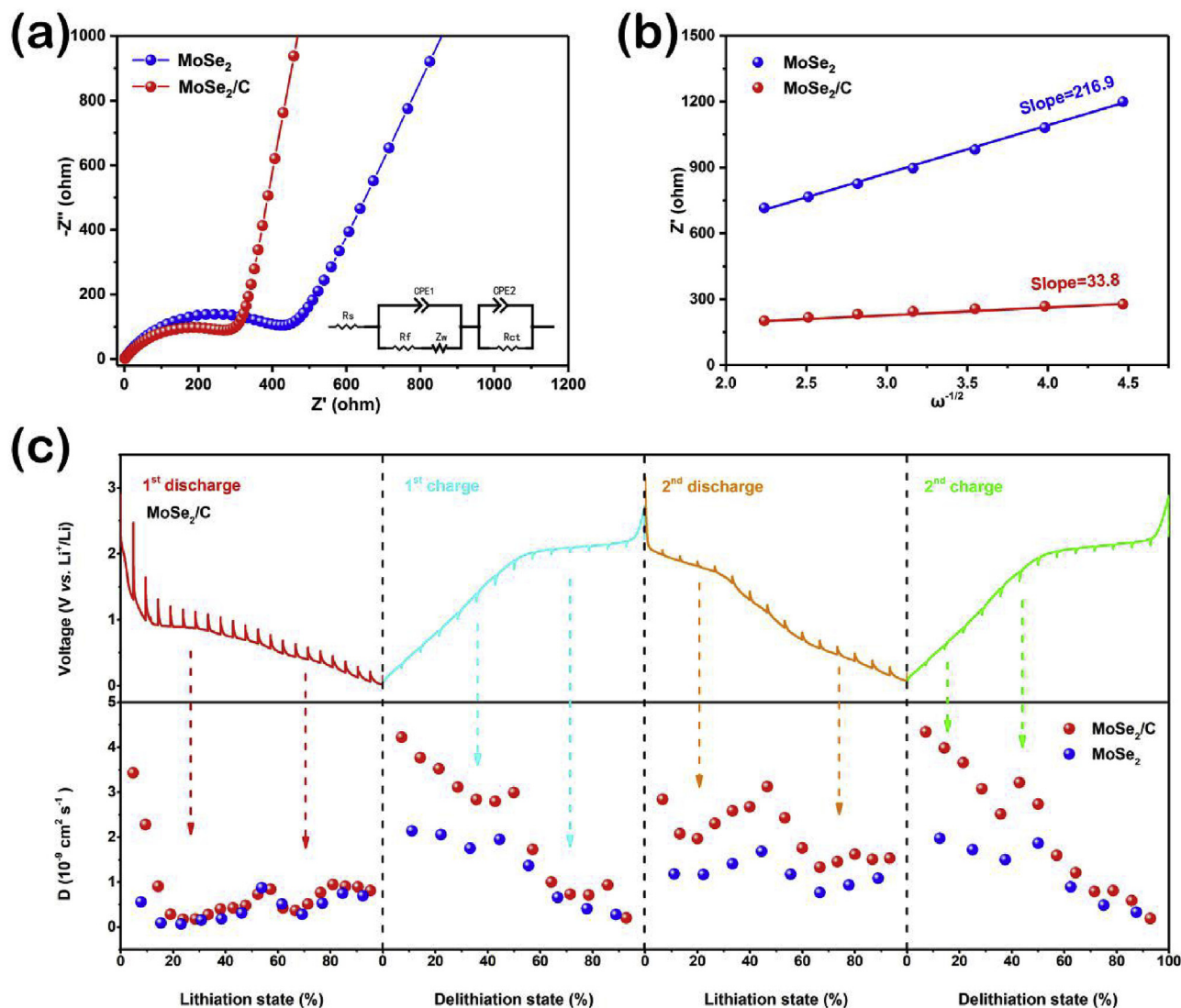


Fig. 6. (a) Nyquist plots of the as-synthesized MoSe₂/C composite and MoSe₂. The bottom inset is the corresponding equivalent circuit model; (b) the corresponding profile of the relationship between Z' and $\omega^{-1/2}$ at low frequency region; (c) GITT curves and the corresponding Li⁺ diffusion coefficient at different discharge/charge voltage of MoSe₂/C electrode.

initial reversible specific capacity (628 mA h g^{-1}). The initial falling may be caused by the formation of the SEI film and the followed rising might result from the activation of the active substance and the increment of the active sites [22,42]. The alternative current impedance measurements were conducted after 10, 20 and 50 cycles as shown in Fig. S4, and the R_{ct} value is 34.99Ω , 46.42Ω , and 33.9Ω , respectively. The R_{ct} value after 20 cycles is higher than that after 10 cycles, which can be attributed to the decomposition of the electrolyte and the stabilization of SEI layer for the first 26 cycles. However, the R_{ct} value after 50 cycles is smaller, which may be attributed to the activation of the electrode materials after electrochemical grinding of the MoSe₂/C composite. To further verify the superior electrochemical performance of the MoSe₂/C composite, the rate performances of the MoSe₂/C and the MoSe₂ nanorods electrodes were performed and shown in Fig. 5d. The MoSe₂/C composite delivered the capacities of 451, 421, 396, 371, 326 and 208 mA h g^{-1} at 100, 200, 500, 1000, 2000, 5000 mA g^{-1} , respectively. After resetting the current density to 100 mA g^{-1} , a capacity of 557 mA h g^{-1} can be recovered. However, although the MoSe₂ nanorods electrode exhibit high capacity at low current densities, the capacities decrease quickly at high rates. In particular,

only a capacity of 28 mA h g^{-1} can be delivered at the current density of 5000 mA g^{-1} . The results demonstrate the greatly improved rate capability of the MoSe₂/C nanorod composite.

The EIS and galvanostatic intermittent titration technique (GITT) measurements were conducted to better understand the intrinsic electrochemical and kinetic mechanisms of the MoSe₂/C composite. Fig. 6a displays the Nyquist plots of the MoSe₂/C composite and MoSe₂ nanorods. Both two samples' plots intuitively demonstrate a semicircle with an inclined line, which are simulated by the equivalent circuit model (inset in Fig. 6a) [23,43]. R_s stands for the electrolyte resistance, R_f and CPE1 represent the SEI layer resistance and the constant phase element, respectively. Z_w is the Warburg impedance, R_{ct} and CPE2 indicate the charge transfer resistance and related double layer capacitor, respectively. According to the fitting result, the R_{ct} value of MoSe₂/C composite is 332.8Ω , which is smaller than that of MoSe₂ nanorods (458.1Ω). On the basis of Eq. S(1) [44], the diffusion coefficient of Li⁺ is in inverse proportion to σ , where σ is the slope of the line $Z' - \omega^{-1/2}$ (Eq. S(2)). As disclosed in Fig. 6b, contrary to the EIS pattern, the slope value of the MoSe₂/C composite (33.8) is smaller than that of MoSe₂ nanorods (216.9). The results demonstrate that the carbon-encapsulated MoSe₂

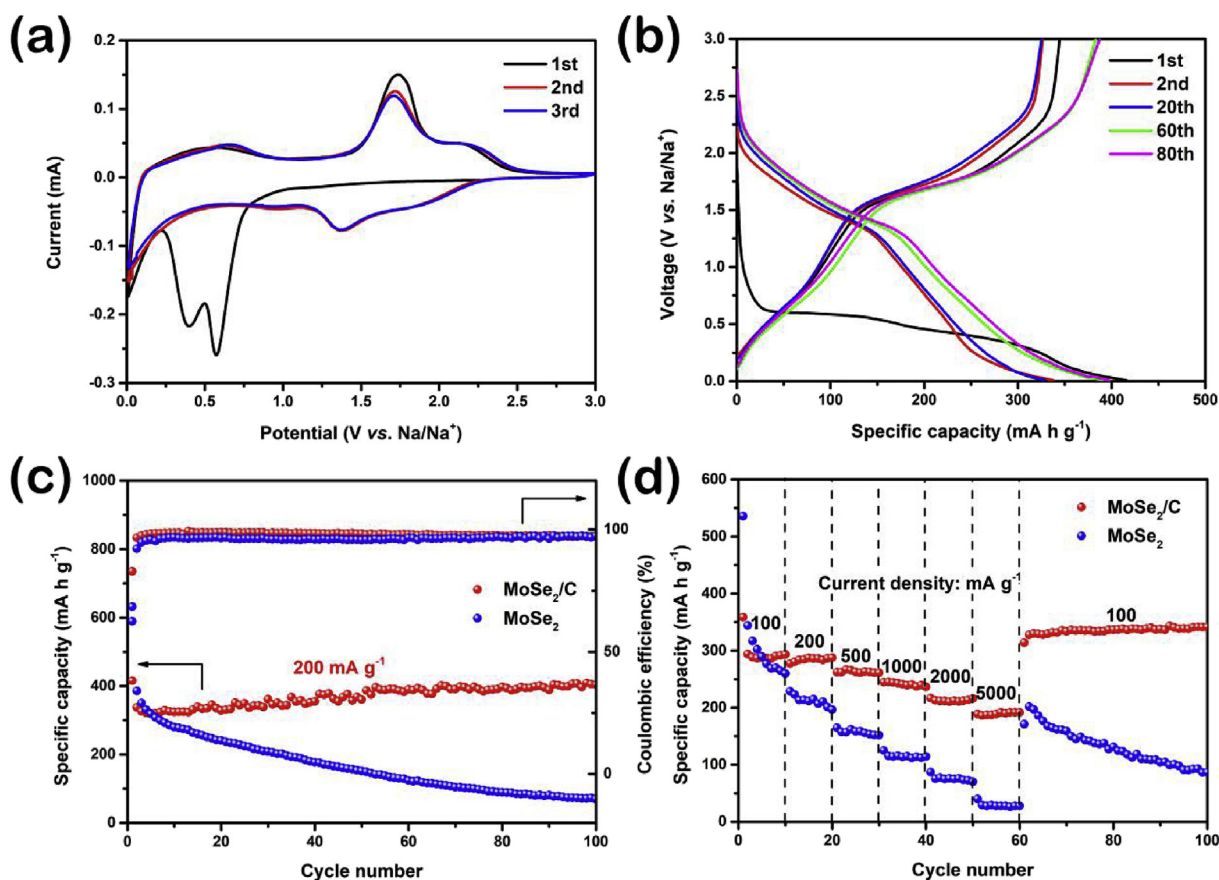


Fig. 7. Electrochemical performances for SIBs: (a) The initial three consecutive CV curves of MoSe₂/C at a scanning rate of 0.1 mV s⁻¹ between 0.01 and 3 V vs Na/Na⁺; (b) GCD profiles of the 1st, 2nd, 20th, 60th and 80th cycle at 200 mA g⁻¹; (c) cycling performances at 200 mA g⁻¹; (d) rate performances at the current densities of 100, 200, 500, 1000, 2000, 5000 mA g⁻¹.

nanorods with good crystallinity greatly facilitate the ion diffusion kinetics and electron transport rate. GITT tests were used to elucidate the effect of multistep de/lithiation on the ion diffusion and conductivity. The diffusion coefficients (*D*) at different discharge/charge voltages were calculated in the light of Fig. S5 and Eq. S(3) [45,46], and the results of the first two cycles are shown in Fig. 6c. The positions around 0.79 V and 0.36 V during the first discharge, and the position at around 2.2 V during the first charge (Fig. S6) are attributed to the Li⁺ insertion and removal process. The MoSe₂/C composite has higher diffusion coefficient compared with MoSe₂ nanorods. The higher Li⁺ diffusion coefficient of the MoSe₂/C is attributed to the carbon-encapsulated nanorod structure, which improved the electronic conductivity.

The SEM images of MoSe₂/C composite and MoSe₂ anodes after 100 cycles at 100 mA g⁻¹ are shown in Fig. S7. The morphology of MoSe₂/C (Fig. S7a) are in good reservation, demonstrating the carbon-encapsulated nanorod structure could tolerate the volume variations upon cycling. However, the MoSe₂ nanorods morphology (Fig. S7b) aggregates or pulverizes seriously. The result demonstrates better structural stability of the MoSe₂/C composite electrode.

Moreover, the electrochemical properties of MoSe₂/C composite and MoSe₂ nanorods for SIBs were also explored and shown in Fig. 7. Fig. 7a presents the CV profiles of the MoSe₂/C composite in the first three cycles. Two cathodic peaks located at 0.57 V involved the intercalation reaction (MoSe₂ + xNa⁺ = Na_xMoSe₂) [39] and 0.40 V involved the conversion reaction (Na_xMoSe₂ + (4-x)Na⁺ = Mo + 2Na₂Se) and SEI film formation [19,39]. And one anodic peak appeared at 1.74 V involved the oxidation of Mo to MoSe₂. The GCD

profiles exhibited in Fig. 7b are also in good agreement with the CV results. Fig. 7c exhibits the cycling performances of the MoSe₂/C composite and MoSe₂ nanorods for SIBs at 200 mA g⁻¹. The discharge capacity of MoSe₂/C composite delivers 416 mA h g⁻¹ in the first cycle with a high coulombic efficiency of 82.9% and still keeps 404 mA h g⁻¹ after 100 cycles. By contrast, the MoSe₂ nanorods displays an obvious declining trend during the cycling process, indicating the carbon coating can greatly improve the cycle stability. Fig. 7d depicts the rate performances of two anode materials at various current densities from 100 to 5000 mA g⁻¹, in which the capacity for MoSe₂/C composite gradually declined with the increase of the current density, and can recover to 342 mA h g⁻¹ when returned to 100 mA g⁻¹. Nevertheless, the capacities for MoSe₂ nanorods sharply decreased and it was almost zero at 5000 mA g⁻¹. The MoSe₂/C composite nanorods exhibit much better capacity retention ability during the cycling process, which may be attributed to the improved structural stability of the electrode materials. Moreover, the better rate capability can be attributed to the electronic conductivity of the MoSe₂/C composite by the carbon coating layer.

4. Conclusion

In summary, MoSe₂/C nanorods composite were successfully prepared by using organic-inorganic hybrid MoO_x-EDA as a sacrificial template. The as-obtained MoSe₂/C composite exhibits excellent performances as anode materials for LIBs and SIBs. The good electrochemical performances are attributed to the smart MoSe₂/C nanorod composite with bicontinuous electron/ion

pathways, low charge transfer resistance, and robust structure stability.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 51874162), Hunan Provincial Natural Science Foundation of China (2018JJ1036), the Innovation Project of Central South University (2017CX001), Central South University Post-doctoral Research Opening Fund.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.electacta.2018.09.154>.

References

- [1] B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: a battery of choices, *Science* 334 (2011) 928–935.
- [2] Q. Wei, F. Xiong, S. Tan, L. Huang, E.H. Lan, B. Dunn, L. Mai, Porous one-dimensional nanomaterials: design, fabrication and applications in electrochemical energy storage, *Adv. Mater.* 29 (2017), 1602300.
- [3] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, Challenges in the development of advanced Li-ion batteries: a review, *Energy Environ. Sci.* 4 (2011) 3243–3262.
- [4] X. Cao, A. Pan, Y. Zhang, J. Li, Z. Luo, X. Yang, S. Liang, G. Cao, Nanorod-nanoflake interconnected LiMnPO₄/Li₃V₂(PO₄)₃/C composite for high-rate and long-life lithium-ion batteries, *ACS Appl. Mater. Interfaces* 8 (2016) 27632–27641.
- [5] S. Liang, X. Cao, Y. Wang, Y. Hu, A. Pan, G. Cao, Uniform 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes for high-performance Li-ion batteries, *Nano Energy* 22 (2016) 48–58.
- [6] K. Chang, W. Chen, L-cysteine-assisted synthesis of layered MoS₂/graphene composites with excellent electrochemical performances for lithium ion batteries, *ACS Nano* 5 (2011) 4720–4728.
- [7] C. Zhao, J. Kong, X. Yao, X. Tang, Y. Dong, S.L. Phua, X. Lu, Thin MoS₂ nanoflakes encapsulated in carbon nanofibers as high-performance anodes for lithium-ion batteries, *ACS Appl. Mater. Interfaces* 6 (2014) 6392–6398.
- [8] P. Zhang, L. Zou, H. Hu, M. Wang, J. Fang, Y. Lai, J. Li, 3D hierarchical carbon microflowers decorated with MoO₂ nanoparticles for lithium ion batteries, *Electrochim. Acta* 250 (2017) 219–227.
- [9] J. Peters, D. Buchholz, S. Passerini, M. Weil, Life cycle assessment of sodium-ion batteries, *Energy Environ. Sci.* 9 (2016) 1744–1751.
- [10] X. Cao, A. Pan, S. Liu, J. Zhou, S. Li, G. Cao, J. Liu, S. Liang, Chemical synthesis of 3D graphene-like cages for sodium-ion batteries applications, *Adv. Energy Mater.* 7 (2017) 1700797.
- [11] J. Li, X. Cao, A. Pan, Y. Zhao, H. Yang, G. Cao, S. Liang, Nanoflake-assembled three-dimensional Na₃V₂(PO₄)₃/C cathode for high performance sodium ion batteries, *Chem. Eng. J.* 335 (2018) 301–308.
- [12] Y. Cai, H. Yang, J. Zhou, Z. Luo, G. Fang, S. Liu, A. Pan, S. Liang, Nitrogen doped hollow MoS₂/C nanospheres as anode for long-life sodium-ion batteries, *Chem. Eng. J.* 327 (2017) 522–529.
- [13] J. Goodenough, K. Park, The Li-ion rechargeable battery: a perspective, *J. Am. Chem. Soc.* 135 (2013) 1167–1176.
- [14] H. Hou, C. Banks, M. Jing, Y. Zhang, X. Ji, Carbon quantum dots and their derivative 3D porous carbon frameworks for sodium-ion batteries with ultralong cycle life, *Adv. Mater.* 27 (2015) 7861–7866.
- [15] G. Zou, H. Hou, G. Zhao, P. Ge, D. Yin, X. Ji, N-rich carbon coated CoSnO₃ derived from *in situ* construction of a Co–MOF with enhanced sodium storage performance, *J. Mater. Chem. A* 6 (2018) 4839–4847.
- [16] M. Chhowalla, H. Shin, G. Eda, L. Li, K. Loh, H. Zhang, The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets, *Nat. Chem.* 5 (2013) 263–275.
- [17] P. Ge, H. Hou, C. Banks, C. Foster, S. Li, Y. Zhang, J. He, C. Zhang, X. Ji, Binding MoS₂ with carbon constrained in carbonous nanosphere towards high-capacity and ultrafast Li/Na-ion storage, *Energy Storage Mater.* 12 (2018) 310–323.
- [18] P. Zhang, F. Qin, L. Zou, M. Wang, K. Zhang, Y. Lai, J. Li, Few-layered MoS₂/C with expanding *d*-spacing as a high-performance anode for sodium-ion batteries, *Nanoscale* 9 (2017) 12189–12195.
- [19] Y. Ko, S. Choi, S. Park, Y. Kang, Hierarchical MoSe₂ yolk-shell microspheres with superior Na-ion storage properties, *Nanoscale* 6 (2014) 10511–10515.
- [20] J. Wang, L. Lu, M. Lotya, J. Coleman, S. Chou, H. Liu, A. Minett, J. Chen, Development of MoS₂-CNT composite thin film from layered MoS₂ for lithium batteries, *Adv. Energy Mater.* 3 (2013) 798–805.
- [21] M. Zhu, Z. Luo, A. Pan, H. Yang, T. Zhu, S. Liang, G. Cao, N-doped one-dimensional carbonaceous backbones supported MoSe₂ nanosheets as superior electrodes for energy storage and conversion, *Chem. Eng. J.* 334 (2018) 2190–2200.
- [22] Z. Luo, J. Zhou, L. Wang, G. Fang, A. Pan, S. Liang, Two-dimensional hybrid nanosheets of few layered MoSe₂ on reduced graphene oxide as anodes for long-cycle-life lithium-ion batteries, *J. Mater. Chem. A* 4 (2016) 15302–15308.
- [23] H. Wang, X. Lan, D. Jiang, Y. Zhang, H. Zhong, Z. Zhang, Y. Jiang, Sodium storage and transport properties in pyrolysis synthesized MoSe₂ nanoplates for high performance sodium-ion batteries, *J. Power Sources* 283 (2015) 187–194.
- [24] D. Xie, W. Tang, Y. Wang, X. Xia, Y. Zhong, D. Zhou, D. Wang, X. Wang, J. Tu, Facile fabrication of integrated three-dimensional C-MoS₂/reduced graphene oxide composite with enhanced performance for sodium storage, *Nano Res.* 9 (2016) 1618–1629.
- [25] J. Li, H. Hu, F. Qin, P. Zhang, L. Zou, H. Wang, K. Zhang, Y. Lai, Flower-like MoSe₂/C composite with expanded (0 0 2) planes of few-layer MoSe₂ as the anode for high-performance sodium-ion batteries, *Chem. Eur. J.* 23 (2017) 14004–14010.
- [26] Y. Liu, M. Zhu, D. Chen, Sheet-like MoSe₂/C composites with enhanced Li-ion storage properties, *J. Mater. Chem. A* 3 (2015) 11857–11862.
- [27] X. Yang, Z. Zhang, Y. Fu, Q. Li, Porous hollow carbon spheres decorated with molybdenum diselenide nanosheets as anodes for highly reversible lithium and sodium storage, *Nanoscale* 7 (2015) 10198–10203.
- [28] B. Mao, T. Bao, J. Yu, L. Zheng, J. Qin, W. Yin, M. Cao, One-pot synthesis of MoSe₂ hetero-dimensional hybrid self-assembled by nanodots and nanosheets for electrocatalytic hydrogen evolution and photothermal therapy, *Nano Res.* 10 (2017) 2667–2682.
- [29] X. Zhao, W. Cai, Y. Yang, X. Song, Z. Neale, H.-E. Wang, J. Sui, G. Cao, MoSe₂ nanosheets perpendicularly grown on graphene with Mo–C bonding for sodium-ion capacitors, *Nano Energy* 47 (2018) 224–234.
- [30] Y. Nien, J. Carey, J. Chen, Physical and electrochemical properties of LiFePO₄/C composite cathode prepared from various polymer-containing precursors, *J. Power Sources* 193 (2009) 822–827.
- [31] Q. Gao, S. Wang, H. Fang, J. Weng, Y. Zhang, J. Mao, Y. Tang, One-dimensional growth of MoO_x-based organic–inorganic hybrid nanowires with tunable photochromic properties, *J. Mater. Chem.* 22 (2012) 4709–4715.
- [32] S. Zhuo, Y. Xu, W. Zhao, J. Zhang, B. Zhang, Hierarchical nanosheet-based MoS₂ nanotubes fabricated by an anion-exchange reaction of MoO₃-amine hybrid nanowires, *Angew. Chem. Int. Ed.* 52 (2013) 8602–8606.
- [33] K. Zhu, X. Wang, J. Liu, S. Lo, H. Wang, L. Yang, S. Liu, T. Xie, Novel amorphous MoS₂/MoO₃/Nitrogen-doped carbon composite with excellent electrochemical performance for lithium ion batteries and sodium ion batteries, *ACS Sustain. Chem. Eng.* 5 (2017) 8025–8034.
- [34] Z. Che, Y. Li, K. Chen, M. Wei, Hierarchical MoS₂@RGO nanosheets for high performance sodium storage, *J. Power Sources* 331 (2016) 50–57.
- [35] Y. Wu, M. Xu, X. Chen, S. Yang, H. Wu, J. Pan, X. Xiong, CTAB-assisted synthesis of novel ultrathin MoSe₂ nanosheets perpendicular to graphene for the adsorption and photodegradation of organic dyes under visible light, *Nanoscale* 8 (2016) 440–450.
- [36] Y. Fang, L. Xiao, J. Qian, Y. Cao, X. Ai, Y. Huang, H. Yang, 3D Graphene Decorated NaTi₂(PO₄)₃ microspheres as a superior high-rate and ultracycle-stable anode material for sodium ion batteries, *Adv. Energy Mater.* 6 (2016), 1502197.
- [37] Q. An, F. Xiong, Q. Wei, J. Sheng, L. He, D. Ma, Y. Yao, L. Mai, Nanoflake-assembled hierarchical Na₃V₂(PO₄)₃/C Microflowers: superior Li storage performance and insertion/extraction mechanism, *Adv. Energy Mater.* 5 (2015), 1401963.
- [38] D. Choi, D. Wang, I. Bae, J. Xiao, Z. Nie, W. Wang, V. Viswanathan, Y. Lee, J. Zhang, G. Graff, Z. Yang, J. Liu, LiMnPO₄ nanoplate grown via solid-state reaction in molten hydrocarbon for Li-ion battery cathode, *Nano Lett.* 10 (2010) 2799–2805.
- [39] Y. Tang, Z. Zhao, Y. Wang, Y. Dong, Y. Liu, X. Wang, J. Qiu, Carbon-stabilized interlayer-expanded few-layer MoSe₂ nanosheets for sodium ion batteries with enhanced rate capability and cycling performance, *ACS Appl. Mater. Interfaces* 8 (2016) 32324–32332.
- [40] L. Ma, X.P. Zhou, L.M. Xu, X.Y. Xu, L.L. Zhang, W.X. Chen, Ultrathin few-layered molybdenum selenide/graphene hybrid with superior electrochemical Li-storage performance, *J. Power Sources* 285 (2015) 274–280.
- [41] L. Yang, S. Wang, J. Mao, J. Deng, Q. Gao, Y. Tang, O.G. Schmidt, Hierarchical MoS₂/polyaniline nanowires with excellent electrochemical performance for lithium-ion batteries, *Adv. Mater.* 25 (2013) 1180–1184.
- [42] K. Chang, D. Geng, X. Li, J. Yang, Y. Tang, M. Cai, R. Li, X. Sun, Ultrathin MoS₂/nitrogen-doped graphene nanosheets with highly reversible lithium storage, *Adv. Energy Mater.* 3 (2013) 839–844.
- [43] Y. Wang, G. Xing, Z. Han, Y. Shi, J. Wong, Z. Huang, K. Ostrikov, H. Yang, Pre-lithiation of onion-like carbon/MoS₂ nano-urchin anodes for high-performance rechargeable lithium ion batteries, *Nanoscale* 6 (2014) 8884–8890.
- [44] X. Kong, Y. Wang, J. Lin, S. Liang, A. Pan, G. Cao, Twin-nanoplate assembled hierarchical Ni/MnO porous microspheres as advanced anode materials for lithium-ion batteries, *Electrochim. Acta* 259 (2018) 419–426.
- [45] B. Yin, X. Cao, A. Pan, Z. Luo, S. Dinesh, J. Lin, Y. Tang, S. Liang, G. Cao, Encapsulation of Co_x nanocrystals into N/S Co-doped honeycomb-like 3D porous carbon for high-performance lithium storage, *Adv. Sci.* (2018), 1800829.
- [46] G. Fang, Z. Wu, J. Zhou, C. Zhu, X. Cao, T. Lin, Y. Chen, C. Wang, A. Pan, S. Liang, Observation of pseudocapacitive effect and fast ion diffusion in bimetallic sulfides as an advanced sodium-ion battery anode, *Adv. Energy Mater.* 8 (2018), 1703155.