

Directionally Assembled MoS₂ with Significantly Expanded Interlayer Spacing: A Superior Anode Material for High-Rate Lithium-Ion Battery

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Despite the great promise of molybdenum disulfide (MoS₂) as storage anodes for rechargeable lithium-ion batteries, the corresponding rate capacity is limited by the low electrical conductivity and kinetic barriers linked to ion diffusion, which prevents MoS₂ from being used in current electrical energy storage devices. A feasible strategy is reported to tackle these challenges by directionally growing MoS₂ nanosheets with expanded interlayer spacing (i.e., 9.4 Å versus 6.15 Å for pristine 2H-MoS₂) on multiwall carbon nanotubes (MWCNTs), which is performed through microwave-assisted solvothermal reduction of ammonium tetrathiomolybdate [(NH₄)₂MoS₄] in dimethylformamide in the presence of MWCNTs. The intimate interfaces between the MoS₂ edges and the MWCNTs as well as the expanded interlayer gaps in MoS₂ offer efficient and rapid pathways for ion and electron transport, which is favorable for improving performance of batteries and enables achieving the highest rate capability. Batteries containing the as-synthesized MoS₂/MWCNT anodes can constantly deliver a reversible capacity of 390 mA h g⁻¹ at a current rate up to 57.312 A g⁻¹ (36C), describing the first class of MoS₂-based anodes promising for high-rate use.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely adopted for powering portable electronics, while current technologies remain inadequate for applications such as hybrid or electric vehicles, electric transportation, in which high rate capability is required. Ideal electrode materials for these emerging applications should possess fast ion and electron transport kinetics in addition to high specific capacity, hence improving energy storage at high charge/discharge rates. Common strategies explored to enhance ion and electron transport in active electrode materials include using nanostructures, which offers exceptionally short transport lengths and significantly reduced lithium ion diffusion time, and hybridizing them with electrical conductive additives such as carbon.¹⁻³ Besides, for layered intercalation hosts, expanding interlayer distance could also effectively improve the intrinsic ion diffusivity owing to the decreased diffusion energy barrier, which has been verified theoretically⁴⁻⁶ and experimentally.^{5, 7-10} However, no significant improvements in rate performance have been observed for the studied layer-

structured materials.

Recently, transition metal dichalcogenides with layered structures have aroused a lot of interest from the viewpoints of their versatile physics and chemistry as well as natural abundance.¹¹⁻¹⁴ Among these materials, molybdenum disulfide (MoS₂) is fundamentally and technologically interesting for a wide variety of applications including electrochemical energy storage,¹⁵⁻¹⁷ catalysis,¹⁸ chemical sensing,^{19, 20} transistors,²¹ and photodetectors,²² thanks to their unique electronic/optoelectronic properties.^{11, 12, 15, 18, 19, 21, 22} The use of MoS₂ as lithium ion storage electrodes of LIBs is highly promising as it presents considerable advantages in terms of high rate capability, high capacity retention, small volumetric expansion and low cost.²³ MoS₂ crystallizes in a graphite-like lamellar structure that coupled by weak van der Waals forces and readily allows ion intercalation chemistry. Considerable effort has been invested to the development of MoS₂ for lithium storage, typically focused on synthesizing highly nanostructured materials to shorten the diffusion path for ions and electrons,^{8, 24-28} and on combining MoS₂ with carbon materials to increase electrical conductivity.²⁹⁻³³ Other strategies to this purpose include introducing dipole molecules (e.g., water) to reduce the polarization of solvated ions, thereby boosting the ion diffusivity,⁵ or incorporating suitable polymer such as poly-(ethylene oxide) (PEO) that possesses ion coordination properties to accelerate lithium ion transportation.³⁴ Nevertheless, using MoS₂-based materials as candidate electrodes for rapidly charging and discharging is still not realized yet.⁸

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In this article, a new class of anode material consisting of interlayer-expanded MoS₂ nanosheets directionally anchored on multiwall carbon nanotubes (denoted as IE-MoS₂/MWCNTs), which enables high specific capacity, excellent capacity retention, satisfied coulombic efficiency, and especially good rate capability. It exhibits a reversible charge/discharge capacity of 1442 mAh g⁻¹ at 1.592 A g⁻¹ (1C) and retains excellent capacity with small polarization at rate as high as 57.3 A g⁻¹ (36C). The successful synthesis benefits from the rational promotion of heterogeneous nucleation of MoS₂ on the controlled oxidized MWCNTs through a microwave-assistant solvothermal reduction of (NH₄)₂MoS₄ in dimethylformamide (DMF). Because of the simplicity, low energy consumption, and ease in scaling up, the method developed for synthesizing IE-MoS₂/MWCNTs offers new opportunities for the rational design of electrode materials with enhanced conductivity and rate performances.

2. Experimental Section

2.1 Chemical Oxidation of MWCNTs

All chemicals were used as received without further purification. The controlled oxidation of MWCNTs was carried out according to the process reported elsewhere.³⁵ In brief, 0.3 g of MWCNT powders were dispersed in 25 mL aqueous solution formed from mixing sulphuric acid (H₂SO₄, 96 wt%) and hydrogen peroxide (H₂O₂, 30 wt%) (V_{H₂SO₄} : V_{H₂O₂} = 7:3) in a 100-mL round-bottom flask equipped with a condenser. The dispersion was constantly stirred for 5 h to completely disperse the MWCNTs. The resulting dispersion was then diluted with appropriate amount of water, followed by filtration. The collected black solid was washed with water thoroughly until the pH of washing water became neutral. The washed solid was then placed in fume hood and dried for 2 days in the ambient environment. The dry solid was re-dispersed in DMF (anhydrous, 99.8%, Sigma-Aldrich) to form a dispersion with concentration of ~3 mg mL⁻¹.

2.2 Synthesis of IE-MoS₂/MWCNTs

In a typical synthesis, 10 mg of (NH₄)₂MoS₄ (99.97%, Sigma-Aldrich) was added to 6 mL of DMF dispersion of oxidized MWCNTs, followed by vigorous magnetic stirring for 15 min under ambient condition. The resulting solution was transferred into a 10-mL microwave reaction vessel, which was sealed and heated to 240 °C at a fast temperature ramp in a Monowave 300 microwave reactor (Anton Paar). The solution temperature was maintained for appropriate time. The reaction solution was then cooled down to room temperature with pressurized nitrogen flow. The synthesized IE-MoS₂/MWCNTs product was collected via centrifugation at 6,000 r.p.m. (revolutions per minute) for 5 min. After removal of the colourless supernatant, the precipitate was washed with distilled water and absolute ethanol for at least 4 times, followed by drying at 60 °C in an oven for 4 h. Elemental analysis indicated that the MoS₂ loading in the IE-MoS₂/MWCNTs composite was 36 wt%. Since the DMF

solution of (NH₄)₂MoS₄ exhibited a brown colour, the colourless supernatant indicated that the synthesis yield reached approximately 100%.

2.3 Characterization

The as-synthesized samples were examined by X-Ray diffraction (XRD), which was carried out on a Bruker D2 Phaser X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV and a current of 10 mA. TEM and HRTEM images were recorded with a JEOL 2010F(s) transmission electron microscope operated at an acceleration voltage of 200 kV. The energy dispersive X-ray (EDX) spectra were collected with an INCA X-ray microanalysis system equipped on the JEOL 2010F(s) microscope. All samples were prepared by drop-casting the ethanol suspensions of interesting nanostructures onto the carbon-coated copper grids, followed by drying in fume hood at room temperature. The synchrotron small-angle X-ray scattering (SAXS) measurement was performed at the beam line 12-ID-B of Advanced Photon Source (APS), Argonne National Laboratory.

2.4 Battery Assembly and Performance Evaluation

In a typical process for fabricating working electrodes with the synthesized IE-MoS₂/MWCNTs, 850 mg of IE-MoS₂/MWCNTs was mixed with N-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich), 50 mg of C45 (Timcal), and 100 mg of polyvinylidene (PVdF, Kureha KF-9300) to form a slurry. This slurry was then coated on a Cu foil (60 cm \times 70 cm) using a doctor blade, followed by drying in a vacuum oven set at 75 °C overnight to evaporate NMP solvent. The loading of IE-MoS₂/MWCNTs for the electrode was ~0.2 mg cm⁻². Punching the film formed electrode discs with size of 0.5 cm in diameter, which were then further dried under vacuum at 110 °C to remove any moisture trapped in the electrode. The 2032-type coin cells were assembled in an argon-filled glove box (O₂, H₂O < 5 ppm) using the as-fabricated electrode discs as anodes and lithium foils as the counter electrodes (cathode). The electrodes were separated with a Celgard 2325 separator soaked with electrolyte (Tomiya Chemical Industry, Japan) consisting of 1.2 M LiPF₆ in Ethylene carbonate (EC):Ethyl methyl carbonate (EMC) with a weight ratio of 3:7. Anodes made of pure IE-MoS₂ nanostructures and MWCNTs were also fabricated and used to assemble coin cells by following the same procedure.

The assembled coin cells were all cycled on a Maccor cycler. They first went through an initial activation step at room temperature, which consisted of three cycles between 3 V and 0.0005 V with C/20 current. Then, the cells were aged within the same voltage range but with 1C rate to evaluate their cycling performance. The specific capacities were calculated based on the mass of the integrated IE-MoS₂/MWCNTs including the mass of both MoS₂ and MWCNTs. After either activation step or targeted 1C aged cycles, the cells were discharge to 0.9 V and held at the potential for more than 15 hours to wait for the AC impedance measurement. An EG&G 273A potentiostat and a Solartron SI1260 frequency response analyzer controlled by ZPLOT

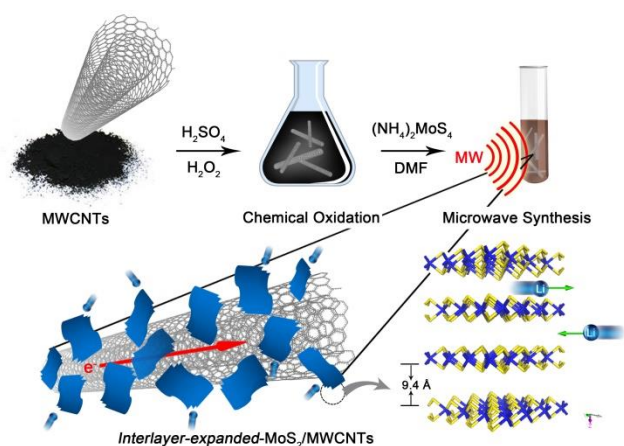


Fig. 1 Schematic illustration of the synthesis of IE-MoS₂/MWCNTs through a microwave-assisted solvothermal reduction of (NH₄)₂MoS₄ in DMF in the presence of oxidized MWCNTs. The resulting MoS₂ nanosheets exhibit an expanded interlayer spacing of 9.4 Å and directionally anchor on the outmost walls of MWCNTs forming intimate interfaces between the MoS₂ edges and the MWCNT walls.

measurement software were used. The impedance spectra were collected between 100 kHz and 10 mHz, with a 10 mV perturbation around the open-circuit voltage.

3. Results and Discussions

3.1. Characterization of the IE-MoS₂/MWCNTs heterostructures

The IE-MoS₂/MWCNTs hybrid structures are prepared by microwave-heating a DMF solution of (NH₄)₂MoS₄ in the presence of MWCNTs under solvothermal condition. Fig. 1 highlights the major steps involved in the synthesis and the structure of the product. It is noteworthy that pure MWCNTs usually present poor wettability with foreign active materials. The MWCNTs are firstly oxidized with a mixture of H₂SO₄ (96 wt%) and H₂O₂ (30 wt%) to provide oxygen-containing groups³⁵ that exhibit increased wettability towards Mo precursor. The enhanced affinity promotes heterogeneous nucleation of MoS₂ upon reduction of MoS₄²⁻ ions at high temperatures, leading to the formation of MoS₂/MWCNTs hybrid structures. Due to the increased reducing ability of DMF at elevated temperatures, oxidized MWCNTs (Ox-MWCNTs) are reduced to MWCNTs by eliminating the oxygen-containing groups. The chemical conversion of Ox-MWCNTs to MWCNTs stops the continuous nucleation of MoS₂ on the Ox-MWCNTs. Therefore, continuous reduction of MoS₄²⁻ ions only grow the existing MoS₂ nuclei into larger MoS₂ nanosheets. The non-wettability between MoS₂ and MWCNTs (i.e., hydrophilic MoS₂ versus hydrophobic MWCNTs) forces the growing MoS₂ nanosheets to protrude out of the MWCNT surfaces, enabling a directional assembly of the as-grown MoS₂ nanosheets on the outmost walls of the MWCNTs with the formation of intimate interfaces between MoS₂ edges and MWCNT walls. Such a directionally aligned growth of MoS₂ nanosheets on the MWCNTs has also been observed in the synthesis of MoS₂/graphene composites.^{36, 37} Similar to the synthesis in the absence of

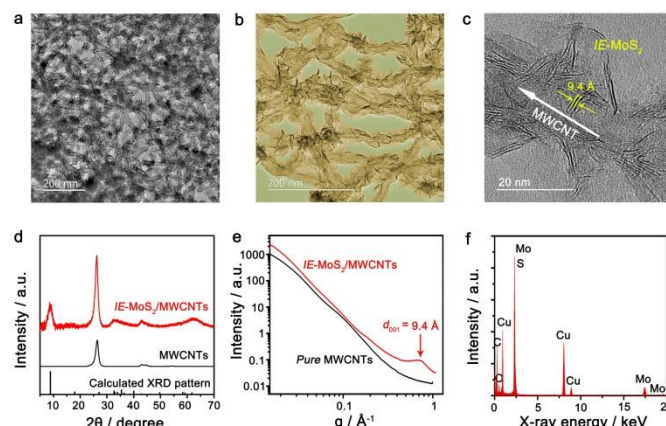


Fig. 2 Characterization of the synthesized IE-MoS₂/MWCNTs hybrid structures. (a,b) Typical TEM images with different magnifications. (c) HRTEM image of a partial MWCNT decorated with IE-MoS₂ nanosheets, showing characteristic features including thin thickness of the MoS₂ nanosheets, expanding MoS₂ interlayer spacing of 9.4 Å, and interfaces between MoS₂ edges and MWCNT wall. (d) Comparison of XRD patterns of the IE-MoS₂/MWCNTs (red) and MWCNTs (black), revealing the formation of MoS₂ with expanded interlayer spacing and the intactness of the MWCNTs in the course of synthesis illustrated in Fig. 1. The sticks represent the theoretical peak positions and their relative intensities corresponding to MoS₂ with an expanded interlayer spacing of 9.4 Å. (e) Comparison of synchrotron SAXS patterns of the IE-MoS₂/MWCNTs (red) and the corresponding MWCNTs (black). (f) EDX spectrum of the IE-MoS₂/MWCNTs.

MWCNTs, the resulting MoS₂ nanosheets on the MWCNTs also exhibit an expanded interlayer spacing of 9.4 Å (versus 6.15 Å for pristine 2H-MoS₂).³⁸ The large interlayer gap is mostly ascribed to the leftover species (e.g., DMF solvent molecules or NH₄⁺ ions) of the synthesis reaction.

Fig. 2 presents a typical sample of IE-MoS₂/MWCNTs synthesized from a reaction performed at 240 °C for 100 min. The corresponding transmission electron microscopy (TEM) images (Fig. 2a, 2b, and 2c) show the sheet-like MoS₂ grown uniformly around each MWCNT. Each MoS₂ nanosheet consists of only a few (3-5) S-Mo-S molecular layers and it links to the MWCNT through its edge rather than its basal surface. Most MoS₂ nanosheets exhibit sizes less than 20 nm. Control experiments illustrate that using MWCNTs without oxidation treatment leads to the failure of anchoring MoS₂ (Fig. S1); while in the absence of MWCNTs, the exact same synthesis produces sphere-like assemblies of MoS₂ nanosheets, where homogeneous nucleation takes place (Fig. S2). Independent from the nucleation process, such microwave chemistry always forms nanostructured MoS₂ with enlarged interlayer spacing of 9.4 Å, which is consistent with the high-resolution TEM (HRTEM) image shown in Fig. 2c.

Fig. 2d shows the X-ray diffraction (XRD) pattern of the synthesized IE-MoS₂/MWCNTs product, in which the strong Bragg peak at 25.8° corresponds to the (002) reflections of the MWCNTs with lattice spacing of 3.4 Å.³⁹ The wide-angle reflections in a 2θ range of 30°-70° can be indexed to the hexagonal MoS₂ (JCPDS 77-1716). The asymmetric nature of the reflections indicates the turbostratic feature of grafted MoS₂ nanosheets, presumably caused by, for example, the presence of stacking faults among S-Mo-S molecular layers as a result of a-b plane gliding.^{38, 40} The symmetric peak at low angle of 9.4° originates from the (002) reflections of the layer-

structured MoS₂ with interlayer spacing of 9.4 Å, which is consistent with the HRTEM observation. Such expanded interlayer spacing is also confirmed with synchrotron small-angle X-ray scattering (SAXS) pattern, which displays a single scattering peak centered at $q = 0.67 \text{ \AA}^{-1}$ (corresponding to 9.4 Å in *d* spacing determined from $q = 2\pi/d$) (Fig. 2e). In contrast, the corresponding MWCNTs do not show any characteristic SAXS peaks, further confirming the interlayer-expanded feature of the MoS₂ nanosheets. Compared to the *d* spacing of 6.15 Å for pristine 2H-MoS₂, about 53% expansion of S-Mo-S interlayer distance is observed in the synthesized IE-MoS₂/MWCNTs, which may facilitate the intercalation/diffusion of lithium ions.^{4,5} Energy-dispersive X-ray (EDX) spectrum (Fig. 2f) identifies Mo, S, and C as the majority of elemental components (Cu and part of C signals emanating from the carbon-coated TEM grid), further demonstrating the formation of IE-MoS₂/MWCNTs hybrid structures.

3.2. Electrochemical performance of the IE-MoS₂/MWCNTs heterostructures

Lithium ion storage performance in the as-synthesized IE-MoS₂/MWCNTs of Fig. 2 has been evaluated in 2032-type coin cells using lithium metal as counter electrode. Each cell is initially discharged at a low rate of C/20 (20 h) to activate the electrode material along with storing lithium ions in IE-MoS₂ (activation process). Fig. 3a presents cyclic voltammograms (CVs) of an IE-MoS₂/MWCNTs electrode conducted at a slow scan rate of 0.5 mV s⁻¹. Two cathodic peaks at 0.99 and 0.45 V in the initial cycle can be attributed to lithium intercalation into layered MoS₂, leading to a possible transition from the trigonal prismatic 2H semiconducting phase to the octahedral 1T metallic phase (Fig. S3),^{41, 42} followed by a conversion reaction and eventually a deep conversion to stoichiometrically equivalent Mo- and Li₂S-rich composition, which is still a reducing derivative of MoS₂ containing Li⁺ (e.g., Li₃MoS₂).^{29, 32, 42} The peakless current variation between 0.99 and 0.45 V is ascribed to the continuous insertion of lithium ions into the expanded MoS₂ interlayer gaps in the course of discharge.^{43, 44} The following anodic process shows two lithium extraction peaks at 1.76 and 2.29 V, which are related to the oxidation of intermediate conversion species (e.g., Li₃MoS₂ containing possible Mo and Li₂S clusters, Li₅Mo₂S₄).^{29, 32, 42, 45} The subsequent CV profiles of the IE-MoS₂/MWCNTs are consistent, showing the disappearance of the two peaks at 0.99 and 0.45 V that are observed in the first cathodic scan. Instead, two pairs of redox peaks show up: the reduction peak at 1.96 V corresponds to the reverse process of the oxidation peak at 2.29 V, highlighting the redox reaction between MoS₂ and LiMo₂S₂ (the shallow insertion intermediate). The reduction peak at 1.23 V corresponds to the reverse process of the oxidation peak at 1.73 V, denoting the reduction/oxidation between the chemical conversion intermediates (e.g., Li₃Mo₂S₄ and Li₅Mo₂O₄) and the shallow insertion intermediate (LiMo₂S₂). The high consistency in CV profiles indicates good anode stability and electrochemical reversibility of the

synthesized IE-MoS₂/MWCNTs. According to the density-functional theory (DFT) simulations, George et al. suggested the stable intermediates in the lithiation process include LiMo₂S₂ (shallow insertion of Li⁺), Li₃Mo₂S₄ and Li₅Mo₂O₄ (intermediate insertion of Li⁺ and chemical conversion), and Li₃MoS₂ with possible Li₂S, Mo atomic chains, and MoLi alloy (deep insertion and chemical conversion).⁴⁵ The lithium intercalation and conversion reaction increases the interlayer gap while the integrity of the layered structure still remains. The calculation results indicate that the expanded interlayer spacing of MoS₂ in the synthesized IE-MoS₂/MWCNTs material benefits the lithium intercalation and conversion reaction yet eliminates the structural failure of the layered MoS₂ structure.

Comparative CV studies on pure IE-MoS₂ and MWCNTs show significant electrochemical differences from IE-MoS₂/MWCNTs (Fig. S4 and S5), strongly suggesting that the synergistic effect between IE-MoS₂ and MWCNTs may enable unique battery performance. Fig. 3b compares the voltage profiles of IE-MoS₂/MWCNTs at the initial cycles. For the first cycle, IE-MoS₂/MWCNTs anode exhibits an impressive specific discharge capacity of 2538 mAh g⁻¹ while the specific charge capacity drops to 1414 mAh g⁻¹, which results in a low coulombic efficiency of ~56%. The coulombic efficiency can rapidly reach 92% in the third cycle with the discharge and charge capacities of 1655 and 1524 mAh g⁻¹, respectively. The difference of CVs between the first scan and the following scans is consistent with the difference of discharge curve between the first cycle and the second cycle, indicating that the initial reduction/discharge of the as-synthesized IE-MoS₂/MWCNTs involves many side reactions such as reaction with solvent molecules adsorbed on surfaces and trapped in the interlayer gaps, adsorbed high-oxidation-state species, and possible crystalline defects. The consistency of profiles of CVs and charge/discharge curves in the 2nd and higher cycles implies that the initial cycle conditions the electrode materials to behave reversibly in electrochemical redox processes relying on the characteristic structure and properties of the IE-MoS₂/MWCNTs (e.g., enlarged interlayer gap).

The rate capability of IE-MoS₂/MWCNTs has been assessed after the initial activation process. Fig. 3c exhibits the variation of discharge capacity from 2686 mAh g⁻¹ to 390 mAh g⁻¹ at the discharge/charge rate varying from C/30 (0.053 A g⁻¹) to 36C (57.312 A g⁻¹). Furthermore, the capacity of 1442 mAh g⁻¹ delivered at 1C (1.592 A g⁻¹) can be recovered and remains stable for numerous cycles after fast-rate operation (Fig. 3c). At a super high current rate of 57.312 A g⁻¹ (i.e., 36C), the electrode is still capable of delivering 390 mAh g⁻¹ capacity in 24.5 s (Fig. 3d). Such high rate capacity value achieved for IE-MoS₂/MWCNTs is remarkable and is far above the documented data for MoS₂-based anodes, in which rates higher than 10 A g⁻¹ are barely reported.⁸ Fig. 3e shows the stable capacity retention of the IE-MoS₂/MWCNTs anode upon cycling at 1C (1.592 A g⁻¹). An increase of the capacity observed in the initial 35 cycles is presumably caused by the delayed wetting of electrolyte into the composite electrode. After activation, it demonstrates a capacity of 1442 mAh g⁻¹ with

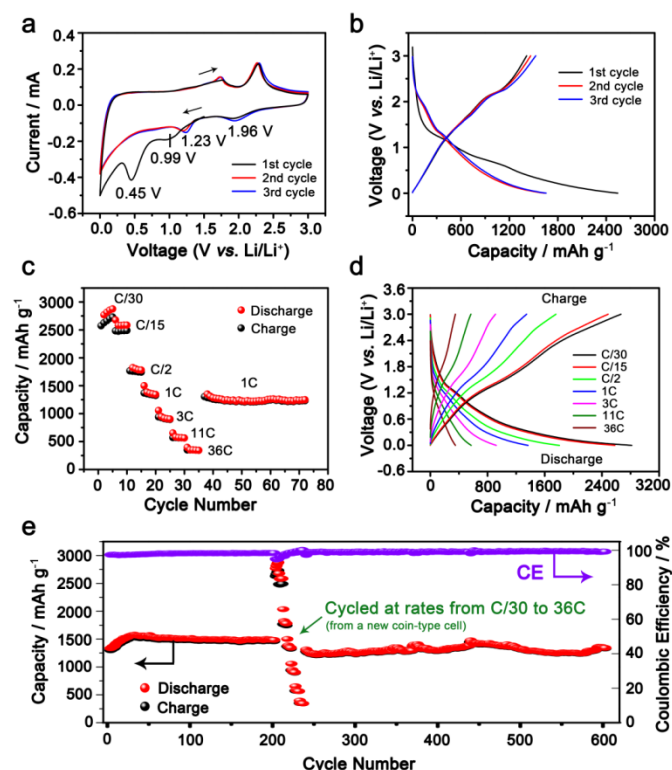


Fig. 3 Electrochemical performance of IE-MoS₂/MWCNTs anodes in lithium-ion batteries. (a) CV measurement of the IE-MoS₂/MWCNTs for the first 3 cycles (i.e., the initial activation step). The sweep rate was 0.5 mV s⁻¹ in the voltage range of 0-3 V versus Li/Li⁺. (b) Discharge-charge voltage profiles recorded in the first three cycles with 1C rate. (c) Comparison of discharge/charge capacities of the IE-MoS₂/MWCNTs anode at various current rates from C/30 to 36C. The measurements were performed after the initial activation step. (d) Representative discharge-charge voltage profiles at various C rates. (e) Discharge/charge capacities and the corresponding Coulombic efficiency measured over 600 cycles in the 0.0005-3 V.

coulombic efficiency of 98.4% and for a life extending 600 cycles with only 6.2% capacity decay (Fig. 3e). The battery performance of IE-MoS₂/MWCNTs is superior to that of pure IE-MoS₂ and MWCNTs (Fig. S6, S7), and also outperforms the reported MoS₂-based anode materials.

The electrode after being deeply cycled has been studied to gain insight into the excellent battery performance of IE-MoS₂/MWCNTs. High-angle annular dark field scanning

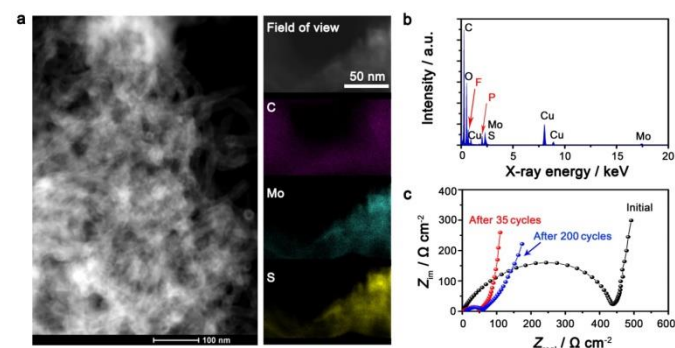


Fig. 4 Characterization of the IE-MoS₂/MWCNTs electrode after discharge/charge cycles. (a) HAADF-STEM image (left) and elements mapping (right) of the IE-MoS₂/MWCNTs electrode after 200 cycles. (b) EDX spectrum of the IE-MoS₂/MWCNTs electrode after 200 cycles. (c) Impedance measurements of the IE-MoS₂/MWCNTs electrode before (black) and after different numbers of cycles.

transmission electron microscopy (HAADF-STEM) image (Fig. 4a, left) reveals that the IE-MoS₂/MWCNTs hybrid structures still well remain after 200 fatigue cycles but with some extent of aggregation, which is likely due to the mixing with binders in the electrode preparation process. EDX elemental mapping over a typical area of the cycled electrode shows that the spatial distributions of Mo and S are completely same while they are different from that of C (Fig. 4a, right), implying the high possibility of that Mo and S atoms still bond together after cycles. Quantitative analysis of the corresponding EDX spectrum (Fig. 4b) reveals that the atomic ratio of Mo/S is ~1:2, close to the stoichiometry of MoS₂. The high-fidelity retention of spatial overlapping and stoichiometry of the Mo and S elements highlights that the long-time (200 cycles) discharge/charge operation does not completely break the original layered geometry of MoS₂ to form segregated nanoparticles. The structural integrity and interlayer distance of the cycled sample can be further studied with TEM and XRD if an appropriate method is developed to prepare clean sample to avoid the interferences of the electrolyte and binder.³⁶ Strong signal of C element is also observed, indicating the good retention ability on electrode constituents. The F and P signals are caused by the residual LiPF₆ electrolyte in the vicinity of the studied electrode material. The impedance change of IE-MoS₂/MWCNTs electrode has tracked before cycling and after 35 and 200 cycles. As shown in Fig. 4c, a tremendous impedance decrease can be observed for the cell after 35 cycles, which is attributed to the slow wetting of the electrolyte into the IE-MoS₂/MWCNTs, and also to exclusion of foreign adsorbates and crystalline defects in the initial discharge process. The decreased impedance agrees well with the capacity increase over first 35 cycles, as observed in Fig. 3e. No significant impedance increase is observed after 200 cycles, indicative of the limited growth of the solid electrolyte interphase during aging,⁴⁶ which further confirms the good cycling stability of IE-MoS₂/MWCNT.

3.3. Mechanism for high rate capability

Theoretically, the specific capacity of MoS₂ is calculated to be ~670 mAh g⁻¹ while the value for MWCNTs is ~340 mAh g⁻¹.^{23, 30, 41} The measured superior capacity of IE-MoS₂/MWCNTs is strongly indicative that a favorable synergistic effect exists in this composite electrode and thus affords capacity gains. Similar improved capacities have also been reported for other nanostructured MoS₂-based composites, for examples, MoS₂ decorated carbon nanofibers,³² MoS₂/polyaniline nanowires,⁴² MoS₂/MoC/carbon nanotubes,³⁰ MoS₂/graphene²⁹ and others. However, for the existing MoS₂-based materials, there is rare published data available for a rate higher than 10 A g⁻¹ (Fig. 5a), and the cycling stabilities are usually demonstrated below 200 cycles. Compared with the reported electrochemical data for MoS₂-based material (Fig. 5a), our IE-MoS₂/MWCNTs offer a capacity of 390 mAh g⁻¹ at a very high rate of 57.3 A g⁻¹ (36C) while capacity loss is barely observed in the course of continuous charge/discharge cycles (Fig. 3c), which represents the highest rate capability of MoS₂-based materials.

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The substantially improved battery performance in terms of the high rate capability and capacity can be attributed to the highly conductive MWCNTs, the advantageous interlayer-expanded MoS₂ structure, and the synergistic effect between them, which allow for enhancing ion and electron transport kinetics in battery. Carbon nanotubes permit nanoscale electrical wiring of active materials to their surfaces due to the striking percolation networks,^{47, 48} creating good composite electrode materials with high surface area and excellent electric conductivity. The high rate behavior significantly benefit from the interlayer expansion of MoS₂ grafted on the MWCNTs. As for layered materials, insertion and transport of lithium ions is mainly determined by diffusion energy barrier formed between polarizing cation and negatively charged host lattice.^{5, 49} For example, bulk MoS₂ with interlayer spacing of 6.2 Å exhibits a calculated diffusion barrier of ~0.49 eV.⁴ Recent studies suggest that such slow kinetics can be circumvented by enlarging the interlayer spacing of MoS₂,^{8, 24, 50} or by reducing dimensionality to monolayer,⁴ thus facilitating insertion and diffusion of lithium ions. Despite these successes, MoS₂-based materials perform at high current rates are rarely demonstrated, owing to the lack of effective approaches to further expand the interlayer spacing that permits an optimized lithium-MoS₂ interaction (reported values often <6.9 Å).^{8, 10, 24, 51-55} Fig. 5b highlights how the high electric conductivity of MWCNTs and expanded interlayer spacing of MoS₂ nanosheets cooperate to enable the fast lithium intercalation/diffusion and the following redox reaction involving electron transfer. The significantly expanded interlayer spacing (9.4 Å) facilitates insertion of lithium into the interlayer gaps in grafted MoS₂ nanosheets as well as the following lithium diffusion in the interlayer gaps.⁵⁶ Once lithium diffuse to the appropriate sites, redox reaction can occur between lithium and MoS₂ and the involving electrons can quickly migrate through individual S-Mo-S layers to the MoS₂ edges interfaced with the MWCNTs, which efficiently guide the electrons to the collecting electrode. Due to the large interlayer gaps allows all the MoS₂ units to (fully) wet with the lithium ions, the molecular layer structure can be maintained even after the IE-MoS₂/MWCNTs undergo a deep chemical conversion. In contrast, deep chemical conversion breaks the molecular layers of MoS₂ to enable lithium ions to diffuse to the buried MoS₂ units of MoS₂ nanosheets with narrow interlayer gaps. The unique features of the synthesized IE-MoS₂/MWCNTs enable outstanding rate capability that outperforms almost all the reported counterpart MoS₂-based electrode materials.

Conclusion

In summary, we have demonstrated a high-performance anode material composed of MoS₂ nanosheets with significantly expanded interlayer spacing, which are directionally assembled around highly percolated MWCNTs to exhibit very short lithium diffusion lengths as well as efficient and rapid pathways for electron and ion transport, boosting

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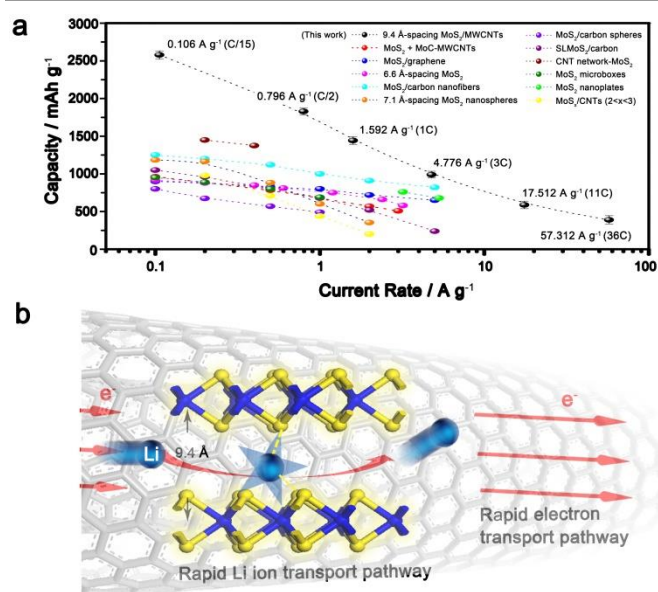


Fig. 5 (a) Comparison of rate capability for various MoS₂-based electrodes, including MoS₂+MoC-MWCNTs,³⁰ MoS₂/graphene,²⁹ 6.6 Å-spacing MoS₂,¹⁰ MoS₂/carbon nanofibers,³² 7.1 Å-spacing MoS₂ nanospheres,⁵⁷ MoS₂/carbon spheres,⁵⁸ single layer MoS₂/carbon,⁵⁹ CNT network-MoS₂,⁶⁰ MoS₂ microboxes,²⁷ MoS₂ nanoplates,⁸ and MoS₂/CNTs (2<x<3).⁶¹ (b) Schematic of the plausible mechanism responsible for the enhanced rate performance of the synthesized IE-MoS₂/MWCNTs.

discharge/charge kinetics. This newly developed composite material displays remarkable capability at high current rate even up to 57.3 A g⁻¹ (36C) and also performs very stable for over 600 cycles, representing the first MoS₂-based material attempting towards high-rate charge and discharge use. These understandings shed light on rational design of high-performance anode materials with superior rate capability that can be achieved by controlling nucleation and growth kinetics of colloidal chemistry. The IE-MoS₂/MWCNT hybrid structures exhibit major features completely different from the widely studied MoS₂/rGO (reduced graphene oxide) composites.⁶²⁻⁶⁴ The MoS₂/rGO composites usually form layer-by-layer stacking structures with the small-sized MoS₂ layers embedded in the stacked rGO sheets, resulting in a difficulty to expose the MoS₂ edges to electrolyte in batteries. Since the intercalation/deintercalation of ions in MoS₂ is dominated by the diffusion of ions through the MoS₂ edges into/out of the MoS₂ interlayer gaps, embedding the MoS₂ in stacked rGO dramatically reduces the diffusion rate of ions (i.e., lower rate capability of the corresponding batteries). In contrast, the IE-MoS₂/MWCNT composite (Fig. 2) completely eliminates the disadvantages of the MoS₂/rGO composites. The IE-MoS₂ nanosheets extend out of the MWCNTs to fully expose the MoS₂ edges to electrolyte, facilitating the intercalation/deintercalation of ions in the MoS₂ interlayer gaps and thus improving the rate capability of the corresponding batteries. The unique geometry of the IE-MoS₂/MWCNT structure and the expanded interlayer spacing of IE-MoS₂ can also benefit the high electric conductivity in individual S-Mo-S molecular layers, through which the electrons can quickly transfer to the highly conductive MWCNTs, to lower the impedance of the corresponding

anodes. It is worthy of note that the high surface area of the nanostructured IE-MoS₂/MWCNT electrode materials may induce a non-negligible capacitive behaviour to make a contribution to the electrochemical energy storage capacity of the materials. The actual contribution of storage capacity associated with lithium intercalation and conversion reaction may be smaller than the measured capacity (Fig. S8).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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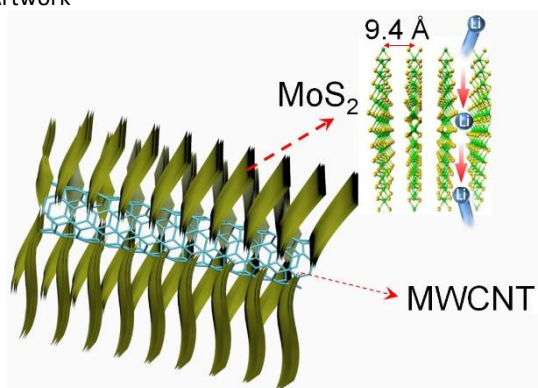
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Interlayer-expanded MoS₂ nanosheets directionally assembled on multi-walled carbon nanotubes represent a new class of anode materials for lithium ion batteries with superior high rate capacity.