MoO$_3$@MoS$_2$ Core-Shell Structured Hybrid Anode Materials for Lithium-Ion Batteries

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Abstract: We explore a phase engineering strategy to improve the electrochemical performance of transition metal sulfides (TMSs) in anode materials for lithium-ion batteries (LIBs). A one-pot hydrothermal approach has been employed to synthesize MoS$_2$ nanostructures. MoS$_2$ and MoO$_3$ phases can be readily controlled by straightforward calcination in the (200–300 °C) temperature range. An optimized temperature of 250 °C yields a phase-engineered MoO$_3$@MoS$_2$ hybrid, while 200 and 300 °C produce single MoS$_2$ and MoO$_3$ phases. When tested in LIBs anode, the optimized MoO$_3$@MoS$_2$ hybrid outperforms the pristine MoS$_2$ and MoO$_3$ counterparts. With above 99% Coulombic efficiency (CE), the hybrid anode retains its capacity of 564 mAh g$^{-1}$ after 100 cycles, and maintains a capacity of 278 mAh g$^{-1}$ at 700 mA g$^{-1}$ current density. These favorable characteristics are attributed to the formation of MoO$_3$ passivation surface layer on MoS$_2$ and reactive interfaces between the two phases, which facilitate the Li-ion insertion/extraction, successively improving MoO$_3$@MoS$_2$ anode performance.

Keywords: core-shell structure; hybrid anode; MoS$_2$; MoO$_3$; hydrothermal synthesis

1. Introduction

For the ever-growing need for renewable resources, the energy storage area has attracted much attention to alleviate environmental catastrophe and energy conditions caused by traditional fossil fuels [1]. In this regard, rechargeable Li-ion batteries (LIBs) have become by far the most promising energy storage systems for portable electronic devices and electric vehicles, due to their comparatively greater energy and power density, and long-cycle life [2–4]. Since the electrochemical properties of the active materials govern the LIB’s performance, the development of new materials for LIBs is a crucial factor. Although LIBs are receiving growing attention, a graphite anode with a theoretical capacity of 372 mAh g$^{-1}$ cannot meet the challenging requirements for higher energy density [5].

To substitute for graphite, various anode materials have been explored to improve the electrochemical performance, including transition metal dichalcogenides (TMDs) [6–10], transition metal oxides (TMOs) [11–13], titanium-based materials [14,15], carbon nanomaterials [16,17], and their composite materials [18,19]. Alloving-type anodes (Si, Sn, Ge) are...
the other alternative candidates that can replace graphite due to their very high theoretical capacity and relatively higher working potential, beneficial for reducing the risk of dendrite formation. However, the major drawback of these alloy-type anode materials is their massive volume expansion during cycling: for instance, Si expands up to 320%, leading to the failure of the active material. Extensive studies are ongoing to fix their volume expansion and stabilize them for LIBs [20–22]. Anode materials of the insertion type, such as carbonaceous materials and titanium-based oxides, have limited specific capacity. Compared to these insertion-type materials, conversion-type materials have a higher theoretical capacity of (600–1000 mAh g$^{-1}$) and may be ideal to meet the energy demand for large-scale energy storages [23]. Over the past several decades, TMOs, one of the conversion-type materials’ families, have been studied extensively in LIBs [23,24]. Recent research has shifted focus from transition metal oxides (TMOs) to transition metal sulfides (TMSs), due to their better electrical conductivity, mechanical and thermal stability, and higher electrochemical activity [25,26]. The majority of TMSs have 2D layered structures with a chemical composition of MS$_n$ (where $n = 1$ or 2, and M = Mo, W, Ti, V, or Sn). With an analogous layered structure to that of graphite anodes, 2D TMSs enable high rate capability via facile Li insertion and extraction, while the strong covalent bonding within the layers provides structural rigidity and robustness, leading to stable cyclability [27]. Even the interlayer spacings of these layer-structured TMSs are wider than graphite (~3.3 Å), for example, ~6.2 Å for MoS$_2$, ~5.9 Å for SnS$_2$, and ~5.7 Å for VS$_2$ [28]. Using 2D TMSs with larger interlayer spacing can significantly reduce the diffusion barriers for Li-ions, and accommodate their expansion upon insertion. Most importantly, TMSs have a higher voltage platform compared to graphite anodes, which prevents the formation of lithium dendrites, and ensures their high safety [26]. Thanks to those advantageous properties, several TMS-based materials have shown larger Li storage capacities than graphite anodes, making them promising candidates for high-performance LIB anodes [25,26]. Molybdenum sulfide (MoS$_2$), one of the most intriguing TMSs, has been studied in a number of applications, including nanoelectronics, electrocatalysis, and energy storage systems [29,30]. The MoS$_2$ anode in LIBs undergoes an intercalation-assisted conversion reaction, where a Mo nanocrystal is embedded in the Li$_2$S matrix as the final lithiated product and displays a high theoretical capacity of 670 mAh g$^{-1}$ [28,31].

Although TMSs materials have many advantages, there are still challenges that need to be urgently solved. A particular problem is the sulfur dissolution in electrolytes caused by soluble polysulfide intermediates that occur during Li$_2$S formation/decomposition, which results in the loss of sulfur components, thus abruptly deteriorating the capacity [26]. Various composite strategies with transition metal oxides have been explored to address the above problems, such as the TiO$_2$@MoS$_2$ [32], SnO$_2$/SnS$_2$ [33], MoO$_2$/MoS$_2$ [34], MoO$_3$/MoS$_2$ [35], MoO$_3$/SnS$_2$ [36], Fe$_2$O$_3$/MoS$_2$ [37], and MoS$_2$/MnO [38], which showed improved electrochemical performance in LIBs. However, making composites with TMO materials would not be optimal for mitigating the severe shuttling of lithium polysulfide (LiPSs), since the sulfide electrode interface remains exposed to the electrolyte. Surface protection, such as introducing a metal oxide protective layer, might help reduce polysulfide shuttling by preventing the dissolution of intermediates and accumulation of the sulfur phase on the lithium counter electrode [39]. W.-H. Ryu et al. reported a WO$_3$ protective layer on WS$_2$ nanofiber anode material, which dramatically improves the cycling performance in a sodium-ion battery [40]. Therefore, the synergistic effect of structurally stable TMOs’ surfaces with conductive TMS cores can be the key characteristic of potentially excellent electrochemical performance.

Herein, motivated by such synergetic effects of the TMO-covered TMS hybrid structure, we have proposed an in situ formation of MoO$_3$ on the MoS$_2$ TMS (denoted as MoO$_3$@MoS$_2$) by simple post-annealing of hydrothermally synthesized MoS$_2$. Structural characterizations have verified the formation of the MoO$_3$@MoS$_2$ hybrid structure. The MoO$_3$@MoS$_2$ hybrid anode has demonstrated much-improved cycling stability compared with the single-phase MoS$_2$ and MoO$_3$ counterparts, without sacrificing the high power and capacity.
2. Experimental Section

2.1. Synthesis of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$

The modified one-pot method was employed to synthesize the MoS$_2$ [41]. First, thiourea (SC(NH$_2$)$_2$, solution A), and ammonium molybdate ((NH$_4$)$_2$MoO$_4$, solution B) were dissolved in separate beakers for 30 min, followed by pouring solution B into solution A. This mixture was stirred moderately for another 30 min. Next, the transparent solution was placed into a 100 mL capacity Teflon-lined, stainless-steel autoclave, which was transferred to a convection oven programmed for the reaction at 200 °C for 12 h. After natural cooling to room temperature (RT), the black precipitates were collected, centrifuged with DI water and ethanol three times, then vacuum-dried at 100 °C for 1 h. Then, the as-synthesized MoS$_2$ was further calcined at (200, 250, and 300) °C at a 5 °C/min rate in a box furnace. As per the structural results, the (200, 250, and 300) °C annealed samples were denoted as MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$, respectively.

2.2. Material Characterizations

High-resolution powder X-ray diffraction (HRPD) data were collected at the 9B beamline of the Pohang Acceleration Laboratory (PAL, Pohang, South Korea), using a monochromated X-ray with a wavelength ($\lambda$) of 1.5183 Å. The Raman spectra were collected using a Renishaw inVia system with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements (Ulvac PHI X-tool spectrometer) were performed with Al–K$_\alpha$ X-ray radiation, to investigate the chemical and valance states of the materials. The Mo K-edge X-ray absorption spectroscopy (XAS) spectra were measured at the Pohang Accelerator Laboratory (PAL) 8C beamline, in transmission mode, and processed with Athena software. The morphology and microstructure of the powders were analyzed by field-emission scanning electron microscopy (FE-SEM, Regulus 8230, HITACHI) and transmission electron microscopy (TEM, Talos F200X, ThermoFisher). Thermogravimetric analysis (TGA) of the as-prepared sample was carried out on a NETZSCH (STA 449F3, Selb, Germany) thermal analyzer with a heating rate of 10 °C/min in open-air conditions. Electrical conductivity was evaluated using a Loresta-GP low-resistivity meter (MCP-T610, Mitsubishi Chemical corp.). The sample porosity characteristics were determined by nitrogen adsorption and desorption measurements at 77 k (Micromeritics, Norcross, GA, USA).

2.3. Electrochemical Measurements

The 2032-coin cells with a two-electrode configuration were used to perform the electrochemical experiments. The MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ powder samples were thoroughly mixed with conductive carbon black and poly(vinylidene) fluoride (PVDF) binder dissolved in N-methyl pyrrolidone (NMP) solution in an 8:1:1 weight ratio to make a viscous slurry. The working electrode was prepared using a doctor blade casting on a Cu foil current collector. The electrode loading level was controlled to be ~2.27 mg cm$^{-2}$ of active material. We used a TMAX roll press machine for calendaring. The density of electrodes was calculated to be 1.8997 g/cm$^3$. The coin cells were assembled inside a glove box filled with Ar gas, with a Li metal counter electrode, a separator (Celgard 3501), and 1.0 M LiPF$_6$ in a 1:1 (v:v) ratio of ethylene carbonate/dimethyl carbonate with 3% FEC additive as the electrolyte. After stabilizing the coin cell for 24 h, electrochemical tests were performed using a Neware (CT-4008–5 V 10 mA-164) battery cycler at RT. A Bio-Logic electrochemical system (VMP-3) was used to measure the cyclic voltammetry (CV). The cells were cycled at different current densities (35 to 700) mA g$^{-1}$ between the potential window of (0.01–3.00) V. A cyclic voltammetry (CV) test was done under a 0.1 mV s$^{-1}$ scan rate within the potential window of (0.01–3.00) V. A PGSTAT 302 electrochemical workstation (Metrohm Autolab) was employed to measure the electrochemical impedance spectroscopy (EIS) in the frequency range (100 kHz to 0.01 Hz) at an open-circuit voltage (OCV).
3. Results and Discussion

Scheme 1 shows a schematic of the hydrothermal reaction followed by post-annealing in the air to synthesize MoO₃@MoS₂ hybrid material. The SEM images in Figure 1a,b demonstrate that the as-prepared MoS₂ exhibits a 2D-sheet-like morphology, reflecting its 2D hexagonal structure, similar to the previous reports [27,41]. These nanosheets are twisted together due to their curved morphology, which causes many voids between them. When annealed at 250 °C in the air, the surface of the 2D-sheet-like structures appears somewhat disrupted, associated with the potential formation of a MoO₃ layer (Figure 1c,d). The presence of Mo, S, and O in the EDS (Energy dispersive spectroscopy) pattern (Figure S1 of the Supplementary Information (SI)) indicates that the MoO₃@MoS₂ hybrid has been successfully formed. Evidently, the MoO₃@MoS₂ hybrids exhibit a morphology that shows a mixture of sheet-like and particle-like characteristics, such that the surfaces appear excessively rough, in apparent contrast to the smooth surface of the pristine MoS₂ nanosheets (Figure 1a). On the other hand, when the sample is further annealed at 300 °C, different sizes of cuboid-shaped grains are observed for pure MoO₃ formation (Figure 1e,f).

Synchrotron-based high-resolution powder diffraction (HRPD) was used to investigate the crystal structure of the MoS₂, MoO₃@MoS₂, and MoO₃ samples, as presented in Figures 2a and S2. The characteristic peaks of the MoS₂ sample annealed at 200 °C match very well with those of the hexagonal-structured 2D MoS₂ with the space group P6₃/mmc (JCPDS # 37–1492), while the intense XRD peaks for MoO₃ annealed at 300 °C confirm the formation of a highly crystalline α-MoO₃ phase with an orthorhombic structure and space group Pbnm (JCPDS # 35–0609). Notably, the MoO₃@MoS₂ sample annealed at 250 °C exhibits the diffraction peaks corresponding to both hexagonal MoS₂ and orthorhombic MoO₃ phases, verifying the hybrid structure formation. Notably, the MoO₃ peak intensity in the MoO₃@MoS₂ hybrid was relatively lower than that of the MoO₃ sample heated at 300 °C, suggesting the relatively lower content of the MoO₃ than the MoS₂. Figure S3a–c depicts the HRPD profile matching data of MoS₂, MoO₃@MoS₂, and MoO₃. The as-prepared hybrid material perfectly matches and contains the well-positioned diffraction peaks of MoS₂ and MoO₃. The lattice volume (v) of the MoS₂ component in MoO₃@MoS₂ hybrid decreased by 0.71% when it was annealed at 250 °C, as shown in Table S1. The lattice volume contraction is due to the formation of the MoO₃ layer, which compresses the core lattice [42]. In the hybrid, however, the MoS₂ phase is not sufficiently crystallized to allow Rietveld refinement for calculating the weight fraction of MoS₂ and MoO₃.

Furthermore, the Raman spectra in Figure 2b also prove the successful formation of the MoO₃@MoS₂ hybrid, agreeing with the XRD results. The MoS₂ spectrum presents the E₁₂g (380.5 cm⁻¹) and A₁g (406 cm⁻¹) peaks corresponding to the in-plane and out-of-plane vibration modes of Mo-S, respectively [43]. The characteristic peak for the MoO₃ phase positioned at 664 cm⁻¹ belongs to B₂g/B₃g mode associated with the triply coordinated oxygen stretching in the 3MoO₆⁻ [44]. The Raman spectrum of the MoO₃@MoS₂ demonstrates the signature of both MoS₂ and MoO₃ peaks, confirming the formation of the MoO₃@MoS₂ hybrid.

![Scheme 1. Schematic of MoO₃@MoS₂ synthesis.](image-url)
Figure 1. FE-SEM images for (a,b) MoS$_2$, (c,d) MoO$_3$@MoS$_2$, and (e,f) MoO$_3$.

Figure 2. (a) HRPD and (b) Raman spectra of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$. 
XPS analysis was further performed to verify the chemical and electronic state at the sample's surface. Figure S4 of the SI shows the survey spectrum of the MoO3@MoS2 sample, supporting the concurrent presence of Mo, S, and O elements in the prepared sample. Figure 3a compares the high-resolution Mo 3d core level XPS spectrum for the MoS2, MoO3@MoS2, and MoO3 samples. Two distinct peaks displayed at 229.3 and 232.5 eV for MoS2 correspond to Mo4+ 3d3/2 and 3d5/2 states, respectively. The high-resolution XPS spectrum of the MoO3 profile exhibits the 236.1 and 233.5 eV peaks corresponding to the Mo6+ 3d3/2 and 3d5/2 states, respectively [45]. The Mo 3d region of the MoO3@MoS2-XPS profile reveals the presence of mixed Mo6+ and Mo4+ oxidation states. Interestingly, the intensity of two distinct peaks at 236.1 and 233.5 eV associated with the MoO3 is predominant in the XPS spectra of the MoO3@MoS2 sample. Meanwhile, the two other peaks correspond to Mo4+ oxidation states associated with the MoS2 shift to low binding energy, suggesting that electron transfer occurs between MoO3 and MoS2 [37]. This finding implies that the hybrid sample shows a strong coupling between the MoS2 and MoO3 interface. Figure 3b shows the S 2p XPS region of MoS2, MoO3@MoS2, and MoO3. For MoS2, the deconvoluted S 2p profile exhibits the doublet at 162.1 and 163.2 eV, while MoO3 shows no peak, confirming that only O and Mo are present in the MoO3 sample. The MoO3@MoS2 hybrid displays a noticeable shift of the two S 2p peaks to a lower binding energy, revealing that the MoO3 surface layer influences the valence states of the S species. The spectrum also includes a weak and broad peak at 168.9 eV, likely corresponding to the S-O bond formed during the post-annealing in air [46,47]. In Figure 3c, the deconvoluted O 1s region clearly establishes the Mo-O bonding in the MoO3 and MoO3@MoS2 hybrid samples [48–50]. Environmental sources and complete oxidation at 300 °C are attributed to the observed weak and strong O 1s peaks of MoS2 and MoO3, respectively. When compared to the MoO3@MoS2 hybrid sample, the shallow O 1s peak supports the evolution of the MoO3 oxide layer at the MoS2 surface.

Figure 3. (a) Mo 3d, (b) S 2p, and (c) O 1s XPS spectra of MoS2, MoO3@MoS2, and MoO3.
Overall, the Raman results are in complete accordance with the XRD results, but XPS results show somehow opposite behavior regarding the crystal structure of the MoO$_3$@MoS$_2$ hybrid sample. While XRD is a bulk probe (detected in the micrometer range), XPS is a surface probe (of a few nanometers). Based on the XPS data recorded in the Mo 3d and S 2p regions, the peak density associated with the sulfur phase dropped while the peak density for the oxide phase strengthened (Figure 3a,b), suggesting the MoS$_2$ surface almost converted to MoO$_3$. XRD results show that the MoS$_2$ phase predominates over the MoO$_3$ phase in bulk, while the XPS peaks show that the oxide phase prevails on the surface of the MoO$_3$@MoS$_2$ hybrid. The ratio of the integral area between oxygen and sulfur obtained from XPS survey data is 9.1 (O$_{2p}$/S$_{2p}$. 90.42/9.58). This ratio asserts our statement that the surface of MoS$_2$ almost converted to MoO$_3$. In contrast, we observed 1.5 wt% loss after the oxidation process above 250 °C in the TGA curve of as-synthesized MoS$_2$ (Figure S5). Based on the calculation (see the SI), the bulk MoO$_3$:MoS$_2$ ratio is approximately 1.5:8.5 in the MoO$_3$@MoS$_2$ hybrid. This finding confirms the results of XRD and Raman. Furthermore, another bulk probe technique, X-ray absorption spectroscopy (XAS), also exhibits a similar tendency to XRD. The Mo K-edge position of the MoO$_3$@MoS$_2$ hybrid is much closer to that of MoS$_2$ spectra, as shown in Figure 4a. There are two notable peaks in the Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra (without phase correction) of MoS$_2$ at approximately 1.91 and 2.92 Å, corresponding to Mo-S and Mo-Mo interaction in the first and second coordination shells, respectively [51]. As expected, the FT-EXAFS spectrum of MoO$_3$@MoS$_2$ matches very well with MoS$_2$, rather than MoO$_3$. This finding further confirms that the MoS$_2$ phase dominates the core of the MoO$_3$@MoS$_2$ hybrid, validating our XRD and Raman results. In light of these results, we conclude that the precise control of the post-annealing procedure (i.e., 250 °C in air) produces a MoO$_3$ surface layer on the MoS$_2$ backbone. Scheme 2 graphically presents the structural changes during the post-annealing. The optimization of the post-calcination temperature (~250 °C) is critical in tuning the surface oxidation degree of the MoO$_3$@MoS$_2$ hybrid, as the sulfide phase completely transforms into MoO$_3$ at 300 °C.

The morphology and phase information of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ nanostructures are further elucidated by TEM/EDS analysis, as depicted in Figure 5. The typical sheet-like morphology of MoS$_2$ is further confirmed by TEM images (Figure 5a,b). The selected area electron diffraction (SAED) patterns in Figure 5c displays three diffraction rings for the (002), (100), and (103) lattice planes, indicating the hexagonal MoS$_2$ polycrystalline structure (JCPDS # 37–1492). After introducing MoO$_3$, the sheet-like structures of MoS$_2$ are partially broken, as seen in Figure 5d,e. An enlarged TEM image shows d$_{002}$ edges of the MoS$_2$ phase (Figure S6 of the SI). The MoO$_3$@MoS$_2$ diffraction ring intensity appears weaker and blurrier than MoS$_2$ on the SAED (Figure 5f), but likely relates to the MoS$_2$ phase. This indicates that the sulfide phases are oxidized on the surface and turn into MoO$_3$ phases, which disrupts the MoS$_2$ crystallinity. These observations are consistent with the XRD and XPS results (Figures 2a and 3). In comparison, the cuboid-shaped MoO$_3$ (Figure 5g,h) shows entirely different SAED patterns (Figure 5i). The TEM-EDS elemental mapping (Figure 5j) indicates the uniform distribution of the Mo, S, and O species in the MoO$_3$@MoS$_2$ particles. It is evident that sulfur (red) exists within the particle’s core bodies, while oxide (green) is present at the surface, entirely covering the core. Figure S7a–c shows the BET sorption isotherm of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ samples. The type-III isotherm profiles and absence of a hysteresis loop suggest the low porosity of all the materials. The BET surface area of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ is only 8.71, 8.42, and 9.85 m$^2$ g$^{-1}$, respectively (Table S2). The pore distribution curve (Figure S7d) indicates the presence of only interparticle porosity.
Figure 4. Mo K-edge (a) XANES, and (b) FT-EXAFS spectra, of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$.

Scheme 2. Schematic of the phase transformation of MoS$_2$ between (~200 and ~300 °C).
Figure 5. TEM images and corresponding SAED pattern of (a–c) MoS₂, (d–f) MoO₃@MoS₂, (g–i) MoO₃. (j) TEM-EDS mapping image of MoO₃@MoS₂.

The electrochemical performance of each sample was tested in the LIB half-cells. The cyclic voltammetry (CV) of the MoO₃@MoS₂ hybrid was measured in the voltage window of 0.01 to 3.0 V with a sweep speed of 0.1 mV s⁻¹; the result is shown in Figure 6a. A reduction peak is located at 1.01 V, attributed to the Li-ion insertion between MoS₂ layers and forming LiₓMoS₂. Another peak positioned at 0.46 V is linked to the conversion reaction of LiₓMoS₂ to (Mo + Li₂S) [52]. These two reduction peaks shifted to a higher potential at about 1.91 and 1.15 V from the second cycle onwards. A shallow reduction peak at 0.1 V in the first cycle is the characteristic of solid electrolyte interface (SEI) formation. In the
anodic scan, peaks located at 1.73 and 2.29 V are linked to the reverse conversion reaction of Mo + Li₂S into MoS₂, respectively [34]. The position of the oxidation peaks remains unchanged in the following cycles. Notably, a small irreversible peak at 2.11 V is found in the first cathodic scan, indicating Li⁺ intercalation into MoO₃ crystals to generate LiₓMoO₃ [53]. Following the first cycle, the corresponding reduction peak did not occur, suggesting that the MoS₂ is the predominant participant in the redox activity of the MoO₃@MoO₃ hybrid anode. Therefore, it seems that the main function of MoO₃ is to stabilize MoS₂. Further, the observed CV shows excellent reversibility from the 2nd to 5th cycles, which indicates superior cycling stability. The observed area under the curve of the MoO₃@MoS₂ composite is higher than that of its pristine components (shown in Figure S8a–b in SI), indicating enhanced capacity. Figure 6b shows the galvanostatic discharge/charge (GCD) curve of MoO₃@MoS₂ at the current density of 50 mA g⁻¹; where the initial cycle reveals a remarkably high reversible (charge) capacity of ~721 mAh g⁻¹. The observed capacity is close to the theoretical limit of MoO₃@MoS₂ (~737 mAh g⁻¹). Based on the TGA data (Figure S5), we estimated the theoretical capacity as described in SI. Figure S9a–c shows the extended discharge/charge curves for MoS₂, MoO₃@MoS₂, and MoO₃. When comparing the GCD curves of the three samples, it can be seen that the MoO₃@MoS₂ hybrid outperforms the MoS₂ and MoO₃ counterparts in terms of cycling stability during 100 cycles, establishing its good stability as an active anode material for LIBs. Moreover, the similar trend of the charge/discharge curve for the hybrid anode from the second cycle indicates excellent electrochemical stability and conversion reversibility. In contrast, the charge/discharge efficiencies of the pristine MoS₂ gradually deteriorated over the 100 cycles. Figure 6c further illustrates the difference in cyclability among MoS₂, MoO₃@MoS₂, and MoO₃ anodes. The MoO₃@MoS₂ anode possesses a higher initial charge (reversible) capacity than MoS₂ and MoO₃, with a Coulombic efficiency (CE) of 80.5, 83.5, and 41.5%, respectively. There is a significant decrease in capacity for the first few cycles of the MoO₃@MoS₂ anode. This phenomenon is commonly observed in the conversion-based anode materials, because during the discharge-charge process of the initial cycles, the SEI layer is not fully formed. This accounts for the low CE and capacity loss during initial cycles, as reported in previous studies [6–20]. The CV result described earlier also accords with this behavior. However, after a few cycles, the MoO₃@MoS₂ anode started to stabilize and the Coulombic efficiency improved, which is a marked difference from the pristine MoS₂ or MoO₃ anodes. The obtained result highlights the superior Li⁺ storage performance of the MoO₃@MoS₂ anode. In addition, the MoO₃@MoS₂ anode demonstrates a notably higher capacity (~564 mAh g⁻¹) than that of MoS₂ (~34 mAh g⁻¹) and MoO₃ (~434 mAh g⁻¹) at the end of 100 cycles. Compared with an anode made of pure MoS₂, the MoO₃@MoS₂ anode exhibits enhanced electrochemical properties because of the MoO₃ passivation layer on the surface of the conductive MoS₂. When we disassembled cells for MoS₂ and MoO₃@MoS₂ electrodes after 30 cycles, we observed the active material residue on the lithium foil (counter electrode) for the MoS₂ anode sample. Contrary to this, there was no active material found on lithium foil (counter electrode) in the hybrid anode sample (Figure S10). During the charge/discharge cycles, MoS₂ and MoO₃@MoS₂ anodes undergo a steady conversion process, as evidenced by their Mo K-edge EXAFS spectra measured after the 50 cycles. The FT-EXAFS spectra peaks from their 50th cycle remain almost identical to those from their pristine state (Figure S11). Figure 6d and S12 show the rate capability of the MoO₃@MoS₂ hybrid and its pristine components (MoS₂ and MoO₃). As the current densities increase from 35 to 700 mA g⁻¹, the capacities of the MoO₃@MoS₂ anode decrease; but when the current density is returned to its initial value (35 mA g⁻¹), the active material retains a high-capacity value (~434 mAh g⁻¹). The pure MoO₃ shows very poor rate performance compared to MoS₂, which is attributed to the poor conductive characteristics of the oxide material, as presented in Table 1.
Figure 6. (a) CV and (b) discharge/charge profiles of MoO$_3$@MoS$_2$ between (0.01 and 3.00) V. (c) Comparative cycling performance at a current density of 50 mA g$^{-1}$ and (d) rate performance of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ anodes in LIBs.

Table 1. Electrical conductivity measurement (by four-point probe) results.

| Serial No. | Material        | Average Electrical Conductivity (µS cm$^{-1}$) |
|------------|-----------------|-----------------------------------------------|
| 01         | MoS$_2$         | 5.2442                                       |
| 02         | MoO$_3$@MoS$_2$ | 0.6443                                       |
| 03         | MoO$_3$         | 0.0282                                       |

Figure 7a,b shows the electrochemical impedance spectroscopy (EIS) data with a fitted profile, measured after the 1st and 30th cycles, respectively. An equivalent electrical circuit is presented, where $R_s$ is the solution resistance, $R_{ct}$ is the charge transfer resistance, $W$ is Warburg impedance, while the (CPE1 and CPE2) are the constant phase elements. Figure 7a clearly shows that the semi-circle of the MoO$_3$@MoS$_2$ hybrid anode Nyquist plot is much smaller than its counterparts (MoS$_2$ and MoO$_3$) after the 1st cycle. The calculated solution resistance ($R_s$) and charge transfer resistance ($R_{ct}$) of the hybrid anode are 2.392 and 284.308 Ω, respectively, which are lower than those of MoS$_2$ and MoO$_3$ (Table S3). Furthermore, after 30 cycles, the resistance of all the materials increases, but among them, MoO$_3$@MoS$_2$ shows much smaller resistivity. The hybrid anode material shows a lower $R_{ct}$ value (304.539 Ω) among the three materials (Table S4) thanks to the chemically resistive nature of oxide, which protects the sulfide phase from the dissolution into the electrolyte.
The outstanding performance of the hybrid anode results from the synergistic interaction between the passivating layer of MoO$_3$ and the active material, ensuring smooth electronic conduction. The work presented in this paper provides a simple, two-step, facile method to synthesize different transition metal oxide/sulfide hybrid nanostructures.

4. Conclusions

A novel, in situ approach to the synthesis of a hybrid nanostructure has been successfully optimized. This involves a two-step process of a hydrothermal reaction with subsequent air annealing. The successful formation of the MoS$_2$ core-MoO$_3$ shell hybrid structure was verified by XRD, Raman, XPS, and XAS results. SEM and TEM studies reveal the morphology evolution with the growth of an oxide layer on the bulk sulfide, which facilitates stable cycling stability without sacrificing the high capacity and fast-charging performance. The MoO$_3$@MoS$_2$ hybrid anode delivered an excellent specific charge capacity of 721 mAh g$^{-1}$, a good rate-capability of 278 mAh g$^{-1}$ at 700 mA g$^{-1}$, and the retained capacity was ~564 mAh g$^{-1}$ after 100 cycles, with excellent (~99%) Coulombic efficiency. The outstanding performance of the hybrid anode results from the synergistic interaction between the passivating layer of MoO$_3$, which eradicates the excessive dissolution of active material, and the conducting core of MoS$_2$, which ensures smooth electronic conduction. The work presented in this paper provides a simple, two-step, facile method to synthesize different transition metal oxide/sulfide hybrid nanostructures.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12122008/s1, Figure S1: EDX spectrum of MoO$_3$@MoS$_2$; Figure S2: XRD of (a) MoS$_2$ and (b) MoO$_3$, including MoO$_3$@MoS$_2$, compared with their corresponding standard (PDF) data; Figure S3: Profile matching of HRPD data of (a) MoS$_2$, (b) MoO$_3$@MoS$_2$, and (c) MoO$_3$; Figure S4: XPS survey spectrum of MoS$_2$, MoO$_3$, and MoO$_3$@MoS$_2$; Figure S5: Thermogravimetric analysis (TGA) curve of as-synthesized MoS$_2$ in air; Figure S6: HR-TEM image of the MoO$_3$@MoS$_2$ sample; Figure S7: (a–c) BET and (d) corresponding BJH profile of MoS$_2$, MoO$_3$, and MoO$_3$@MoS$_2$; Figure S8: CV curves of (a) MoS$_2$ and (b) MoO$_3$ anodes; Figure S9: GCD curves of the (a) MoS$_2$, (b) MoO$_3$@MoS$_2$ and (c) MoO$_3$; Figure S10: Photos of Li counter electrodes for the MoS$_2$ and MoO$_3$@MoS$_2$ electrodes half-cells; Figure S11: Ex-situ Mo K-edge FT-EXAFS spectra of MoS$_2$ and MoO$_3$@MoS$_2$ after 50 cycles; Figure S12: The galvanostatic voltage profiles (rate performance) of MoS$_2$ and MoO$_3$@MoS$_2$ anodes at different current densities in LIBs; Table S1: Unit cell parameters of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$; Table S2: Result of BET analysis of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$; Table S3: Fitted solution resistance ($R_s$) and charge transfer resistance ($R_{ct}$) values of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ after 1$^{st}$ cycle; Table S4: Fitted solution resistance ($R_s$) and charge transfer resistance ($R_{ct}$) values of MoS$_2$, MoO$_3$@MoS$_2$, and MoO$_3$ after 30$^{th}$ cycle; Table S5: Comparative table depicting electrochemical performance of selected TMO/TMS and/or carbon hybrids. References [33,36,54–58] were cited in Supplementary Materials.
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