

Article

Molten Salt-Assisted Catalytic Preparation of MoS₂/α-MoO₃/Graphene as High-Performance Anode of Li-Ion Battery

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Abstract: We report on the facile and scalable catalytic conversion of natural graphite and MoS₂ minerals into α-MoO₃ nanoribbons incorporated into hexagonal MoS₂ and graphene nanosheets, and evaluate the structural, morphological and electrochemical performances of the hybrid nanostructured material obtained. Mechanochemical treatment of raw materials, followed by catalytic molten salt treatment leads to the formation of nanostructures with promising electrochemical performances. We examined the effect of processing temperature on the electrochemical performance of the products. At 1100 °C, an excellent Li-ion storage capacity of 773.5 mAh g^{−1} is obtained after 180 cycles, considerably greater than that of MoS₂ (176.8 mAh g^{−1}). The enhanced capacity and the rate performance of this electrode are attributed to the well-integrated components, characterized by the formation of interfacial molybdenum oxycarbide layer during the synthesis process, contributing to the reduced electrical/electrochemical resistance of the sample. This unique morphology promotes the charge and ions transfer through the reduction of the Li-ion diffusion coefficient (1.2×10^{-18} cm² s^{−1}), enhancing the pseudocapacitive performance of the electrode; 59.3% at the scan rate of 0.5 mV s^{−1}. This article provides a green and low-cost route to convert highly available natural graphite and MoS₂ minerals into nanostructured hybrid materials with promising Li-ion storage performance.

Keywords: natural graphite; MoS₂; molten NaCl; graphene; MoO₃; molybdenum oxycarbide



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1. Introduction

The development of efficient and low-cost energy storage devices is a key towards the electrification of various sectors, including the transportation and grid services [1–3], supporting the sustainable development goals. Lithium-ion battery (LIB) is the state of the art energy storage device in a wide variety applications and, therefore, its modifications in terms of performance, cost and availability of raw materials are of great importance [4–6]. Graphite, including synthetic graphite (SG) and modified natural graphite (NG) is a commonly used material for the fabrication of the anode of LIBs, due to its modest theoretical capacity of 372 mAh g^{−1} and high cycle stability [7,8]. SG is made by the graphitization of carbonaceous material at extremely high temperatures (≈3000 °C) [9], which is an extremely energy-intensive approach. NG originating from carbon-rich organics formed through the prolonged geological interactions [9] is considered as a promising alternative anode material mainly due to its high availability and low cost [10–12]. In fact, the world's NG reserves are huge, exceeding 800 million tons of recoverable graphite [13], with a typical low price of around USD 750 per metric ton (≈94% purity) [11] making NG highly attractive for energy applications. Despite these advantages, however, NG minerals often undergo expensive, energy intensive and time-consuming processes, including high-temperature treatments (>2300 °C), and/or treatment with hazardous chemicals such as HF [13–15]. Therefore, the direct application of NG minerals for the fabrication of anode materials

without going through expensive/environmentally problematic processes is required in order to appropriately utilize NG for future developments of LIBs.

Apart from NG, other naturally available materials such as molybdenum disulfide (MoS_2) have also attracted attentions due to their high availability and low-cost. In particular, the theoretical Li-ion storage capacity of MoS_2 is approximately three times greater than that of commercial graphite anodes [16,17]. Despite its potential capability, the application of MoS_2 as the anode of LIBs is challenging due to the low reversible capacity of the material at large cycle numbers. In contrast to MoS_2 , other molybdenum compounds such as molybdenum trioxide (MoO_3) have also been evaluated as the anode of LIBs. However, the cycling performance of MoO_3 is not satisfactory due to the low conductivity of the compound, and its disintegration during discharge/charge cycles [18–20]. These issues might be reduced by combining MoO_3 and MoS_2 so that the latter can enhance the conductivity of the nanocomposite and prevents the rapid disintegration [21–23]. The methods suggested for the synthesis of $\text{MoS}_2/\text{MoO}_3$ nanocomposites comprise of chemical vapor deposition [24], hydrothermal methods [25,26], in-situ growth [23], sulfur transfer [27], anion-exchange [28], and annealing treatment [29] using the precursor materials such as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and thiourea [23,28], organic amine, and MoO_3 [24], Mo metal powder and H_2O_2 [27] as well as MoO_3 powders, sulfur and N_2 [29]. These synthesis methods are typically complicated and require long processing periods involving expensive and/or environmentally problematic raw materials, limiting their capability at large scales.

With this background, the clean and facile preparation $\text{MoS}_2/\text{MoO}_3$ nanocomposites with enhanced Li-ion storage performance using low-cost and highly available minerals is an interesting goal. In a recent work, we suggested the mechanochemical–molten salt treatment of pure synthetic graphite with MoS_2 as a possible green way of producing nanostructures with promising Li-ion storage performance [30]. However, the application of pure synthetic graphite would greatly influence the economic and sustainability of the process. In this study, we show that the wet high-energy ball-milling of commercial MoS_2 , non-purified natural graphite and NaCl, followed by a heat-treatment at temperatures above the melting point of NaCl leads to the formation of well-integrated nanostructured hybrid materials, in which MoO_3 nanoribbons are incorporated with hexagonal MoS_2 and graphene nanosheets. We further study on the effect of heating regime on the microstructural evolution of the nanocomposite materials, and find out that at 1100 °C, the nanocomposite contains the highest amount of well-integrated $\alpha\text{-MoO}_3$ nanoribbons providing a promising Li-ion storage performance of 773.5 mAh g^{−1} after 180 charge/discharge cycles, considerably greater than that of MoS_2 (176.8 mAh g^{−1}). We suggest the formation of interfacial molybdenum oxycarbide that reduces the internal impedance, and promotes the ion/electron transfer within the nanostructured material, and its interface with the electrolyte. Furthermore, this article reports on the molten salt synthesis of hexagonal MoS_2 nanosheets, which are well incorporated into the nanocomposite and contribute to the high performance of the electrode by improving the electron and ion transportation across the material. The formation of hexagonal MoS_2 nanosheets, presented here, is in contrast with alternative techniques reported in the literature for the fabrication of such MoS_2 morphologies based on prolonged sulfurization of $(\text{NH}_4)_2\text{MoS}_4$ using H_2S at 800 °C [31,32]. Other techniques reported on the preparation of hexagonal WS_2 nanoflakes include thermal conversion of W_xO_y nanorods in the presence of S at 750 °C (6 h) under high-vacuum [33], and the electrochemical exfoliation of WS_2 in Na_2SO_4 [34]. Also, the preparation of hexagonal nanosheets of CdI_2 [35] and SnS_2 [36] have been reported using chemical vapor deposition and steam vapor etching. In this paper, we report on the facile preparation of hexagonally-shaped MoS_2 nanosheets incorporated with MoO_3 nanoribbons and graphene nanosheets ($\text{MoO}_3/\text{MoS}_2@\text{Graphene}$) by a simple mechanochemical–molten salt approach using natural graphite and MoS_2 minerals, with promising Li-ion storage performance. The mechanism involved in the preparation and the electrochemical performance of the nanostructured materials are investigated.

2. Results

2.1. Preparation of Materials

In this work, $\text{MoO}_3/\text{MoS}_2@\text{Graphene}$ samples were prepared using natural graphite mineral without conducting extensive modification/purification processes which are often performed to fabricate battery-grade materials. The details of the process are mentioned in “Materials and Methods” and summarized in Figure 1.

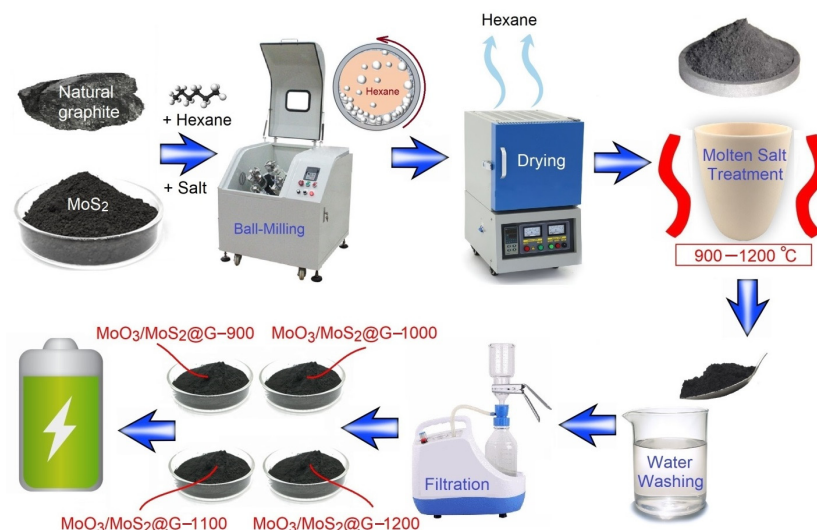


Figure 1. The process employed to convert natural graphite mineral and commercially available MoS_2 into nanostructured materials for energy-storage application.

2.2. Characterization of the Natural Graphite Mineral

It is useful to provide insights on to the chemical and microchemical composition of the NG used as the raw material in this research. Figure 2 shows the SEM/EDS element mapping analysis recorded on the sample. As can be seen from Figure 2a, the material contains graphitic flakes with lateral dimensions typically larger than $20\ \mu\text{m}$. According to the EDS analysis, in addition to carbon, other elements comprising Ca, Fe, O, S, Si, Al, and K could also be detected, indicating the impurity of the natural graphite material.

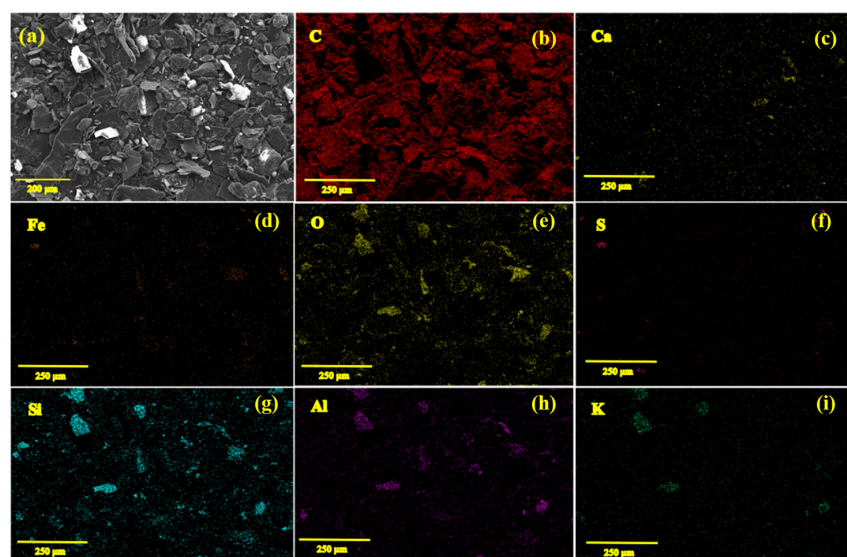


Figure 2. (a) SEM micrograph of the non-purified natural graphite material, and (b–i) corresponding elemental EDS mapping analysis exhibiting the distribution of various elements.

The presence of oxide impurities can clearly be recognized from the EDS analysis. The data obtained could be confirmed by the X-ray fluorescence (XRF) quantitative analysis recorded on the natural graphite sample, as exhibited in Table 1. The analysis performed shows that the carbon content of the material is 74.3 wt%. Other components include SiO₂ (9.27 wt%), Al₂O₃ (6.92 wt%), CaO (2.97 wt%), Fe₂O₃ (2.29 wt%), K₂O (2.17 wt%) and S (2.08 wt%). The natural graphite mineral was employed for the synthesis of MoO₃/MoS₂@graphene samples without purification, as explained in the next section.

Table 1. Quantitative XRF analysis of the natural graphite material (wt%).

C	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	S
74.3	9.27	6.92	2.97	2.29	2.17	2.08

2.3. Catalytic Phase Transitions during the Molten Salt Treatment

MoS₂ and natural graphite precursors were subjected to a ball-milling process (2 h) in the presence of hexane, and the BMed samples were heat treated with NaCl at 900, 1000, 1100 and 1200 °C in air for 20 min. These temperatures are greater than the melting point of NaCl (~800 °C), causing the progress of the reactions in a molten salt environment. This simple molten salt process led to the formation of MoS₂/MoO₃@Graphene nanocomposites, as can be realized from Figure 1, and the XRD patterns of Figure 3. Moreover, the XRF quantitative analysis of various samples, namely MoO₃/MoS₂@G-900, MoO₃/MoS₂@G-1000, MoO₃/MoS₂@G-1100 and MoO₃/MoS₂@G-1200 are shown in Table 2. From the XRD patterns, the graphite and MoS₂ materials do not show any change of crystalline structure after ball milling, while a reduction in the thickness of their flakes can be expected under the influence of the shear forces applied during the ball milling process. However, various phases can be detected in products obtained after the heat-treatment process at different temperatures, namely MoS₂ (PDF#03-065-0160), orthorhombic-MoO₃ (PDF#01-089-5108), monoclinic-MoO₃ (PDF#01-085-2405) and graphite (PDF# 01-075-2078).

Figures S1–S3 show high resolution XRD patterns of diffraction peaks corresponding to monoclinic and orthorhombic MoO₃ which are close to each other. In addition, Table S1 shows the intensity ratios of various phases in MoO₃/MoS₂@G-900, MoO₃/MoS₂@G-1000, MoO₃/MoS₂@G-1100 and MoO₃/MoS₂@G-1200. One observation from Figure 3 and Figures S1–S3 is that the monoclinic-MoO₃ (PDF#01-085-2405) could be formed only at 1200 °C. Moreover, the combination of Table S1 and Table 2 can lead to the conclusion that the amounts of sulfur, molybdenum, carbon and other elements in the samples heated at 900 and 1000 °C are nearly similar. In the samples heated at 1100 °C, however, the amount of sulfur is less, but the contents of other elements are more than those in the samples prepared at 900 and 1000 °C. Therefore, the amount of sulfur reaches to its maximum in the sample prepared at 1200 °C, while the proportions of other elements in this sample are the lowest among all samples.

Based on the observations mentioned above, it can be concluded that the content of MoS₂ gradually decreases, while the temperature is increased from 900 to 1100 °C. On the contrary, the content of MoO₃ gradually increases upon the temperature increase. When the temperature exceeds 1100 °C, the content of MoS₂ increases, leading to the assumption that MoO₃ would further transform into MoS₂. The mechanism involved in this phase transition will be discussed in this paper. As the result, the maximum amount of MoO₃ could be achieved at the heating temperature of 1100 °C.

Further characterization of samples was performed using Raman spectroscopy, and the results are shown in Figure S4. For C-MoS₂, the Raman spectrum shows two major E_{2g}^1 (380 cm⁻¹) and A_{1g} (406 cm⁻¹) activation modes. E_{2g}^1 is due to the in-plane vibration of S and Mo atoms, and A_{1g} is attributed to the relative vibration of S atoms in the out of plane direction. The other two relatively weak peaks observed at 285 and 450 cm⁻¹ belong to E_{1g} and longitudinal acoustic phonon mode in C-MoS₂, respectively, as shown in Figure S4a. After the ball milling process, the E_{1g} peak of C-MoS₂ disappears, and the A_{1g} -LA (M)

peak is promoted. However, the structure of C-MoS₂ and natural graphite phase has no significant change, as shown in Figure S4a. The Raman spectra of the products obtained at various temperatures are shown in Figure S4b. As can be seen from Figure S4b, in addition to peaks related to graphite and MoS₂, there are also peaks related to MoO₃, which are marked with red asterisks on the spectrum of the sample prepared at 1100 °C. Therefore, Raman spectra confirm the formation of MoO₃/MoS₂@Graphene.

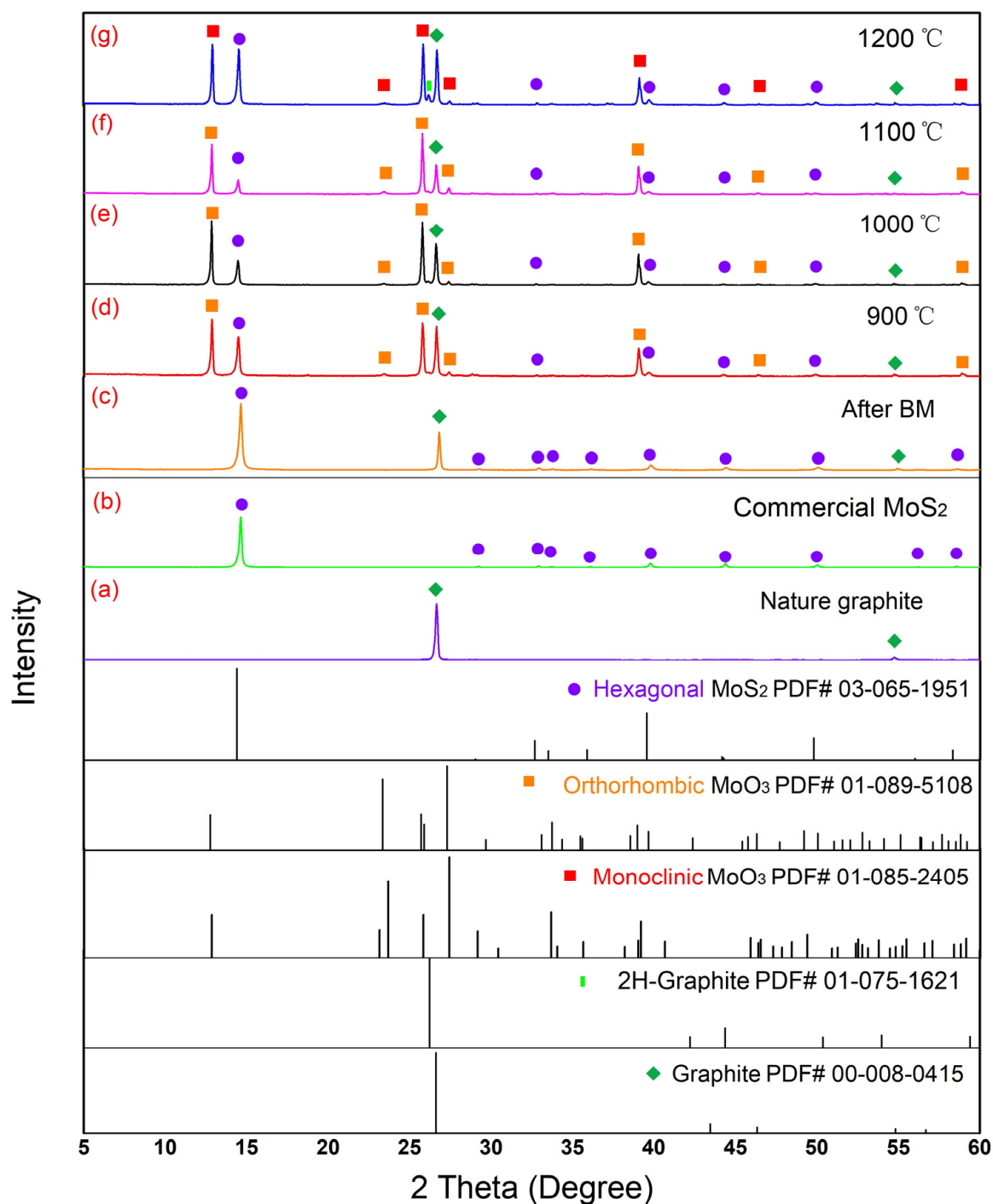


Figure 3. XRD patterns of various precursor materials and products: (a) the non-purified natural graphite material, (b) the commercial MoS₂, (c) the mixture after ball milling; and (d–g) nanostructured materials obtained at various temperatures.

Table 2. XRF quantitative analysis of the MoO₃/MoS₂@G samples prepared at various temperatures.

Sample	S	Mo	C	Si	Al	Fe	Ca	O
MoO ₃ /MoS ₂ @G-900	5.78	44.33	22.6	5.15	1.92	1.65	1.69	16.88
MoO ₃ /MoS ₂ @G-1000	5.59	45.18	23.3	6.36	2.42	1.15	1.74	14.26
MoO ₃ /MoS ₂ @G-1100	2.72	46.01	17.8	6.78	2.48	1.56	1.65	21.00
MoO ₃ /MoS ₂ @G-1200	10.2	48.48	15.6	5.96	2.07	1.82	1.18	14.69

On the other hand, the band gap energy indicates the energy required for the excitation of an electron to be moved from the valence band up to the conduction band. The Tauc method of evaluating the band gap using UV Vis spectroscopy was used to measure the values of the band gap, as shown in Figures S5 and S6 and Table S2. It can be concluded that the values of band gap energy gradually increase with the increase of the content of molybdenum trioxide. The reason behind this variation is based on the fact that MoO₃ is an n-type wide band gap (≈ 3 eV) semiconductor [37], so the value of energy band gap in the sample produced in 1100 °C is the largest.

2.4. SEM Characterization

To investigate the effects of the processing temperature on the morphology and microstructure of the nanocomposite materials prepared in this study, SEM characterization was carried out on commercial molybdenum disulfide (C-MoS₂), natural graphite and products comprising of MoO₃/MoS₂@G-900, 1000, 1100, and 1200. The results are shown in Figure S7 and Figure 4. The SEM micrograph of C-MoS₂ is shown in Figure 4a, indicating that the material consists of irregularly-shaped flakes with the sizes of typically around 2 μ m. SEM micrograph of natural graphite (Figure 4b) shows the sample is made of agglomerated flakes with typical sizes of several tens of micrometers. These two materials in combination with NaCl were used to fabricate MoO₃/MoS₂@G samples. As shown in Figure S7b–g, the morphology of the synthesized materials is different from those of starting material due to the formation of molybdenum oxides, hexagonal MoS₂ and graphene nanosheets. In MoO₃/MoS₂@G-900, the presence of orthorhombic-MoO₃ was already confirmed based on XRD analysis of Figure 3c. The oxide phase can be distinguished in Figure S7b as crystals with sizes of around 1 μ m, scattered within natural graphite and MoS₂ flakes. The presence of orthorhombic-MoO₃ is attributed to the partial oxidation of MoS₂, leading to the formation of the molybdenum oxide and gaseous sulfur dioxide, under the influence of atmospheric air. According to Figure 2, as the temperature increases to 1000 °C, MoS₂ is almost fully oxidized into orthorhombic-MoO₃. Moreover, the dimensions of resulting oxide are increased to form rod-like particles with dimensions in range of around 5–30 μ m, as shown in Figure S7c. The directional growth of orthorhombic-MoO₃ particles may lie on the preferential growth occurred along the-(001) direction in the orthorhombic structure of MoO₃, as further observed in TEM micrograph of Figure S8. By increasing the temperature to 1100 °C, the MoO₃ nanoribbons could grow even further, to form sheet-like particles with dimensions of around 50 μ m, as shown in Figure S7d and Figure 4c,d. This observation suggests that at 1100 °C, other crystallographic directions in the orthorhombic lattice of MoO₃ nanoribbons contribute to the growth phenomenon observed, forming sheet-like particles, which is in contrast to the rod-like particles observed in Figure S7c.

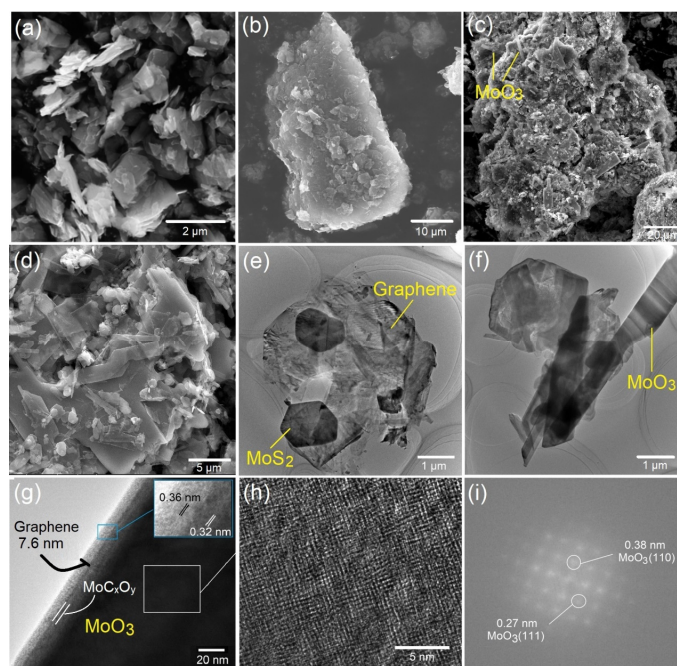


Figure 4. SEM micrographs of (a) commercial MoS_2 , (b) natural graphite, and (c,d) $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$. (e–h) TEM micrographs of $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$. (i) FFT pattern recorded on the micrograph (h).

According to Figure S7e,f, by raising the temperature to 1200 °C, large-sized MoO_3 crystals observed in Figure S7d disappear, and instead, a large number of hexagonally-shaped MoS_2 crystals form. This morphological evolution may be described based on the possible reaction between the natural graphite flakes and sulfur dioxide released by the oxidation of the original MoS_2 flakes, leading to the formation of elemental sulfur. Then, sulfur formed reacts on the surface of MoO_3 nanoribbons particles to form hexagonal MoS_2 nanosheets. As exhibited from Figure S7f, the hexagonal MoS_2 nanosheets grow from the surface of the MoO_3 nanoribbons particles, possibly, by replacing the oxygen of MoO_3 with S [28]. The size of hexagonal MoS_2 nanosheets is typically less than around 2 μm , as shown in the high-magnification image of Figure S8g. Figure S7h shows the EDS analysis recorded on the hexagonal MoS_2 nanosheet shown in Figure 5, providing further evidence for the nature of such hexagonal crystals.

The in-situ formation of hexagonal MoS_2 nanosheets on the surfaces of MoO_3 nanoribbons leads to the disintegration of the MoO_3 into smaller particles, as can be observed in SEM micrographs of Figure S7e,f. This phenomenon also causes the phase transition of MoO_3 from the orthorhombic crystalline structure ($\alpha\text{-MoO}_3$) to the monoclinic modification ($\beta\text{-MoO}_3$), as shown in Figure 2f. This hypothesized mechanism will be discussed further in next sections in this article. The combination of XRD and XRF analyses suggested that the MoO_3 content of the samples reaches its maximum value at 1100 °C. This behavior can be related to the action of molten NaCl to protect the MoO_3 particles from being excessively converted into hexagonal- MoS_2 nanosheets at 1100 °C, while this temperature allows the maximum oxidation of the original MoS_2 into MoO_3 nanoribbons. Considering the higher contentment of MoO_3 in the sample prepared at 1100 °C, the Li-ion storage capacity of this sample is expected to be greater than other samples, and this will be shortly discussed later in this article.

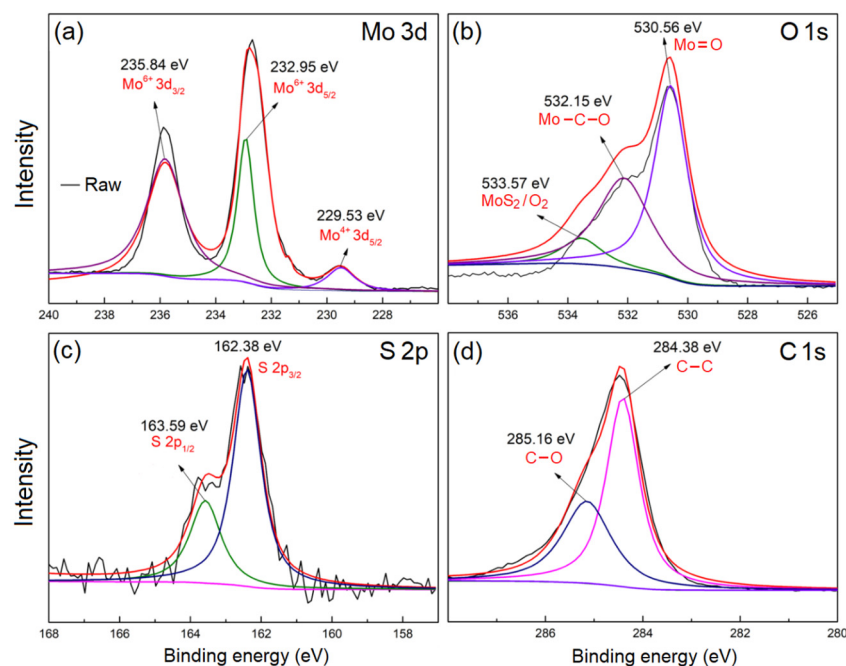


Figure 5. High resolution XPS spectra of MoO₃/MoS₂@G-1100, around (a) Mo 3d, (b) O 1s, (c) S 2p, and (d) C 1s peaks.

2.5. TEM Characterization

As observed in Figure 4c,d, the SEM morphology of MoS₂-MoO₃@G-1100 could be characterized by the presence of agglomerated nano-entities. TEM studies were performed to further investigate this morphology, and the results are shown in Figure 4e–i, where the presence of hexagonal MoS₂ nanoflakes ($\approx 1 \mu\text{m}$), graphene nanosheets and α -MoO₃ nanoribbons ($W \approx 400\text{--}800 \text{ nm}$; $L > 10 \mu\text{m}$) can be realized. The formation of such nanoribbons can be related to the presence of oxygen vacancies on the surface of MoO₃ crystals, providing the driving force for the solid-phase growth of oxides into nanoribbons [38,39]. The MoO₃ nanoribbons appears to be formed as the result of dominant crystal growth along the [001] direction, as shown in Figure S8. In TEM images, the presence of graphene nanosheets (originating from the natural graphite material) combined with hexagonal MoS₂ nanoflakes and MoO₃ nanoribbons is evident. Figure 4g–i provide further insights into the interface between graphene and MoO₃. Figure 4g shows a MoO₃ nanoribbon, where the presence of a graphene layer with the thickness of around 7.6 nm on its surface can be seen. The high magnification TEM image shown as the inset of Figure 4g shows the presence graphene layers with the interlayer spacing of 0.36 nm, representing (002) planes of hexagonal carbon. In addition, toward the bulk of sample, the interlayer spacing of 0.32 nm can be assigned to the (021) crystalline planes of orthorhombic-MoO₃. Moreover, there is an amorphous interface between the graphene nanosheets and MoO₃ which could be assigned to molybdenum oxycarbide formed during the molten salt processing of the sample. Formation of this interfacial phase will be further discussed by XPS analysis in this article. Figure 4h shows a high resolution TEM micrograph recorded on the MoO₃ nanoribbons, where the crystalline structure of the materials can clearly be observed. Figure 4i exhibits the fast Fourier transform (FFT) recorded on the micrograph of Figure 4h, where the spots related to the crystalline planes of orthorhombic-MoO₃ are indexed. Overall, XRD, SEM and TEM analyses suggest the formation of nanostructured MoO₃/MoS₂@G-1100, in which orthorhombic-MoO₃ nanoribbons, hexagonal MoS₂ nanoflakes and graphene nanosheets are well-integrated. The presence of interfacial molybdenum oxycarbide was also suggested.

2.6. Surface Characterization

The structural and microstructural characterizations mentioned above could demonstrate the formation of MoO₃ nanoribbons incorporated into hexagonal MoS₂ and graphene. The Li-ion storage performance of the products will be evaluated shortly in this article. However, before that, it would be interesting to shed light on to nature of the interface between the above mentioned phases. This was examined using XPS analysis, as shown in Figure 5. As can be observed, the characteristic peaks of Mo, O, S and C are debatable in the XPS spectrum of MoO₃/MoS₂@G-1100. High-resolution XPS spectra obtained on Mo 3d, O 1s and S 2p peaks are exhibited Figure 5a–c. As observed, the strong peak at 229.53 eV corresponds to Mo⁴⁺ 3d_{3/2}, and peaks at about 163.1 eV and 161.5 eV to S 2p_{1/2} and S 2p_{3/2}, respectively, revealing the existence of MoS₂ [40,41]. On the other hand, the peaks located at 235.79, 232.95, 530.56 and 532.15 eV correspond to the Mo⁶⁺ 3d_{3/2}, Mo⁶⁺ 3d_{5/2}. These peaks together with that appeared at 530.65 eV (corresponding to O1s components) indicate the presence of MoO₃ [27]. Moreover, the C 1s core level shown in Figure 5d could be deconvoluted into two peaks at 284.38 and 285.16 eV, which originate from the C–C and C–O bonds, respectively [41]. The presence of C–C bond is related to the graphene nanosheets, and C–O bond to the local interaction between graphene nanosheets and MoO₃.

Moreover, the presence of peak at 532.15 eV in Figure 5b indicates the presence of Mo–O–C [42] corresponding to the formation of interfacial molybdenum oxycarbide (MoC_xO_y) at the interface between MoO₃ and graphene nanosheets, as also suggested by the TEM micrograph of Figure 4g. Density functional theory calculations have confirmed the possibility of formation of molybdenum oxycarbide by reacting between zeolite-supported Mo and CO₂ [43]. Zhu et al. [42] suggested that MoO_xC_y can be formed from MoO₃, when vacancies available on the surface of MoO₃ are filled by carbon atoms. In our case, MoO₃ nanoribbons are wrapped with graphene nanosheets (Figure 4). Under this condition, the diffusion of carbon atoms into the surface of MoO₃ at high-temperatures such as 1100 °C is possible, leading to the formation of interfacial MoO_xC_y. It should be mentioned that molybdenum oxycarbide is generally considered to possess low electrical resistivity of 3 μΩm at room temperature [44]. The interfacial molybdenum oxycarbide is likely to promote the electrochemical performances of the nanostructured materials. This will be discussed later in this article. The well-incorporated phases in MoO₃/MoS₂@G-1100, and the possible presence of interfacial molybdenum oxycarbide, can lead to the reduced specific surface area (1.74 m² g^{−1}) and pore volume (0.008 cm³ g^{−1}). In agreement with these observations, the nitrogen adsorption–desorption isotherms of MoO₃/MoS₂@G-1100, shown in Figure 6, provide features corresponding to the type III isotherms, characteristic of the non-porous materials [45].

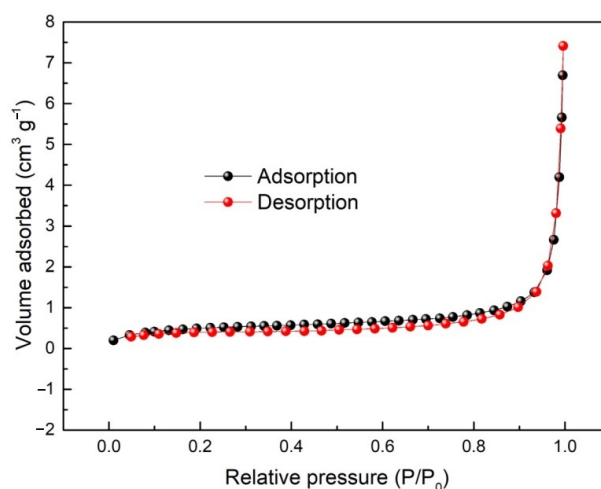
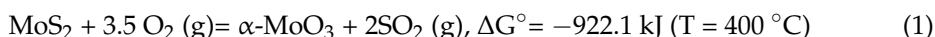


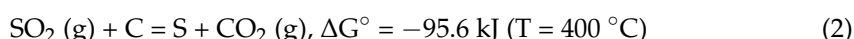
Figure 6. Nitrogen adsorption–desorption isotherms of MoO₃/MoS₂@G-1100.

2.7. Catalytic Formation of Hexagonal MoS₂ Nanocrystals and α -MoO₃

In this research, commercially-available MoS₂ flakes and natural graphite mineral were utilized as the initial material, and the product contained hexagonal MoS₂ nanocrystals. The conversion of flake MoS₂ into hexagonal nanocrystals is an interesting phenomenon discussed in this section. It is known that MoS₂ flakes start to oxidize at around 400 °C, leading to the formation of orthorhombic molybdenum trioxide (α -MoO₃) [46]. Therefore, the thermochemical reactions occurred in the process initiates with the formation of α -MoO₃ through the involvement of oxygen from the atmosphere:



In the presence of graphite, the SO₂ gas formed based on the reaction (1) is likely to be fixed by graphite flakes to generate elemental sulfur and carbon dioxide gas, as shown in Equation (2).



The combination of reactions (1) and (2) can lead to the reaction (3):



The generated elemental sulfur adhered to the surface of MoO₃ is likely to in-situ reduce the MoO₃ into hexagonal MoS₂ nanocrystals:



The reactions (1)–(4) demonstrates the thermodynamic possibility of the formation of α -MoO₃ and hexagonally shaped MoS₂ at temperatures greater than 400 °C initiating with the oxidation of MoS₂. In this research, the heating process was performed at temperatures above the melting point of NaCl. Therefore, the molten salt is likely to exfoliate the graphite flakes [47,48]. The formation of graphene nanosheets is evident from the TEM micrographs of Figure 4 and Figure S7. Figure S13 illustrates the possible mechanism involved in the catalytic formation of hexagonal MoS₂ nanocrystals and MoO₃ observed in this study.

To highlight the role of NaCl in the process, the sample prepared at 1100 °C was washed to remove its NaCl content, and the product (MoO₃/MoS₂@G-1100) was heated to 1200 °C for 5 min, without the involvement of NaCl. The appearance and X-ray diffraction pattern of the resulting sample are shown in Figures S9 and S10, respectively, providing evidence that the sample heated at 1200 °C mainly contains molybdenum oxide, without the participation of molten NaCl. In this case, carbon and molybdenum disulfide content of the sample are oxidized during the heat-treatment process to form molybdenum oxide and gas species at high temperature.

It should be mentioned that oxidation in air of graphitic carbon materials typically occurs at temperatures in the range 400–800 °C, depending on their grain size, level of crystallinity and presence of impurities that can catalyze the oxidation process [49,50] leading to the formation of gashouse species and ash. It is known that the oxidation of bulk and few-layer MoS₂ flakes does not readily take place at ambient conditions due to the high energy barrier involved [51–54]. However, non-isothermal oxidation of MoS₂ flakes initiates at temperatures as low as 350 °C with a limited rate, and increases by enhancing the temperature under an apparent activation energy of ≈ 1 kcal/mol, representing the bulk oxidation event. The oxidation process leads to the increase of the molybdenum oxide content (typically MoO₃), by increasing the temperature [55,56]. This is in agreement with our observation exhibited in Figure S10. Based on the observations mentioned above, the presence of NaCl provides an essential support toward the formation of MoO₃/MoS₂@G samples at high temperatures. First, molten NaCl provides an ionic environment to enhance the chemical reactions, while preventing the oxidation of species and supporting the exfoliation of graphite into graphenen nanosheets; the latter is discussed elsewhere [57].

2.8. Electrochemical Characterization of MoO₃/MoS₂@G Samples

We further investigated the Li-ion storage performances of MoO₃/MoS₂@G samples prepared at various temperatures, namely MoO₃/MoS₂@G-900, -1000, -1100 and -1200 in comparison with those of the initial commercial MoS₂ flakes, named as C-MoS₂. In the half-cell configuration, the driving force for the Li-ion insertion/extraction into/out of the electrode during the discharge/charge processes is provided by the negative/positive polarization applied on the electrode, respectively.

The electrochemical performances of the electrodes are shown in Figure 7. The electrodes were fabricated using the water-based polystyrene acrylic-acrylate as the binder, as explained in the Experimental section. Figure 7a shows the cycle performances of MoO₃/MoS₂@G electrodes, and selected outcomes are summarized in Table 3. As can be seen, MoO₃/MoS₂@G-1100 electrode shows a greater initial coulombic efficiency (CE) of 79.58% compared with other electrodes. After 100 cycles, this electrode exhibits a reversible capacity of 616.3 mAh g⁻¹ at 100 mA g⁻¹.

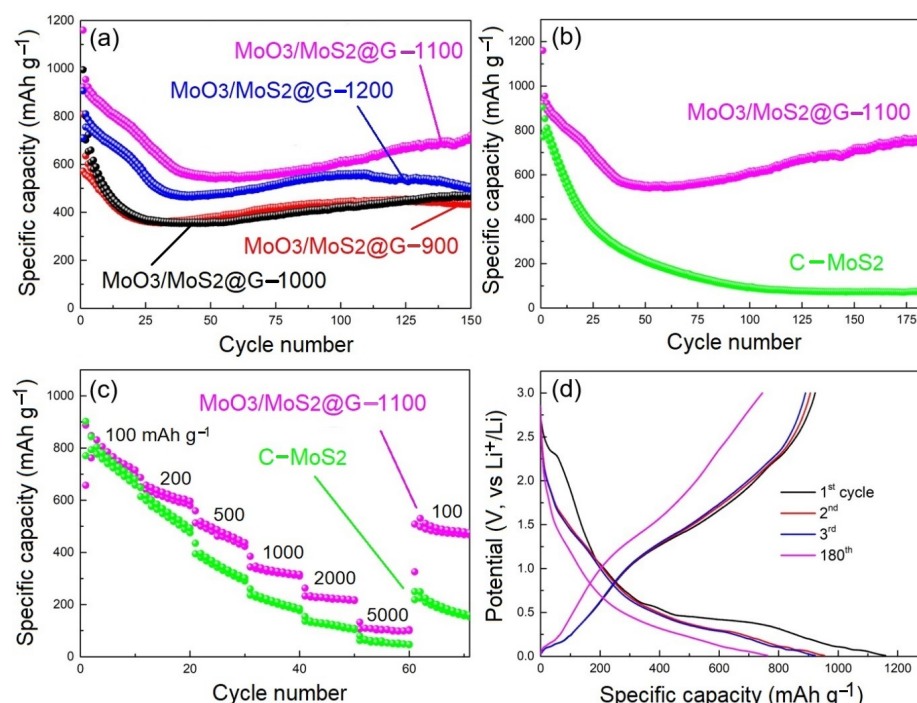


Figure 7. Li-ion storage performances of various electrodes. (a) Cycle performance of various electrodes. (b) Cycle performance, and (c) rate performance of C-MoS₂ in contrast with those of MoO₃/MoS₂@G-1100. (d) Potential-capacity curve of MoO₃/MoS₂@G-1100 electrode. All measurements were recorded at 100 mA g⁻¹, unless indicated otherwise.

Table 3. The electrochemical performance of commercial MoS₂ (C-MoS₂) in comparison with those of MoO₃/MoS₂@G nanostructured materials.

Electrode	Initial Coulombic Efficiency (%)	Specific Capacity after 100 Cycles (mAh/g)	Specific Capacity after 150 Cycles (mAh/g)
C-MoS ₂	85.13	94.8	73.5
MoO ₃ /MoS ₂ @G-900	70.64	444.1	442.8
MoO ₃ /MoS ₂ @G-1000	71.13	422.2	472.7
MoO ₃ /MoS ₂ @G-1100	79.58	616.3	721.2
MoO ₃ /MoS ₂ @G-1200	78.36	560.1	505.9

The performance MoO₃/MoS₂@G-1200 electrode can be evaluated to be greater than those of -900 and -1000 electrodes, but lower than that of -1100. The greater performance of MoO₃/MoS₂@G-1100 can be attributed to the greater amount of MoO₃ in this sample as realized from Figure 2 and Table 2. The other point that deserves attention is that by increasing the temperature to 1200 °C, the amount of MoO₃ in the sample reduces to reach its minimum among all samples, as evidenced from the relative low intensity of MoO₃ reflections observed in Figure 3. Despite having the minimum amount of MoO₃, the performance of the electrode is greater than samples prepared at 900 and 1000 °C. This observation can be assigned to the formation of β-MoO₃ with monoclinic crystalline structure at 1200 °C. This is known that the metastable β-MoO₃ has a highly ionically conductive open-structure [41], enhancing the electrochemical performance of MoO₃/MoS₂@G-1200, despite the lower MoO₃ content of the sample.

As can be seen in Figure 7d, the first discharge/charge specific capacity of MoO₃/MoS₂@G-1100 is recorded at 1159.6 mAh g⁻¹/953.8 mAh g⁻¹ (coulombic efficiency = 79.58%). This capacity loss can mostly be related to the generation of solid electrolyte interphase (SEI) layers on the electrode. The specific reversible capacity of the electrode could still be recorded at 773.5 mAh g⁻¹ after 180 cycles, as exhibited in Figure 7d. Figure S11 shows the durability of MoS₂/MoO₃/G-1100 sample in lithium-ion battery. As seen, the specific capacity after 400 cycles is still maintained at 240 mAh g⁻¹ under the current density of 500 mA g⁻¹.

Figure 8 shows the CV curve of the MoO₃/MoS₂@G-1100 electrode, providing detailed information about the Li-ion insertion and extraction processes. During the first cathodic scan, there is a cathodic peak at 0.56 V. This cathodic event cannot be observed in the subsequent cycles, providing evidence that this peak mainly corresponds to the formation of SEI. Moreover, the presence redox peaks at 1.56/1.76 V and 1.25/1.48 V in the first cycle can be related to the lithiation and delithiation of MoO₃, and to the metallization/oxidation of metallic molybdenum:

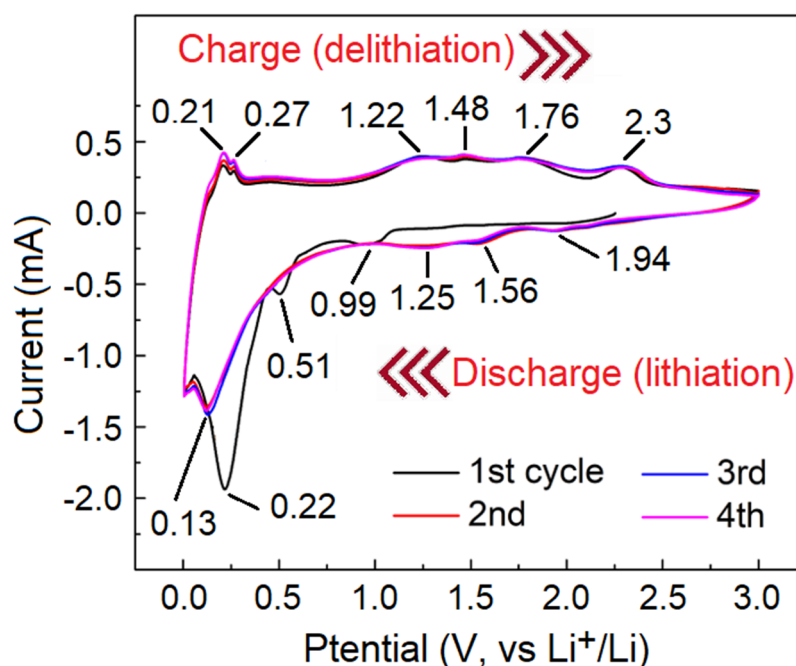
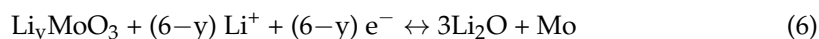
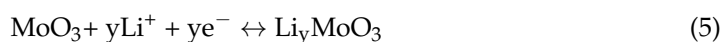
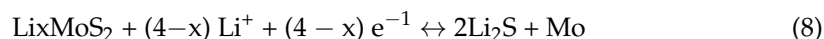
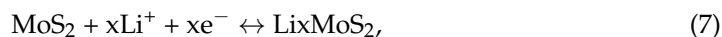


Figure 8. CV curve of MoO₃/MoS₂@G-1100 electrode recorded at 0.5 mV/s.

Moreover, the cathodic peak at 1.94 V might be attributed to the conversion from S_8 to Li_2S , and the oxidation peak at 2.3 V to the decomposition of Li_2S [58,59]. On the other hand, the redox peaks at 0.99/1.22 V corresponded to the following electrochemical reactions [60]:



Furthermore, the reduction/oxidation peaks at 0.21/0.22 V are related to adsorption/desorption of lithium ion on the surfaced of graphene nanosheets [61]. Overall, in agreement with Figure 7d, the CV curve of Figure 8 provides evidence for the electrochemical contribution of all the components of the electrode to the Li-ion storage performance observed.

2.9. Impedance Spectroscopy and Electrode Kinetics

Impedance spectroscopy performed on $MoO_3/MoS_2@G$ and C- MoS_2 . Figure 9a exhibits the Nyquist plots of the electrode. The plots show a semicircle in the high frequency range. The diameter of this semicircle can be related to the charge-transfer resistance (R_{ct}). In the low frequency range, the plots also show sloping straight lines. This part reflects the diffusion characteristics of lithium ions within the electrode [62]. The electrode made of $MoO_3/MoS_2@G-1100$ exhibits a smaller semi-circle diameter (40.71 Ω) than other samples, namely -900, -1000, -1200 and C- MoS_2 ; 63.65, 53.65, 62.9 and 263.8 Ω , respectively. This indicates the higher charge transfer resistance in the latter. The smaller electrochemical resistance observed in the $MoO_3/MoS_2@G-1100$ is consistent with the micrographs of Figure 4, indicating to the presence of integrated components with interfacial molybdenum oxycarbide that reduces the interfacial resistance across the sample.

The Li-ion diffusion (D_{Li}) involved in the electrochemical process discussed above can be calculated as follows [63]:

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (9)$$

Here, R and F represent the gas and Faraday constants, respectively, T is temperature (298 K) and n is the number of participating electrons ($n = 1$). C represents the concentration of Li^+ . The electrode surface area of the electrode (A) was calculated based on the diameter of the electrode (1.1 cm^2). Moreover, σ represents the Warburg factor which is determined based on the slope of the line $Z' \sim \omega^{-1/2}$ shown in Figure 9b, considering that $\omega = 2\pi f$ (f = frequency, Hz). The kinetic parameters of the electrode were determined from the equivalent circuit fitting of Nyquist plots (Figure 9a), and shown in Table 4. At low values of frequency, the $MoO_3/MoS_2@G-1100$ electrode exhibits a high slope (9.77 $\Omega s^{-1/2}$) which demonstrates the relatively high lithium ion diffusion coefficient [64]. The lithium ion diffusion coefficient of $MoO_3/MoS_2@G-900$, -1000, -1100, -1200 and C- MoS_2 electrodes could be calculated to be 8.7×10^{-21} , 1.8×10^{-20} , 1.2×10^{-18} , 5.3×10^{-21} and 1.0×10^{-21} , respectively. The larger D_{Li} in the earlier can be related to the shorter diffusion pathways available in the electrode, brought about by the presence of integrated hexagonal MoS_2 nanocrystals and graphene nanosheets as shown in Figure 4.

Table 4. Electrode kinetic parameters for the $MoO_3/MoS_2@G$ and C- MoS_2 electrodes.

Sample	R_e (Ω)	R_{ct} (Ω)	σ ($\Omega s^{-1/2}$)	D_{Li} ($cm^2 s^{-1}$)
$MoO_3/MoS_2@G-900$	6.90	63.65	114.61	8.7×10^{-21}
$MoO_3/MoS_2@G-1000$	6.56	53.56	79.39	1.8×10^{-20}
$MoO_3/MoS_2@G-1100$	2.21	40.71	9.77	1.2×10^{-18}
$MoO_3/MoS_2@G-1200$	3.92	62.9	146.53	5.3×10^{-21}
C- MoS_2	3.56	263.8	334.49	1.0×10^{-21}

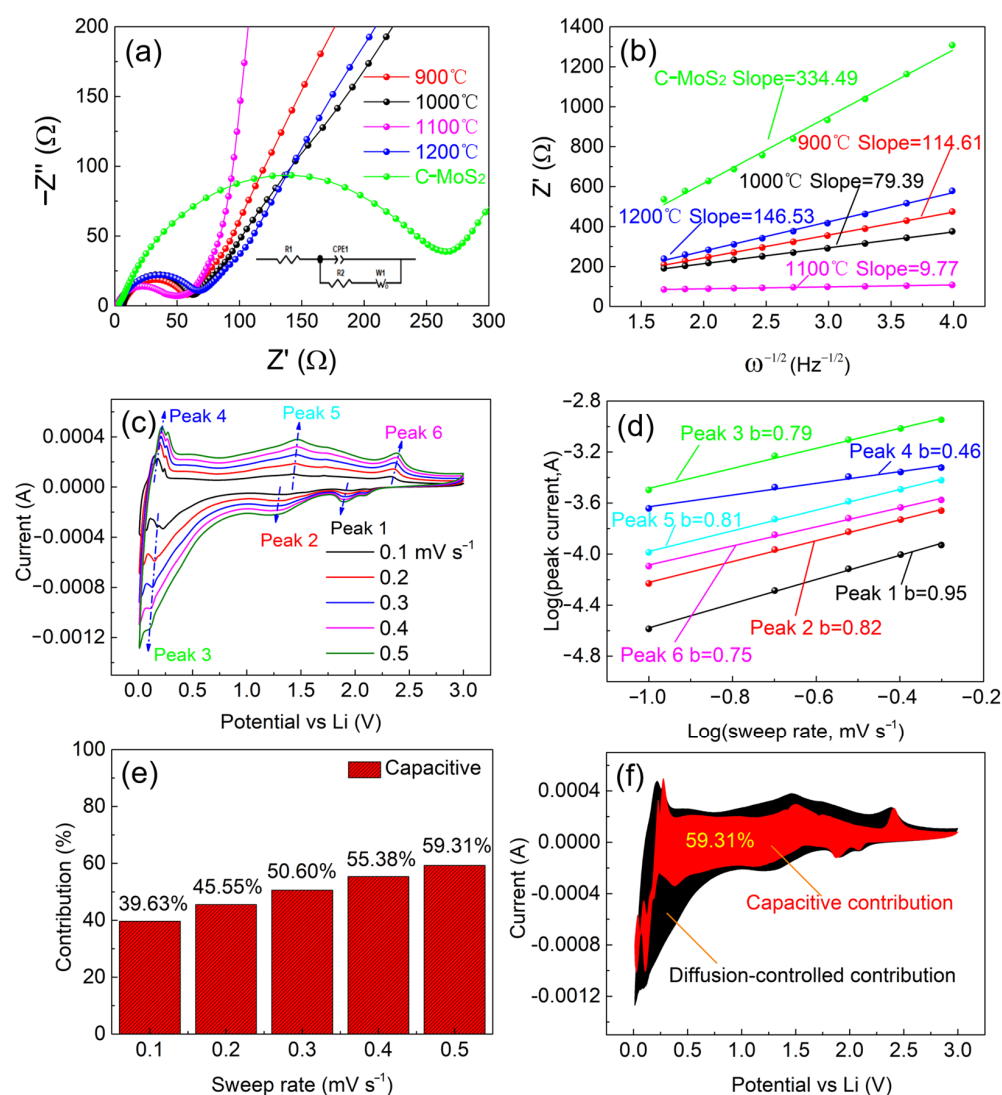


Figure 9. (a) AC impedance spectra of $\text{MoO}_3/\text{MoS}_2@\text{G}$ and C-MoS_2 electrodes. (b) The values of Z' vs. $\omega^{-1/2}$ ($\omega = 2\pi f$) for $\text{MoO}_3/\text{MoS}_2@\text{G}$ and C-MoS_2 . (c–f): Contribution of pseudocapacitive Li-ion storage to the total capacity of the $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ electrode: (c) CV curves with scan rates ranging 0.1 to 0.5 mV s^{-1} ; (d) the logarithmic dependence between the peak current and sweep rate; (e) contribution of pseudocapacitive and diffusion-based processes to the total current at different sweep rates, and (f) the pseudocapacitive contribution at 0.5 mV s^{-1} .

2.10. Contribution of Diffusion- and Surface-Phenomena

We also evaluated the contribution of diffusion- and surface-phenomena to the overall Li-ion storage performance of the $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ electrode. Figure 9c exhibits CV curves recorded on the electrode at various scan rates from 0.1 to 0.5 mV s^{-1} . It should be mentioned that the current intensity (i) and the sweep rate (v) can be related by Equations (10) and (11) [65]:

$$i = a \times v^b \quad (10)$$

$$\log i = \log a + b \times \log v \quad (11)$$

Here, a and b are dimensionless variables. Figure 9d could be established by plotting the logarithmic dependence between the current values related to various peaks shown in Figure 9c and the corresponding values of sweep rates. Based on the results obtained, the relative contributions of pseudocapacitive (vs. the diffusion-controlled events)

to the total current could be found to be in the range 39–60% at different sweep rates, as exhibited in Figure 9e.

It can be seen that the contribution of pseudocapacitive processes to the total current is proportional to the scan rate: higher scan rate, the greater contribution. As such, the pseudocapacitive contribution can directly influence the high-rate performance of the electrode, as shown in Figure 7c. Figure 9f exhibits the pseudocapacitive contribution to the total current at 0.5 mV s^{-1} .

Moreover, in Equation (11), the b value depends on the Li-ion storage mechanism. The value of $b = 0.5$ represents a diffusion-dominated process, while $b = 1$ represents the pseudocapacitive processes. The b values between 0.5 and 1 represent process involving both pseudocapacitive and diffusion-based process with various contribution ratio depending of the b -value [66,67]. As can be seen from Figure 9d, the value of b for the peaks 1, 2, 3, 4, 5, and 6 are obtained to be 0.95, 0.82, 0.79, 0.46, 0.81 and 0.75, respectively. It confirms that all current peaks are mainly dominated by pseudocapacitive processes, unless the anodic peak 4 with the b value of 0.46, representing diffusion based processes. The pseudocapacitive-oriented nature of the peaks mentioned above can be explained based of the integrated nanostructure of the sample (Figure 4) that promotes the Li-ion diffusion and charge transfer the electrode/electrolyte interfaces across the electrode. In contrast, the anodic peak 4 located at 0.20 V, with the b -value of 0.46, corresponds to de-intercalation of Li^+ out of the thicker graphitic flakes present in the sample.

3. Discussion

We have successfully developed a green, simple process for the conversion of the abundant and low-cost natural graphite and widely available MoS_2 into nanostructured $\text{MoO}_3/\text{MoS}_2@\text{Graphene}$. In this process, the oxidation of MoS_2 in the presence of graphite leads to the formation of $\alpha\text{-MoO}_3$ with orthorhombic crystalline structure, as well as hexagonal MoS_2 nanocrystals. At 900 and 1000 °C, the molten salt promotes the catalytic exfoliation of the natural graphite into graphene nanosheets, incorporated with hexagonal MoS_2 crystals and $\alpha\text{-MoO}_3$, denoted as $\text{MoO}_3/\text{MoS}_2@\text{G-900}$, and -1000, respectively. The further development of MoS_2 oxidation at 1100 °C, resulted in the formation of $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$, containing the maximum amount of MoO_3 among all samples. The highest amount of MoO_3 in this sample combined with the presence of integrated graphene nanosheets and hexagonal MoS_2 provide the sample with the greatest value of Li-ion storage capacity about 773.5 mAh g^{-1} after 180 cycles at a current density of 100 mA g^{-1} . The formation of molybdenum oxycarbide between MoO_3 and graphene nanosheets was suggested as the cause of reduced charge-transfer resistance (53.56Ω).

At the processing temperature of 1200 °C, the content of MoO_3 is the minimum among all samples, but the electrochemical performance of the sample ($\text{MoO}_3/\text{MoS}_2@\text{G-1200}$) is second only to that of the sample prepared at 1100 °C, with a Li-ion storage capacity of about 505.9 mAh g^{-1} after 180 cycles at a current density of 100 mA g^{-1} (Table 3). Interestingly, the high Li-ion storage capacity of the sample prepared at 1200 °C was corresponded to the formation of thermodynamically metastable monoclinic molybdenum trioxide ($\beta\text{-MoO}_3$), instead of conventional orthorhombic $\alpha\text{-MoO}_3$ which appears at 900–1100 °C. $\beta\text{-MoO}_3$ is known to have a highly ionically conductive open structure [41], improving the electrochemical performance of the material. Selected number of methods employed in the literature for the preparation of molybdenum compounds, and their electrochemical performances are compared with those of $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ in Table 5. Methods shown in this table typical use expensive and/or hazardous materials such as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ [27,28], MoO_3 [29], $(\text{NH}_4)_2\text{MoO}_4$ [32], and metallic Mo powders [33], in combination with materials such as $\text{CH}_4\text{N}_2\text{S}$ [27], HNO_3 [28], glacial acetic acid [29], HCl [32], and H_2O_2 [33]. The excessive use of such chemicals limits the large-scale implementation of these methods. In the method reported here, ball milling is applied to incorporate natural graphite and MoS_2 in the presence of hexane and NaCl. Both hexane and NaCl can be retrieved from the mixture after ball-milling, and the final washing step,

respectively. Nevertheless, the method reported here requires heating at elevated temperatures which might provide some limitations. Utilization of industrial heat waste can be an option to enhance the economic features of the method.

Table 5. A comparison between selected MoO₃/MoS₂ materials extracted from the literature, and MoO₃/MoS₂@G-1100 prepared here, in terms of the precursor materials, preparation method, and the electrochemical performance.

Mo-Oxide Based Material	Precursor Materials	Preparation Process	Performance
			Capacity (mAh/g)/Cycle/Current Density (mA/g)
Core–sheath structured MoO ₃ @MoS ₂ composite [23]	Rhododendron petals, (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O, CH ₄ N ₂ S	In situ growth at 550 °C (2 h) + 180 °C (24 h)	400/30th/200
Ternary MoS ₂ /MoO ₃ /C nanosheets [24]	Organic amine, MoO ₃	CVD at 800 °C (3 h) under N ₂	961.4/120th/430
MoO ₃ /MoS ₂ nanoribbons [25]	Molybdic acid, glacial acetic acid	Hydrothermal treatment at 800 °C (30 min)	-
MoS ₂ /MoO ₃ nanosheets [26]	CdCl ₂ , (NH ₄) ₂ CS, (NH ₄) ₂ MoO ₄ , NH ₂ OH.HCl	Hydrothermal treatment at 180 °C (30 h)	-
MoS ₂ coated MoO ₃ nanobelts [27]	Mo metal powder 10 mL H ₂ O ₂	Hydrothermal treatment at 180 °C (12 h)	1400/50th/100
MoS ₂ nanosheets on MoO ₃ nanowires [28]	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O, HNO ₃ , thiourea	Hydrothermal treatment at 180 °C (24 h)	800/100th/100
Core-shell MoO ₃ /MoS ₂ nanowires [29]	MoO ₃ powders, sulfur, N ₂	Thermal treatment at 700 °C	
MoS ₂ /MoO ₃ @graphene [This work]	MoS ₂ , natural graphite, NaCl	Heating at 1100 °C (20 min)	316/40th/1000
			774/180th/100

In this research, the structural, morphological and optical properties of raw materials and products obtained at various temperatures were evaluated using a combination of various techniques, based on which the possible mechanism involved in the catalytic formation of hexagonal MoS₂ nanocrystals upon the thermal treatment of MoS₂ in the presence of natural graphite flakes in the molten salt environment was proposed. The formation of hexagonal MoS₂ observed in this work is interesting, in comparison with alternative methods used for the preparation of hexagonally-shaped crystals from the literature, as exhibited in Figure S12 and Table S3. These methods include high-temperature sulfidation [31,32], electrochemical exfoliation [34], and chemical vapor deposition [35,36], using chemicals such as (NH₄)₂MoS₄ [31], pure Mo and S [32], W_xO_y [26], and Na₂SO₄ [34]. In contrast, this work proposes a simple and facile method for the preparation of hexagonal MoS₂, and ultimately MoO₃/MoS₂@G samples using highly available and low-cost precursors comprising of MoS₂, natural graphite minerals and NaCl, as highlighted in Tables 6 and S3. The process is rapid and requires only a short-time heating at 1100 °C. Despite the simple and clean preparation method, the electrode made of MoO₃/MoS₂@G-1100 exhibits a decent Li-ion storage performance. Modification of naturally available materials for energy-storage [68–70] and other demanding applications [71–73] is a viable strategy to meet the increasing green energy demand. In this research, we explored the effect of heating at various temperatures on the ball-milled natural graphite/MoS₂/NaCl mixture for a short period of 20 min to demonstrate that the process of fabricating MoO₃/MoS₂@G samples is considerably fast. The influence of heating time on characteristics of the products needs to be explored in future studies. It should be mentioned that at 900–1200 °C, the interaction between components occurs in molten NaCl, which can effectively reduce the reaction between carbon and oxygen forming CO/CO₂ species. According to Figures S9 and S10, further heating of MoO₃/MoS₂@G-900 in the absence of NaCl to 1200 °C in air leads to the oxidation of carbon and MoS₂ to form CO/CO₂ species and MoO₃, respec-

tively, highlighting the effect of NaCl. The influence of other salts on the process is worth investigation in future.

Table 6. Amounts of raw materials used and the resultant products obtained at various temperatures.

Raw Material	MoS ₂ (10 g)-NaCl (100 g)-Graphite (5 g)			
Ball-milled sample	112.00 g			
Heat-treatment Temperature	900 °C	1000 °C	1100 °C	1200 °C
Sample	MoO ₃ /MoS ₂ @G-900	MoO ₃ /MoS ₂ @G-1000	MoO ₃ /MoS ₂ @G-1100	MoO ₃ /MoS ₂ @G-1200
Before heat-treatment	28.00 g	28.00 g	28.00 g	28.00 g
After washing	3.31	2.60	2.29	2.45

4. Materials and Methods

4.1. Synthesis of MoS₂/MoO₃@Graphene Nanocomposites

A simple and scalable ball-milling–molten salt strategy was used to synthesize MoS₂/MoO₃@Graphene nanocomposites. In a typical experiment, molybdenum disulfide (MoS₂ 99.5%, Aladdin CAS-1317-33-5), natural graphite powder (collected from a graphite mine in Hunan province of China) and sodium chloride (NaCl, >99%) (10:5:100 g, respectively) were thoroughly mixed, and the mixture was placed into 500 mL polymeric jars. The ball-milling was performed using zirconia balls with ball: powder weight ratio of 10:1, in the presence of *n*-hexane. The latter was employed to prevent the occurrence of agglomeration during the ball milling process [74], and partial exfoliation of the non-purified natural graphite and MoS₂ [75,76]. The ball milling was performed for 2 h at 230 rpm using a high-energy planetary mill (MITR QM-QX-2L). After ball milling, the samples obtained were dried at 100 °C for 5 h to remove the hexane, and heat-treated at various temperatures of 900–1200 °C for 20 min in air. The heating was performed at 6 °C min^{−1}. The samples obtained were employed for various characterizations as described below. Figure 1 exhibits the process used to fabricate the samples. The amount of raw materials used and products obtained through the process are shown in Table 6.

4.2. Morphological, Structural and Surface Characterizations

A scanning electron microscope (SEM, Zeiss Ultra Plus, Oberkochen, Germany) equipped with energy dispersive X-ray spectrometer (EDS, Oxford Instruments, High Wycombe, UK) and a transmission electron microscope (TEM, JEOL JEM-F200, Tokyo, Japan) were used for morphological studies. X-Ray diffractometry (XRD, Malvern Panalytical, Malvern, UK) and fluorescence spectrometry (XRF, ZSX Primus, Rigaku, Japan) were used for phase and chemical analysis, respectively. N₂ adsorption-desorption evaluation was performed using a Micrometrics Tristar II 3020 to examine the surface characteristics of the samples, where the pore size distribution was obtained using the desorption branch of the isotherms. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Instrument, East Grinstead, UK) was employed for surface evaluation using Al-K_α rays as the excitation source (1486.6 eV).

4.3. Electrochemical Characterizations

Various electrochemical evaluations were performed on the synthesized MoS₂/MoO₃@Graphene samples and MoS₂. Accordingly, cycling and rate performances as well as cyclic voltammetry were evaluated using two-electrode half-cells. For the fabrication of the working electrode, a mixture of active materials (MoS₂/MoO₃@Graphene or MoS₂), C45 conductive carbon and polystyrene acrylic-acrylate (mass ratio of 7:2:1) were thoroughly ground employing water solvent. Then, the slurry was distributed uniformly onto a copper foil (200 µm). After drying at 80 °C (10 h), the electrodes with the active material mass loading of around 1.1 mg cm^{−2} were obtained. CR-2025 coin cells were

assembled using metallic Li discs as both the reference/counter electrode. For this, the solution containing 1.0 M lithium LiPF_6 in EC:DEC:EMC (1:1:1 wt%) was used as the electrolyte. In addition, Celgard 2400 films were employed as the separator. Coin cells were assembled in a glove-box (Mikrouna) under high purity Ar (O_2 and $\text{H}_2\text{O} < 0.1$ ppm). The cells were left for 10 h to equilibrate at room temperature, and subsequently evaluated using various techniques. Galvanostatic discharge/charge tests were performed within on a Land CT2001A battery testing instrument. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry at various scan rates and were conducted using a CHI 660E electrochemical interface.

5. Conclusions

In summary, we proposed a green and simple catalytic molten salt strategy for the conversion of commercial MoS_2 , natural graphite and NaCl into MoO_3 nanoribbons crystals integrated with hexagonal MoS_2 nanocrystals and graphene nanosheets. The formation of interfacial molybdenum oxycarbide between graphene and MoO_3 is suggested, contributing to the reduced resistance of the hybrid material. The method is simple, involving the mechanochemical processing of the precursor materials, followed by a heat treatment process at 900–1200 °C in air for the duration of 20 min. The temperature was found to have a significant influence on the composition and morphology of the products. In this process, the thermal oxidation of MoS_2 causes the formation of molybdenum oxides, and also the formation of highly crystalline hexagonal MoS_2 nanocrystals integrated with graphene nanosheets. The Li-ion storage performances of hybrid nanostructures fabricated at various temperatures 900–1200 °C, namely $\text{MoO}_3/\text{MoS}_2@\text{G-900}$, -1000, -1100 and -1200 were evaluated. $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ was found to be capable of delivering a relatively high initial coulombic efficiency of 79.58% with a reversible capacity of 773.5 mAh g^{-1} (100 mA g^{-1}) after 180 cycles, outperforming other electrodes. This behavior was attributed to the highest content of MoO_3 in $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ and its unique microstructure. It was observed that $\text{MoO}_3/\text{MoS}_2@\text{G-1200}$ has the lowest amount of MoO_3 among all samples, but its Li-ion storage performance was second only to $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$, recording at 505.9 mAh g^{-1} after 150 cycles at 100 mAh g^{-1} . The high performance of this sample was attributed to the presence $\beta\text{-MoO}_3$ with a highly ionically conductive open-structure monoclinic crystalline structure that only formed at 1200 °C. The formation of $\beta\text{-MoO}_3$ was concluded to contribute to the enhanced electrochemical performance of $\text{MoO}_3/\text{MoS}_2@\text{G-1200}$, despite its relatively low MoO_3 content. Graphene generated from the natural graphite and the hexagonal MoS_2 could be well-integrated, promoting both the electron and ion transportation across the electrode. Consequently, the contribution of pseudocapacitive Li-ion storage of the $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ electrode was characterized to be high at 59.31% under the scan rate of 0.5 mV s^{-1} . This resulted in the high rate performance of the electrode, providing a capacity of 216 mAh g^{-1} after 50 cycles at 2 A g^{-1} , and 106 mAh g^{-1} after 60 cycles at 5 A g^{-1} . This paper proposes a green and low-cost synthesis route for the conversion of highly available MoS_2 and non-purified natural graphite minerals into hexagonal molybdenum disulfide nanocrystals integrated with molybdenum trioxide and graphene nanosheets with enhanced Li-ion storage performance.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13030499/s1>, Figure S1: XRD patterns of $\text{MoO}_3/\text{MoS}_2@\text{G-900}$, $\text{MoO}_3/\text{MoS}_2@\text{G-1000}$, $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ and $\text{MoO}_3/\text{MoS}_2@\text{G-1200}$ around the (2 0 0) reflection of orthorhombic MoO_3 , and the (0 0 1) reflection of monoclinic MoO_3 ; Figure S2: XRD pattern of $\text{MoO}_3/\text{MoS}_2@\text{G-900}$, $\text{MoO}_3/\text{MoS}_2@\text{G-1000}$, $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ and $\text{MoO}_3/\text{MoS}_2@\text{G-1200}$, around the (4 0 0) reflection of orthorhombic MoO_3 , and the (0 0 2) reflection of monoclinic MoO_3 ; Figure S3: XRD patterns of $\text{MoO}_3/\text{MoS}_2@\text{G-900}$, $\text{MoO}_3/\text{MoS}_2@\text{G-1000}$, $\text{MoO}_3/\text{MoS}_2@\text{G-1100}$ and $\text{MoO}_3/\text{MoS}_2@\text{G-1200}$, around the (6 0 0) reflection of orthorhombic MoO_3 , and the (0 0 3) reflection of monoclinic MoO_3 ; Figure S4: Raman spectra of various precursor materials and products obtained at various temperatures; Figure S5: UV-vis spectra of various precursor materials and products obtained at various temperatures; Figure S6: $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots according to UV-vis spectra of

various precursor materials and products obtained at various temperatures; Figure S7: SEM image of (a) commercial MoS₂ and the samples prepared at (b) 900, (c) 1000, (d) 1100, and (e–f) 1200 °C. (g) High magnification image taken of the sample prepared at 1200 °C, and (h) the EDS analysis recorded on hexagonal MoS₂ shown in (g).; Figure S8: TEM micrographs of rod-like MoO₃ observed in MoO₃/MoS₂@G-900; Figure S6: Summary of methods proposed for the preparation of hexagonally-shaped nanocrystals extracted from the literature; Figure S9: Appearance of MoO₃/MoS₂@G-1100, the same sample after heating at 1200 °C for 5 min.; Figure S10: XRD patterns of MoO₃/MoS₂@G-1100 and the sample obtained by heating of MoO₃/MoS₂@G-1100 at 1200 °C for 5 min; Figure S11: Cycling performance of MoO₃/MoS₂@G-1100 at 500 mA g^{−1}; Figure S12: Summary of methods proposed for the preparation of hexagonally-shaped nanocrystals extracted from the literature; Table S1: XRD peak intensity ratio corresponding to various peaks in MoO₃/MoS₂@G-900, MoO₃/MoS₂@G-1000, MoO₃/MoS₂@G-1100 and MoO₃/MoS₂@G-1200; Table S2: Band gap values of various precursor materials and products obtained at various temperatures. and Table S3: A comparison between precursor materials and the methods used for the preparation of hexagonal crystals extracted from the literature, with those produced in the current study [31–36,77,78].

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