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Article

Efficient and Facile Synthetic Route of MoO₃:MoS₂ Hybrid Thin Layer via Oxidative Reaction of MoS₂ Nanoflakes

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Abstract: In the present study, MoO₃:MoS₂ hybrid thin layers have been synthesized through partial oxidation of MoS₂. We have demonstrated that the reaction requires darkness conditions to decrease the oxidation rate, thus obtaining the hybrid, MoO₃:MoS₂. A simple liquid-phase exfoliation (LPE) is carried out to achieve homogenous MoS₂ nanoflakes and high reproducibility of the results after MoS₂ oxidation. XPS analyses reveal the presence of MoO₃, MoS₂, and MoO_xS_y in the hybrid layer. These results are also confirmed by X-ray diffraction and high-resolution TEM. Optical absorbance reveals that the absorption peaks of the MoO₃:MoS₂ hybrid are slightly redshifted with the appearance of absorption peaks in the near-infrared region due to the defects created after the oxidation reaction. The composition and atomic percentages of each component in the hybrid layer as a function of reaction time have also been reported to give perspective guides for improving electronic and optoelectronic devices based on 2D-MoS₂.

Keywords: hybrid layer; thin films; 2D nanomaterials; transition metal dichalcogenide; molybdenum disulfide; molybdenum trioxide; partial oxidation



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1. Introduction

From the success of graphene to the development of transition metal dichalcogenides (TMDs), inorganic compounds with layered structures have received impressive attention because of the unique properties that meet in two-dimensional structures (2D). Among the 2D nanomaterials, TMDs consisted of MX₂, where M is a transition metal (M: Mo, W, etc.), and X is chalcogen (X: S, Se, and Te). As one of the inorganic graphene analogs, its layer nature is characterized by a strong in-plane bonding and weak Van der Waals interaction between the layers [1–3]. Molybdenum disulfide (MoS₂) is categorized as a semi-conducting material. Its stable structure consists of hexagonal layers co-bonded via Van der Waals forces, and each layer has covalent bonds between Mo and S (S-Mo-S). The tunable bandgap energy from 1.2 eV for bulk MoS₂ material to 1.8 eV in monolayer and the transition of the bandgap from indirect to direct bandgap has generated massive attention in exploring MoS₂ for various applications, such as hydrogen production [4–6], optoelectronic [7,8], lubrication [9], batteries [10], photocatalysis [11], and transistors [12].

It is worth noting that over the past years, many efforts have been devoted to exploring MoS₂ as an absorber layer for photovoltaic cells (PVs) since MoS₂ can efficiently

absorb visible light. However, the failure of this approach brings the scientists to develop another way to use MoS₂ as a hole transport layer (HTL) in organic photovoltaic cells (OPVs) [8]. Currently, MoS₂ represents an alternative material that could combine several essential characteristics of an ideal interlayer for the next solar cell generation and OLED applications [13–16]. Thanks to the development achieved in terms of a synthetic route to obtain controllable synthesis and a large-scale and uniform atomic layer. Among the preparation techniques of the MoS₂ layer, we can find liquid-phase exfoliation (LPE) [17], sol-gel/spin-coating [18], thermal decomposition of ammonium tetrathiomolybdate ((NH₄)₂MoS₄)/spin-coating [19], electrochemical process [8], and chemical vapor deposition (CVD) [20]. However, the use of a pure MoS₂ thin layer is still unsatisfactory to reach a good band matching between the electrode and active layer in OPVs and a high electrochemical performance and electrode stability for LIBs. Thus, it opened up the use of heteroatomic doping or combination of 2D-MoS₂ with another material, such as MoS₂/Polyaniline and MoS₂/C for LIBs [21], MoS₂/WS₂ for photoelectrochemical water oxidation [5], and MoS₂/PEDOT:PSS and MoO₃:MoS₂ as HTL for OPVs [22,23].

The interesting properties of n-type semiconductor molybdenum oxide (MoO₃) offer a highly effective combination with the MoS₂ layer, and this hybrid can be helpful and useful for many applications. For this purpose, Yun et al. reported an oxidation/exfoliation process to prepare the MoO₃:MoS₂ hybrid as HTL for polymer solar cells; this oxidation/exfoliation technique can replace the disadvantage of classical methods of MoO₃ thin-layer preparation, such as sol-gel and spray pyrolysis. The solution processable MoO₃:MoS₂ hybrid offers a high OPV performance compared with only the MoO₃ thin layer or the MoS₂ thin layer as HTL [23]. Another way to elaborate the MoO₃:MoS₂ hybrid layer is the use of electrochemical deposition method; this work was done in our laboratory, and the hybrid layer was applied in planar OPVs as HTL. The hybrid synthesized combines both advantages of the use of MoO₃ as an efficient hole transporter layer and MoS₂ as a good electron extractor layer [8]. D. Lei et al. reported a synthesis by the hydrothermal method of MoS₂/carbon shells and oxidation of the MoS₂ which gives a composite consisting of hybrid MoS₂-MoO_x combined with carbon shells for lithium-sulfur batteries. The use of MoS₂-MoO_x results in the enhancement of Li-S battery performances because first, the MoS₂ coupled with MoO_x can improve the absorption toward polysulfides. Additionally, the heterostructure can provide better electron mobility and high catalytic activity, which can promote the redox reaction of polysulfide [10]. Inspired by these previous works, we report a facile and controllable synthetic strategy to prepare the hybrid MoO₃:MoS₂ layer. The synthesis is achieved by exfoliation/oxidation of MoS₂ using H₂O₂ as an oxidizer. Hydrogen peroxide (H₂O₂) promotes a facile, fast, and low-temperature MoS₂ oxidation, which is why it is often employed as an oxidizing agent for 2D materials, including MoS₂ [23]. Based on our previous work, the MoO₃:MoS₂ hybrid thin film as HTL synthesized by the chemical vapor deposition coupled rapid thermal annealing (CVD-RTA) technique reaches good PV performance when the MoO₃ content exceeds 60%. This indicates the importance of controlling the hybrid composition. Therefore, in our work, the idea behind the use of H₂O₂ as an oxidizer is to discover and provide a controlled method to synthesize the MoO₃:MoS₂ hybrid thin layer and to reach a high content percentage of MoO₃ in the prepared hybrid thin film [24]. The free organic solvent liquid phase exfoliation was adopted to obtain MoS₂ nanoflakes, and a homogeneous hybrid layer was grown on a flexible substrate from aqueous dispersion via simple coating/centrifugation techniques. The percentage ratio of MoO₃:MoS₂ was controlled through the control of H₂O₂ concentration and reaction duration at ambient conditions. Moreover, the structural, morphological, and optical properties of the hybrid MoO₃:MoS₂ were studied as well.

2. Materials and Methods

2.1. Experimental Method

The experimental method in the present study was divided into two main parts. Before working on the exfoliated MoS₂ as the starting reactive to produce the hybrid thin film and

evaluate their structural, optical, and morphological properties, the partial oxidation was first checked with the MoS₂ nanopowder.

2.1.1. Partial Oxidation of Nanodispersed MoS₂

The hybrid MoO₃:MoS₂ nanopowder was prepared through partial oxidation of molybdenum disulfide (MoS₂) using hydrogen peroxide (H₂O₂) as the oxidant. MoS₂ nanopowder (90 nm) was purchased from Sigma Aldrich (ref: 804169). In a beaker of 25 mL, MoS₂ (5 mg) was dispersed in distilled water with molar mass of C_{MoS₂} = 6 × 10⁻³ mol L⁻¹ under constant and continuous magnetic stirring for 48 h at 50 °C. During stirring, the beaker was covered by parafilm to avoid any contact with dust and moisture. Then, H₂O₂ was added to the MoS₂ dispersion with a volume ratio of 3:1 *v/v* under stirring at ambient temperature. The reaction was performed in daylight or in the dark. In the dark condition, the beaker containing the solution was totally covered by aluminum foil. After the reaction, the solution (2 mL) was drop-casted on glass and/or ITO-coated glass substrates, followed by drying on a hotplate at 80 °C for 30 min for XPS analysis and further characterizations. The reaction times were taken as variable parameters to control the evolution of the reaction and to subsequently investigate their effect on the hybrid stoichiometry.

2.1.2. Preparation of MoS₂ and MoO₃:MoS₂ Hybrid Thin Films

MoS₂ exfoliation: Using the LPE method, MoS₂ was simply exfoliated in distilled water. The MoS₂ nanopowder (160 mg) was stirred in distilled water with initial mass concentration of 8 mg·mL⁻¹ for 2 h at 80 °C. Then, the dispersion was transferred to a beaker of 25 mL, placed inside a water bath, and sonicated for 6 h using an ultrasonic processor (bioblock scientific, vibra cell) with 500 W maximum power, and 20% amplitude of power with 6 s on and 3 s off pulses. Throughout the whole sonication process, the temperature was kept between 40 °C and 60 °C. The resulting green-dark suspension was settled without disturbance for 2 h, and the upper suspension was collected and centrifuged for 30 min to obtain MoS₂ nanosheets. Two solutions were obtained depending on the centrifugation speed at 2377 rpm, which corresponds to 600× *g* relative centrifugal forces (RCF), and 3069 rpm, which corresponds to 1000× *g*. The final mass concentrations are 1 mg mL⁻¹ and 0.8 mg mL⁻¹ obtained using relative centrifugation force of 600× *g* and 1000× *g*, respectively, and were estimated from the final mass of the unexfoliated nonpowered. The supernatants containing nanosheets of MoS₂ exfoliated/centrifuged at 1000× *g* were carefully collected and directly transferred to another centrifuge tube to proceed with a centrifugation-coating, described below.

Thin films preparation: Growth of the MoO₃:MoS₂ and MoS₂ thin films was achieved using centrifugal force as a coating technique; this technique is reported in the reference [25], and the exfoliated MoS₂ is used as the starting dispersion. The deposition process is described in Figure 1.

The hybrid MoO₃:MoS₂ thin films were obtained according to the oxidation of MoS₂, and all the used parameters were kept as described above, except the starting nanodispersion, where the commercial MoS₂ nanopowder was replaced by the exfoliated MoS₂ dispersion intending to obtain homogenous thin films. The exfoliated MoS₂ centrifuged at 600× *g* was used to keep the same mass concentration, 1 mg mL⁻¹, as it is adopted in the first protocol of the partial nanopowder oxidation. Note that all the reactions have been released in the dark condition during the hybrid thin film preparation.

The obtained MoS₂ dispersions after exfoliation/oxidation and the exfoliated MoS₂ were transferred to another centrifuge tube with graduation of 50 mL where an ITO-coated PET flexible substrate was introduced and stuck on the edge bottom of the centrifuge tube using an adhesive tape. Due to the centrifugal force applied to the dispersion, thin films were deposited uniformly on the flexible substrates that have a dimension of 2.5 × 2.5 cm² or 1 × 2.5 cm². All the thin films were deposited at the relative centrifugal force of 8000 for 10 min using a Sigma 2–16 p centrifuge. With no annealing, the obtained thin films,

MoO₃:MoS₂ and MoS₂ layers, were stored in the primary vacuum under pressure of 2.10^{-2} mbar.

The details of the characterization techniques used in this work are given in Appendix A.

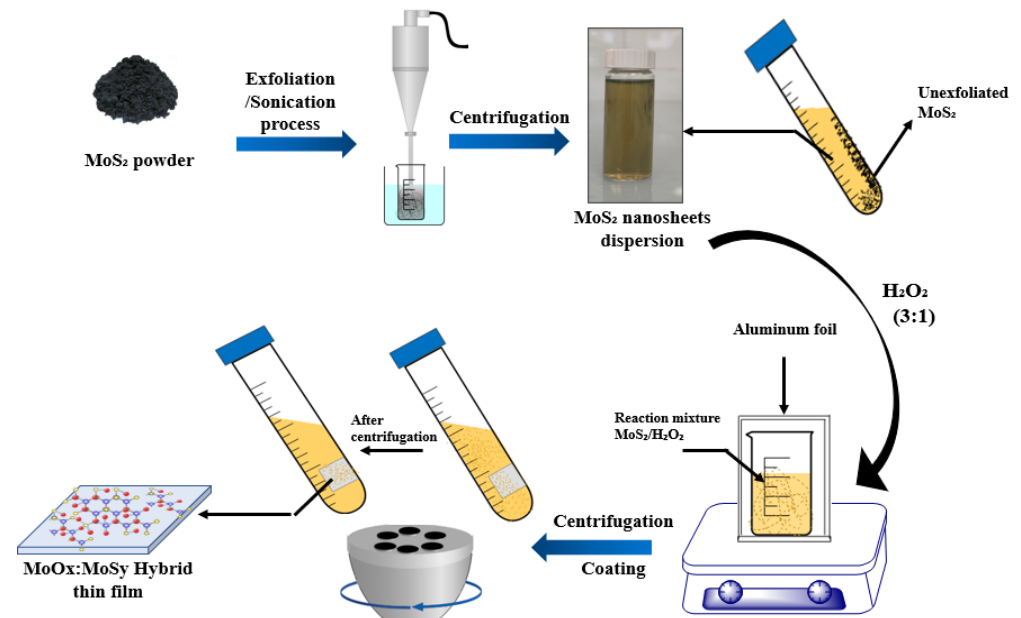


Figure 1. Schematic illustration of MoS₂ exfoliation and hybrid thin film preparation by centrifugation-coating.

3. Results

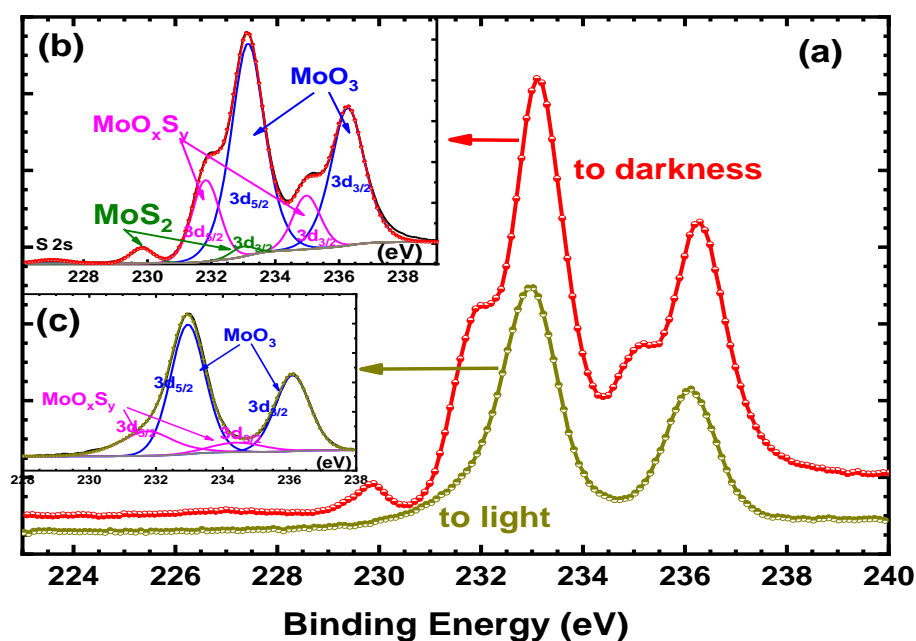
The hybrid MoO₃:MoS₂ nanomaterial was synthesized through partial oxidation of MoS₂ using H₂O₂ as an oxidizer. The XPS analyses were performed to check and identify the samples chemical composition after the oxidation process.

The binding energies of the main peaks detected in the XPS spectra and their corresponding components, MoS₂, MoO₃, and MoO_xS_y, extracted from the literature are listed in Table 1.

First, MoS₂ was oxidized at room conditions by H₂O₂, whose concentration was 10%, for different durations, 30–15 min. Unfortunately, whatever the reaction duration, as shown in Figure 2a,c, no more MoS₂ was detected. Actually, the Mo 3d spectrum corresponds to two doublets; the first one, situated at 232.9 and 236.0 eV can be attributed to the Mo3d_{5/2} and Mo3d_{3/2} of MoO₃, while the second one, at 231.7 and 234.8 eV corresponds to MoO_xS_y (see Table 1) [26]. From these results, MoS₂ is nearly completely converted to MoO₃, suggesting full oxidation of MoS₂, and even if these results indicate that MoS₂ is oxidized in the appropriate path to MoO₃, it does not allow us to achieve one of the main objectives of our work, which is obtaining the hybrid MoO₃:MoS₂. Therefore, to try to slow down the oxidation reaction, the samples were put to darkness during the reaction. As visible in Figure 2a,b, for a reaction time of 15 min, some MoS₂ is still present, indicating that the MoS₂ oxidation rate decreases when the reaction is carried out in the dark.

Table 1. XPS-binding energies of MoS₂, MoO₃, and MoO_xS_y.

Components		Binding Energies (eV)	References
MoS ₂	Mo 3d _{5/2}	229	[23]
	Mo 3d _{3/2}	233	
MoO ₃	Mo 3d _{5/2}	233	[27,28]
	Mo 3d _{3/2}	236	
MoO _x S _y	Mo 3d _{5/2}	232	[26]
	Mo 3d _{3/2}	235	

**Figure 2.** Mo3d spectra of MoS₂ oxidized by H₂O₂ (10%) for 15 min to light and to darkness (a). Inset (b) Mo3d decomposition after oxidation to darkness and inset (c) Mo3d decomposition after oxidation to light.

To be able to control more easily the percentage of MoS₂ still present at the end of the reaction, we decided to use a small concentration of H₂O₂ for the oxidation reaction. Therefore, we proceeded to an oxidation using H₂O₂ concentrations of 6%. To confirm the influence of light on the oxidation reaction, we compared the Mo3d spectra obtained after 30 min with and without light. The results of the deconvolution of the Mo3d spectra are summarized in Table 2. The atomic percentage of MoS₂ after 30 min of reaction is nearly double when the reaction is carried out in darkness. Thus, as expected, the MoS₂ oxidation rate decreases when the synthesis was performed in the dark conditions. Therefore, it is easier to manage the composition of the hybrid material by working in the dark. Therefore, we decided to proceed with oxidation in darkness.

Table 2. Composition of the hybrid nanopowder after oxidation of MoS₂ by H₂O₂ 6% for 30 min, in function of light environment: to light or in the dark.

Experimental Conditions	MoS ₂ (at%)	MoO ₃ (at%)	MoO _x S _y (at%)
To light	17	71	12
To darkness	30	60	10

The idea was to sweep the composition of the nanopowder from 100% of MoS₂ not oxidized to 0% after oxidation, using the reaction time as parameter. Unfortunately, when

the reaction duration increases beyond 30 min, the oxidation reaction tends to saturate; thus, the longer the reaction duration increases, the faster the oxidation rate decreases. Thereby, while for the 30 min reaction time only 30% of MoS₂ remains, for 45 min or more, the measured value remains above 20–25%. Indeed, it is an average value because the result changes significantly from one point to another, which suggests that the samples are not homogeneous. If the nominal grain size of MoS₂ nanopowder is 90 nm, it is in fact an average value, and some grains are far much larger, reaching a size up to 3 μm, as shown in Figure 3a.

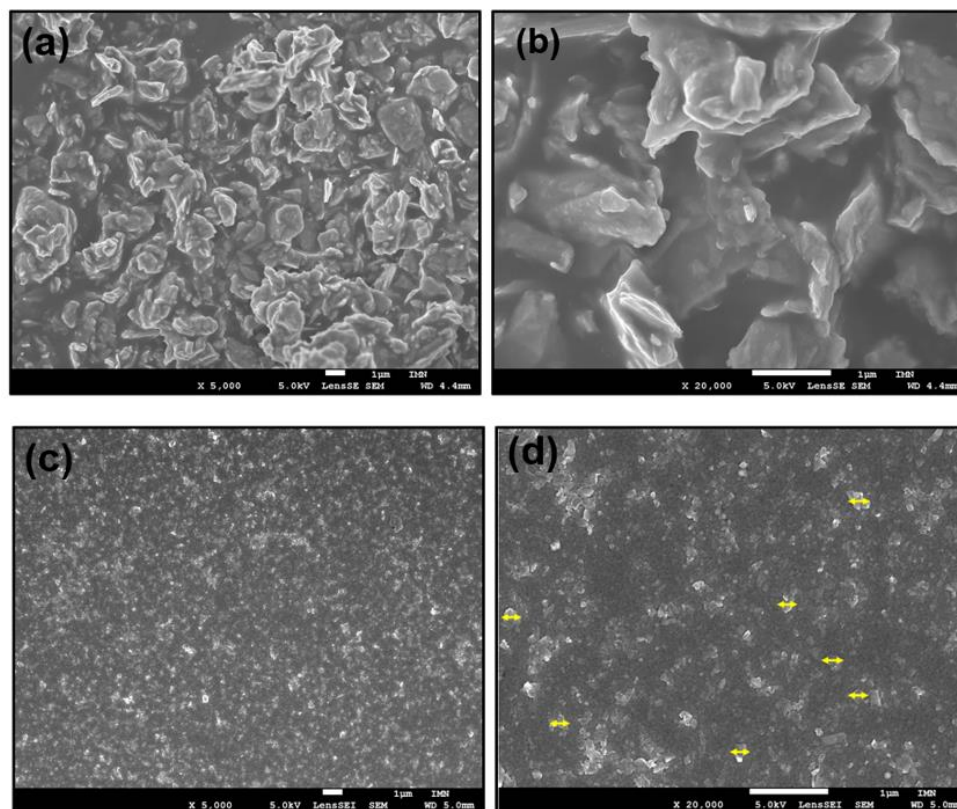


Figure 3. FESEM images of (a) MoS₂ nanopowder and (b) MoS₂ nanopowder at high magnification, (c) exfoliated MoS₂, (d) exfoliated MoS₂ at high magnification, and the yellow arrows indicate the grain lateral sizes.

The presence or not of such big MoS₂ grains explains the inhomogeneity of the results and the saturation tendency of the oxidation reaction since it is more difficult to achieve complete reaction in the case of grains of several microns in diameter than in the case of grains of a few tens of nanometers. Since the XPS analysis is essentially a surface analysis, we used the SEM backscattered electron mode [29] to verify the homogeneity of the samples and especially the presence of the MoS₂ after the oxidation reaction.

Images of MoS₂ nanopowder crystal after oxidation by H₂O₂ 6% for 45 min in the secondary mode and in the backscattering mode are shown in Figure 4a,b. Lighter areas are visible in Figure 4b; they correspond to non-oxidized MoS₂ since the heavier atoms backscatter the electrons more than lighter atoms. The dark spots are supposed to correspond to the lightest components, which are the oxidized MoS₂; thus, these images clearly show the limits of the XPS analysis, as mentioned above. However, a vital point that can be extracted from these results is MoS₂ does not react homogeneously due to the non-homogenous distribution of MoS₂ grain size. Starting from the point that H₂O₂ can be oxidized and spontaneously exfoliate MoS₂, as given in previous work [30], it is not beneficial and not easy to directly prepare a homogenous hybrid from MoS₂ nanopowder;

thus, the synthetic process requires another step to keep the control on the reproducibility of the results regarding the critical dependence between oxidation reaction rate and nanoparticles size.

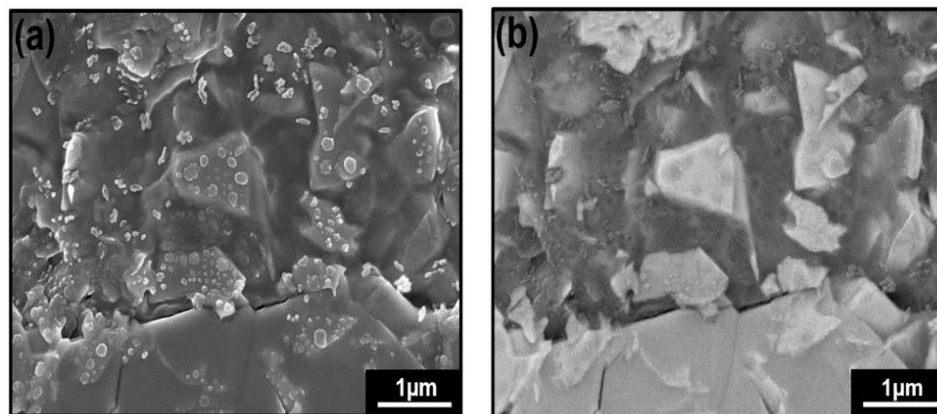


Figure 4. FESEM images of MoS₂ powder crystal after oxidation of MoS₂ by H₂O₂ 6% for 45 min: (a) in the secondary mode and (b) in the backscattering mode.

It can be concluded from this study of that it is possible to convert MoS₂ into MoO₃ by H₂O₂ oxidation, but in addition, we showed that to be able to better manage the reaction rate it was desirable to carry out the oxidation in darkness. Nevertheless, the reaction tends to saturate even when the reaction time increases due to the samples non-homogeneity, as shown by SEM analyses. Therefore, for a controllable oxidation rate, it was necessary to work with a MoS₂ nanopowder more homogeneous and of real nanometric dimensions. For that reason, we exfoliated MoS₂ to obtain smaller particles exhibiting more homogeneous dimensions.

Keeping the same preparation strategy of the hybrid MoO₃:MoS₂, the liquid phase exfoliation (LPE) was first carried out for MoS₂ initial powder. LPE, as one of the top-down approaches, is a way to control the 2D MoS₂ flake morphology and proceed our hybrid synthetic strategy based on MoS₂ oxidation. Based on recent studies, we believe that the LPE free organic solvent may be a promising technique for specific applications; thus, we proceed in our work for an exfoliation of MoS₂ in water [17,31,32]. The details of the exfoliation procedure are described in the experimental section.

From the photographs showed in Figure 5, the change of the dispersion color from dark gray to yellow color after exfoliation indicate the exfoliation of MoS₂. To confirm the exfoliation and identify the crystallinity of exfoliated MoS₂ thin film, the X-ray diffraction technique was conducted on commercial MoS₂ and exfoliated MoS₂ samples. Based on the XRD patterns presented in Figure 5a,b, exfoliated MoS₂ shows a peak with high intensity at $2\theta \sim 14^\circ$ corresponding to the (002) plane of MoS₂ (PDF.04-004-1905), suggesting that the hexagonal structure of MoS₂ is retained after exfoliation [17]. The widening of the peak (002) and disappearance of the rest of the peaks after exfoliation compared to MoS₂ nanopowder indicates the efficient exfoliation of MoS₂ [33,34].

Before going through the oxidation reaction of the exfoliated MoS₂, we checked first the sample morphologies using SEM analysis. From the images shown in Figure 3b, we can clearly observe that the particles size was reduced from several microns for commercial powder to 200–250 nm in lateral size at the maximum and with thin flakes for exfoliated MoS₂. Thus, it confirms the exfoliation of the MoS₂ nanopowder accompanied the flakes fragmentation during the exfoliation process. As well, we can see the homogenous distribution of the nanoparticles for the sample after exfoliation which is another decisive and important point for our hybrid preparation procedure.

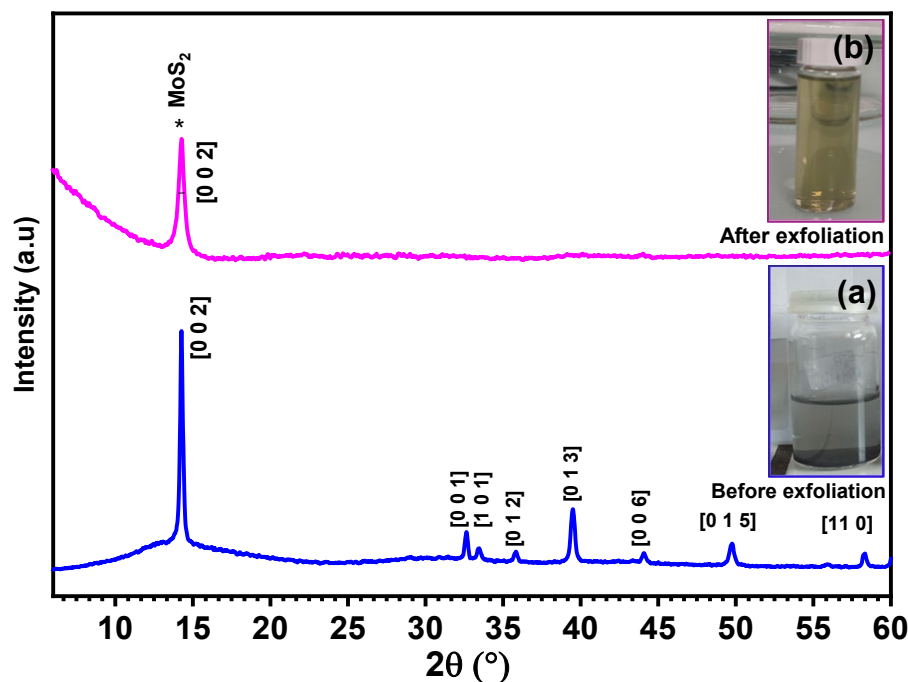


Figure 5. X-ray diffraction of MoS₂ commercial nanopowder (a) and after exfoliation (b). The inset figures represent dispersions (a) before and (b) after exfoliation.

After exfoliation, the nanoparticles are much smaller and more homogeneous than those of the nanopowder; thus, to avoid too rapid oxidation, we used 3% concentration of H₂O₂ to achieve the reaction. The oxidation reaction of MoS₂ and the synthetic route of the hybrid MoO₃:MoS₂ thin layer is illustrated in the above scheme (Figure 1).

First, we looked at the reproducibility of the results. To do this, we chose a reaction time of 10 min and a concentration of H₂O₂ of 3%. As shown by the atomic percentage of MoS₂ in Table 3, the results obtained with the exfoliated MoS₂ are far more reproducible than those obtained with MoS₂ nanopowder. Changes in the relative concentrations of MoO₃ and MoO_xS_y are because the energies of the corresponding doublets are close, which induces a certain margin of uncertainty when the corresponding signal is decomposed.

Table 3. Atomic percentages extracted from Mo 3d XPS spectra of the components present in the MoO₃:MoS₂ hybrid thin film after 10 min of reaction in the darkness, the H₂O₂ concentration being 3%.

Sample	MoS ₂ (at%)	MoO ₃ (at%)	MoO _x S _y (at%)
N°1	18	62	20
N°2	17	56	27
N°3	16	66	17

To better understand the reaction process, we looked at the XPS spectra of all components of the hybrid layer. Firstly, Mo 3d spectra of MoO₃:MoS₂ and MoS₂ thin films deposited on the ITO/PET substrate are presented in Figure 6. From the Mo3d spectrum of MoS₂ thin film, we can observe two doublets, the first at almost 229 eV and 232 eV corresponding to MoS₂ and the second doublet at almost 232 eV and 235 eV which correspond to the Mo⁵⁺ oxidation state that can be attributed to the MoO_xS_y (Table 1); the presence of a low quantity of this intermediate product in MoS₂ thin film is coming from MoS₂ oxidation during the exfoliation process [35]. After MoS₂ oxidation using H₂O₂, we can observe a doublet peak with high intensity at 232.6 eV and 235.6 eV corresponding to MoO₃ [27] and MoS₂ at binding energies of 229 eV and 232 eV. The conversion of MoS₂ to MoO₃ is accompanied by the third compound at energies of 232 eV and 235 eV corresponding to MoO_xS_y.

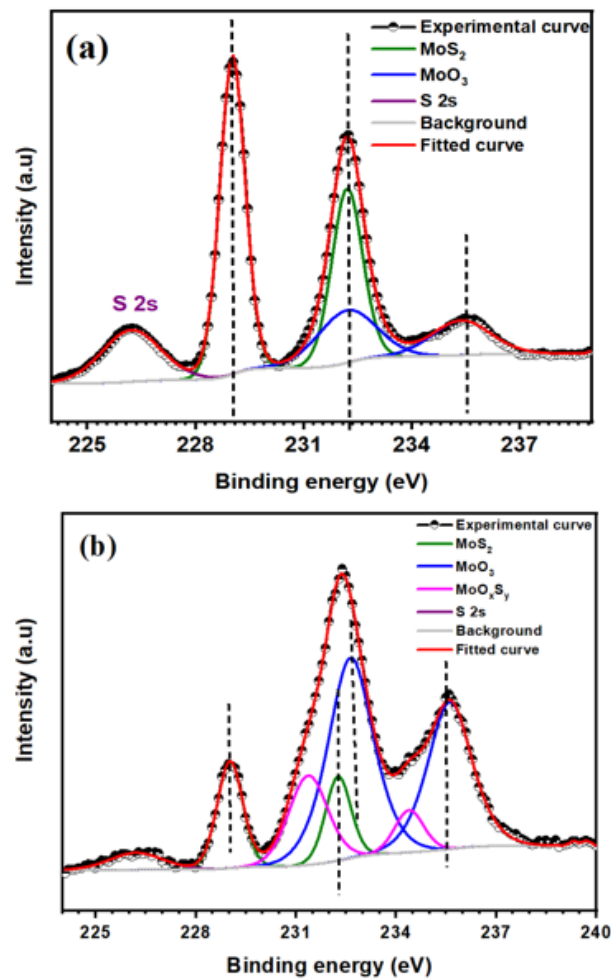


Figure 6. Mo 3d XPS spectra of (a) MoS₂ thin layer and (b) MoO₃:MoS₂ reaction duration of 10 min.

The reaction mechanism of MoS₂ oxidation is generally described through the reaction of a free hydroxyl radical coming from H₂O₂, involved in Mo-S breaking and oxidation of S²⁻ and Mo⁴⁺ leading to the formation of MoO₃ [10,36]. However, the oxidation of Mo⁴⁺ may not be totally achieved since the decomposition of the Mo3d peaks reveals the presence of an intermediate product in the hybrid layer that corresponds to the oxidation state of Mo⁵⁺; as reported by S. Shin et al., this intermediate corresponds to MoO_xS_y named molybdenum oxysulfide, which is related to the incomplete substitution of sulfur by oxygen [37,38]. To discuss the reaction process, S 2p and O1s spectra of the hybrid thin film are illustrated in Figure 7; it can be seen in the S2p spectrum that there is a spin-orbit doublet at the binding energy of 161 eV and 163 eV corresponding to the oxidation state S²⁻ which also confirms the existence of MoS₂ moieties in the hybrid thin film [26]. Moreover, we have detected an additional weak peak at binding energy around 169 eV for the MoS₂ layer before oxidation [26,38]; the presence of this peak at higher binding energy is mostly attributed to the presence of sulfate (SO₄²⁻) due to air contamination and the exfoliation process of MoS₂ as reported in the previous works [35,39]. This peak becomes dominant at almost the same binding energy for the hybrid layer with the appearance of the Mo⁵⁺ oxidation state which is attributed to the existence of MoO_xS_y. This finding was also reported by S. Ho Song et al. in their work, where the presence of MoO_xS_y is accompanied with the appearance of the sulfur peak at higher binding energy of almost 169 eV [26]. Based on the Mo 3d and S 2p spectra, the presence of MoO_xS_y is related to the association of sulfur and molybdenum with oxygen, which means that the oxygen environment in the hybrid layer is composed of Mo and sulfur. Thus, the presence of Mo-O-S bonds showed after the peak's deconvolution, giving the new intermediate product

the name of oxo-bridge molybdenyl sulfate rather than O-Mo-S bonds. For further details, the deconvolution of O 1s peaks presented in Figure 7a,c showed the presence of three types of bonding for both oxidized and not oxidized MoS₂; the peak situated at almost 530 eV is attributed to metal-oxygen (Mo-O), the peak at an energy >531 eV is mostly due to oxygen-sulfur (O-S), and the middle peak detected at an energy of 531 eV which is indicated by “contamination” is attributed to adsorbed contamination and oxygen-carbon that is present in the PET substrate [37]. The peak area of oxygen-sulfur indicates that the amount of O-S bonds increases after MoS₂ oxidation, and the S2p peak at higher binding energy becomes dominant; this confirms the presence of a small amount of free sulfur oxide accompanied with the new composite oxo-bridge molybdenyl sulfate MoO_xS_y. A hypothetical structure of this new component produced during the process is illustrated in Figure 9c.

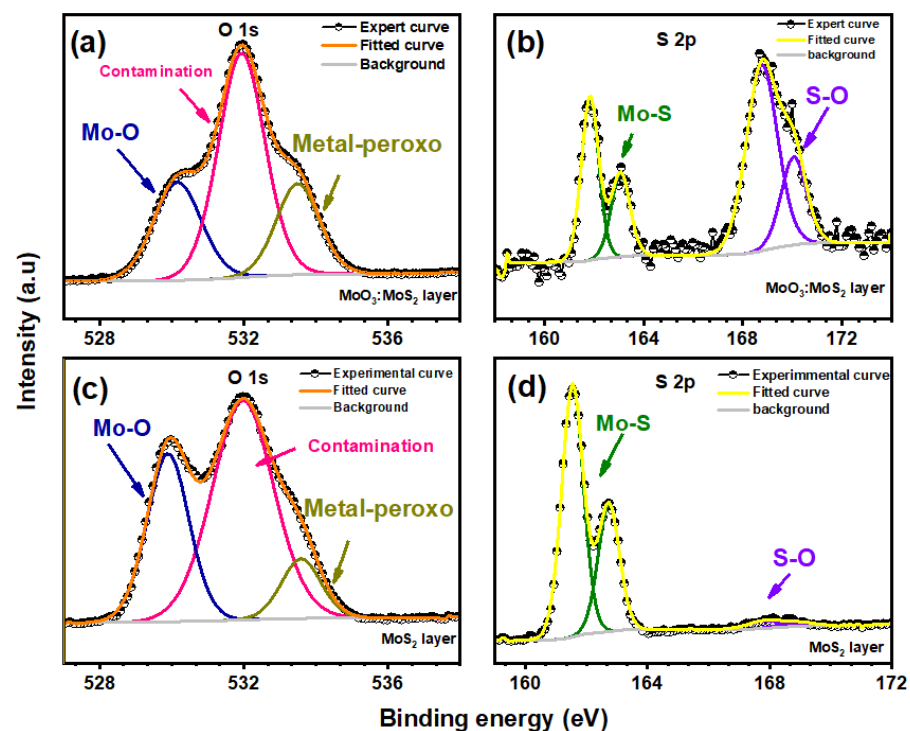


Figure 7. S2p and O 1s zone spectra of MoS₂ after reaction duration of 10 min (a,b) and MoS₂ before reaction (c,d).

To determine the crystallinity of the MoO₃:MoS₂ hybrid layer, we did the XRD characterizations; the XRD patterns (not shown) present a weak peak at 14° corresponding to (002) peak of hexagonal structure of MoS₂ for both the MoS₂ layer and MoO₃:MoS₂ hybrid layer with the presence of peaks derived from the ITO/PET substrate. Thus, this confirms the crystalline structure of MoS₂ present in the hybrid layer. The absence of additional peaks corresponding to MoO₃ or the intermediate product, MoO_xS_y, may be due to the amorphous structure of those compounds or an amount below the detection limit. Furthermore, high-resolution TEM was used to verify the crystalline structure of the studied samples. Figure 8 shows the HRTEM image of the MoO₃:MoS₂ hybrid obtained after MoS₂ oxidation with 30 min of reaction duration; from this image we can observe different zones with a highly crystalline structure as indicated by squares on the image (Figure 8c,d) and other areas with a disordered structure as we can see in Figure 8g. Using fast Fourier transform (FFT) patterns of the selected areas, b₂, c₂, and g₁, we can confirm that the slightly dark color contrast TEM (Figure 8c) is attributed to the crystalline structure of MoO₃ with a lattice spacing of 0.27 nm, which corresponds to the plan (1–11). The selected area with the orange square (d) reveals the presence of a hexagonal structure of MoS₂ with a lattice

parameter of 0.31 nm [40,41]. As evident in the FFT pattern (Figure 8g₁), the disordered areas indicate the presence of an amorphous structure which may correspond to the oxo-bridge molybdenyl sulfate, MoOxSy, as already revealed by XPS measurements. Briefly, through the oxidation reaction, we obtained nanosheets consisting of a heterostructure containing the three components, MoO₃, MoS₂, and MoOxSy.

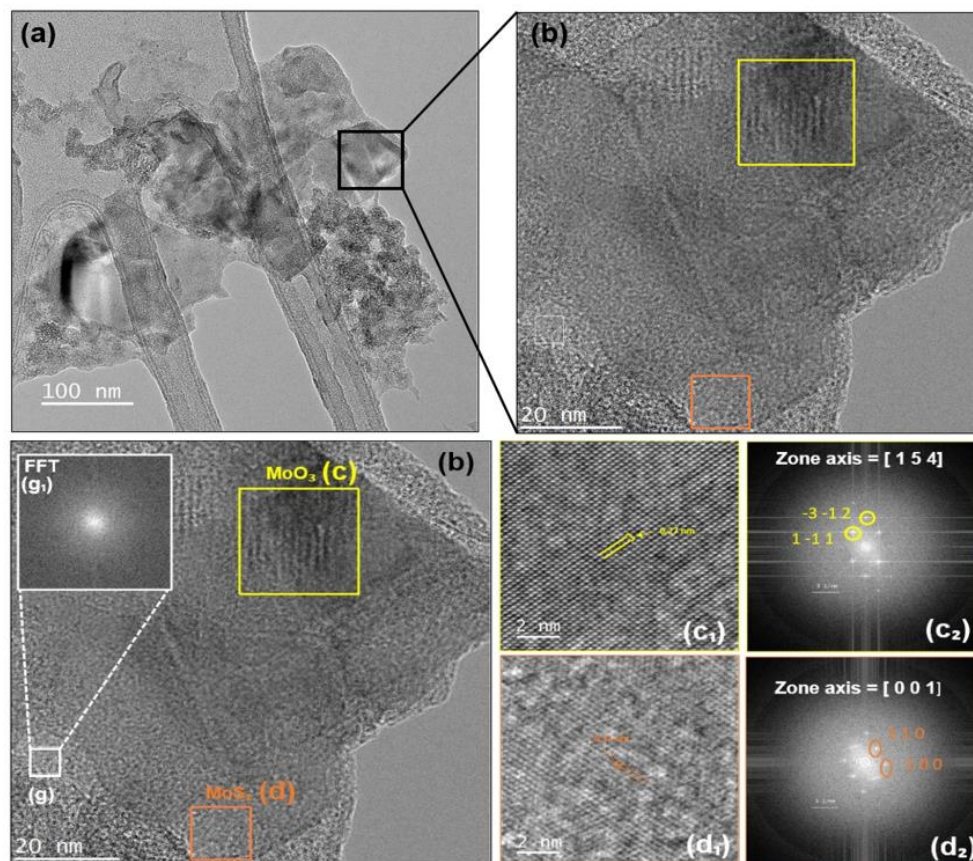


Figure 8. (a) HRTEM of MoO₃:MoS₂ hybrid nanosheet; (b) high magnification image of MoO₃:MoS₂ hybrid nanosheet. The (c) and (d) selected areas with their corresponding high magnification (c₁,d₁) and FFT (c₂,d₂) images indexed with JEMS software [42], respectively; (g₁) FFT image of the selected area (g).

Based on the above results, the synthetic process of the hybrid MoO₃:MoS₂ produced during the MoS₂ nanoflakes oxidation can be illustrated as follows (Figure 9).

The absorbance spectra of exfoliated MoS₂ and the hybrid after reaction durations of 10 min and 30 min are shown in Figure 10. As it is expected, MoS₂ exhibited four absorption peaks; these peaks are attributed to the excitonic transitions, A, B, C, and D (see Table 4) [43]. From the absorption spectra the estimated bandgap is 1.77 eV for exfoliated MoS₂. It is known that the thickness reduction shifts the band gap from indirect to direct transition; therefore, herein the increase in the bandgap to 1.77 eV indicates the exfoliation of MoS₂ to monolayers [17]. Whereas, after the oxidation reaction, the excitonic transitions A and B are almost invariable, which means that the MoS₂ unreacted during the reaction remains highly crystalline, which is characterized by good absorption in the visible region. Furthermore, in the NIR the hybrid shows two absorption bands at wavelengths of 959 nm and 1150 nm, corresponding to the energies of 1.29 eV and 1.07 eV (inset Figure 10). However, the absorption peaks become weaker when the reaction duration increases due to the decrease in the density of oxygen vacancies [44].

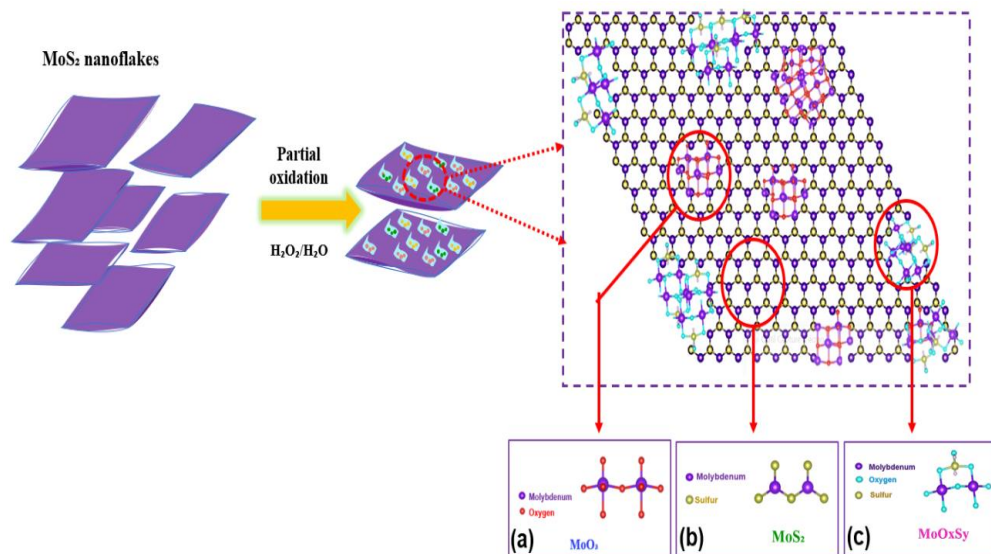


Figure 9. Illustration of the hybrid $\text{MoO}_3:\text{MoS}_2$ synthetic process, and the chemical structure of (a) MoO_3 (b) MoS_2 and (c) MoO_xS_y .

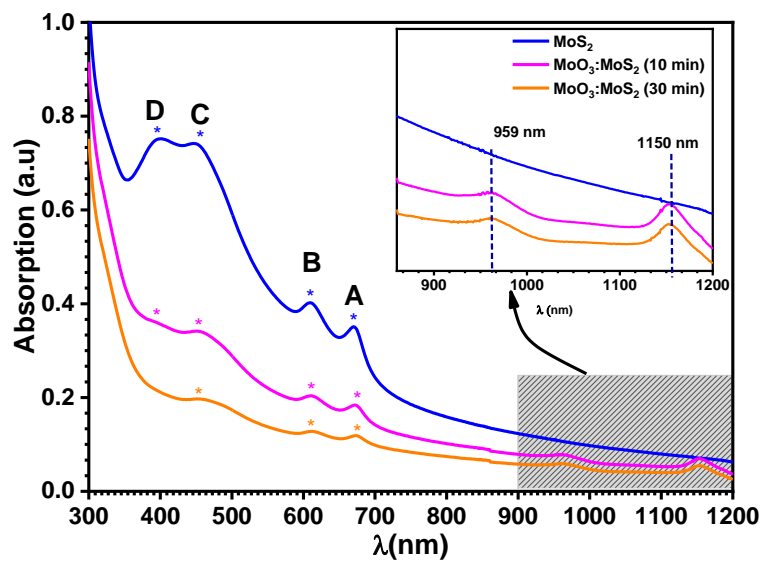


Figure 10. Absorbance spectra of exfoliated MoS_2 (blue line) and $\text{MoO}_3:\text{MoS}_2$ dispersion as function of reaction durations of 10 min (pink line) 30 min (orange line).

Table 4. Positions of the excitonic peaks.

Excitonic Transition	Exfoliated MoS_2	Hybrid $\text{MoO}_3:\text{MoS}_2$	
		10 min	30 min
A	670	673	673
B	607	610	610
C	448	454	454
D	398	398	—

Considering these results, we have studied the evolution of the composition of the hybrid with the time reaction at fixed H_2O_2 concentration of 3%. The XPS results are summarized in Table 5.

Table 5. Evolution with the reaction time of the composition of the hybrid thin film (3% H₂O₂, in the darkness), based on decomposition of Mo 3d peaks.

Reaction Duration (min)	MoS ₂ (at%)	MoO ₃ (at%)	MoO _x S _y (at%)
5	25	56	19
10	17	60	23
15	5	52	43
30	4	66	30
45	2.5	75	23

It can be seen in Table 5 that with the reaction with a H₂O₂ concentration of 3% it is possible to manage the atomic concentration of MoS₂ present in the hybrid layer from 25% after 5 min of reaction to 2.5% after 45 min. It is thus possible to obtain the desired composition for the hybrid layer according to its intended use.

From Figure 6 and Table 5, after 10 min of reaction duration, 60% of MoO₃ was produced from the MoS₂ oxidation process after 10 min and 66% after 30 min, giving the MoO₃/MoS₂ ratios of 3.5 and 16, respectively. Hence, the MoO₃:MoS₂ ratios increase with the time reaction suggesting that there is a relation between the atomic percentage and the reaction duration, where the MoS₂ atomic percentage decreases and MoO₃ increases by increasing the reaction duration. The new component MoO_xS_y atomic percentage increases with the reaction duration until its saturation at 15 min with a maximum percentage of 43%, and then the atomic percentage starts to decrease with the reaction duration; this indicates that the MoO_xS_y content also depends on the reaction and the content of oxygen incorporated. Regarding these results, the control of the reaction duration allows us to obtain a high MoO₃ atomic percentage, which is an essential advantage for the use of the hybrid MoO₃:MoS₂ in optoelectronic application and especially in OPVs as the hole transport layer (HTL). The operation of the HTL hybrid layer depends on the atomic percentage of MoO₃ which must be dominant and that is confirmed by our previous work. We note that, the synthesis of the hybrid MoO₃:MoS₂ layer in our previous work was carried out using sulfidation of MoO₃ thin film, and the control of its composition was achieved by varying the annealing temperature of the substrate. The application of this hybrid as the hole transport layer in the planar heterojunction solar cells gives better results when the atomic percentage of MoS₂ in the hybrid layer does not exceed 5%, which corresponds to 65% of the MoO₃ atomic percentage; therefore, the presence of a high MoS₂ content (>5%), which means low MoO₃ concentrations in the hybrid MoO₃:MoS₂, could limit the positive effect of the hybrid layer when used as HTL. Taking into account these previously obtained results, the presence of such a high MoO₃ percentage of about 65% in the MoO₃:MoS₂ layer as HTL is beneficial for enhancing the photovoltaic performances due to the improvement of the band matching at the electrode and photoactive layer interface [24]. On the basis of this finding, we can conclude that controlling the atomic percentage of such a component of the hybrid layer is necessary to achieve good device performances when the hybrid is introduced; thus, the successful control of the composition achieved in the present work could open up the use of the hybrid prepared by wet chemical synthesis as the hole transport layer (HTL) in the organic solar cells.

Herein, the measurements of the bandgap from the absorption spectra are uncertain; hence, the bandgap is stable at 1.77 eV ± 0.02 for MoS₂ and oxidized MoS₂. However, the presence of defects under the bandgap due to the presence of the oxo-bridge molybdenyl sulfate, MoO_xS_y, can improve the holes extractions when it is applied as HTL in solar cells [8]. In a previous report, the MoS₂ bandgap can be tuned after its oxidation depending on the MoO_xS_y atomic percentage where they find that the bandgap extended into the visible range when the MoO_xS_y contents increased. The MoO_xS_y reaching 50 at.% induces an increase of the bandgap by 0.25 eV, proving that the modulation of the bandgap is possible by controlling the MoO_xS_y contents [26]. Thus, this indicates that the presence of the MoO_xS_y composite can be efficient to reach a wide bandgap energy. In addition, the

presence of these defects in the hybrid layer can effectively enhance the absorption ability of MoS₂ towards polysulfides, as reported for Li-S batteries [10].

4. Conclusions

In conclusion, we have reported a facile synthetic route to prepare the hybrid MoO₃:MoS₂ layer via exfoliation/partial oxidation of MoS₂ under ambient temperature. Before investigation of the properties of the hybrid layer, the first part was detected in the partial oxidation of MoS₂ nanopowder where we found that the reaction can be controlled efficiently in the darkness, and the homogeneity of the grain sizes is needed to obtain high reproducibility of the results. To overcome the non-homogenous results, the second part was dedicated to the exfoliation by LPE to control the grain size homogeneity and therefore, the morphological, optical, and structural properties of the MoS₂ and the hybrid MoO₃:MoS₂ layer.

In the present study, an original method of LPE was done in pure water as the solvent; the use of water is beneficial as it is not only cost-effective in industrial and commercial applications but also facilitates the hybrid synthesis via the MoS₂ oxidation. A possible growth mechanism of MoS₂, the MoO₃:MoS₂ thin layer was achieved using centrifugation/coating method.

The Investigation of XPS analyses revealed the presence of the three compounds, MoO₃, MoS₂, and MoO_xS_y; this heterostructure was also confirmed by HRTEM analyses. Based on the evolution of the reaction, we found that the atomic percentage of each component depends on the reaction duration; the MoO₃ atomic percentage can exceed 60%, and the presence of the oxo-bridge molybdenyl sulfate, MoO_xS_y, in the hybrid layer justifies the possibility to use this hybrid for large potential applications, especially solar cells, Li-batteries, and catalysis.

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Appendix A

Chemical compositions of the synthesized hybrid MoO₃:MoS₂ nanopowder and thin films were investigated by X-ray photoelectron spectroscopy (XPS) analysis at room temperature using the Axis Nova spectrometer (Kratos Analytical) and employing Al K α line as the excitation source. The spectra were adjusted according to the fixed binding energy of carbon C 1 s at 284.8 eV as a reference. The XPS data were treated using CasaXPS software, the fitting was obtained by a mixed Gaussian–Lorentzian product with 30% and 70% as the contribution of Lorentzian and Gaussian, respectively, for Mo 3d fitting the area ratio of 2:3 was fixed for Mo 3d 5/2 and Mo 3d 3/2, respectively, after the extraction of the Shirley

background. The core-level spectra were recorded using a constant pass energy of 20 eV with an energy step of 0.1 eV.

The morphology of the studied hybrid nanomaterials was analyzed using a scanning electron microscopy (SEM) with a JEOL JSM 7600F field-emission scanning electron gun microscope (Centre de micro-caractérisation, Institut des Matériaux de Nantes Jean Rouxel IMN, Nantes université). Images were recorded using a secondary electron detector and a backscattered electron detector, and the accelerating voltage was set to 5 KV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected by a S/TEM Themis Z G3 (thermo Fisher Scientific) microscope with an operating voltage at 300 KV. The samples analyzed by TEM were prepared by the deposition of a droplet on Cu lacey carbon grid.

Optical absorption spectra were measured at room temperature using a UV-visible-NIR spectrophotometer (Perkin Elmer Lambda 1050 setup) at a normal incidence in the spectral range 300 nm–1200 nm.

X-ray diffraction was done with Diffractometer Burker D8 A25 “Da Vinci” setup using Cu K α radiation ($\lambda_{K\alpha} = 1.5418 \text{ \AA}$); the diffractometer is equipped with a second-generation Si strip detector (“LynxEye XE”).

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