Hydrogen reduction of molybdenum oxide at room temperature

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The color changes in chemo- and photochromic MoO\textsubscript{3} used in sensors and in organic photovoltaic (OPV) cells can be traced back to intercalated hydrogen atoms stemming either from gaseous hydrogen dissociated at catalytic surfaces or from photocatalytically split water. In applications, the reversibility of the process is of utmost importance, and deterioration of the layer functionality due to side reactions is a critical challenge. Using the membrane approach for high-pressure XPS, we are able to follow the hydrogen reduction of MoO\textsubscript{3} thin films using atomic hydrogen in a water free environment. Hydrogen intercalates into MoO\textsubscript{3} forming H\textsubscript{x}MoO\textsubscript{3}, which slowly decomposes into MoO\textsubscript{2} + 1/2 H\textsubscript{2}O as evidenced by the fast reduction of Mo\textsuperscript{6+} into Mo\textsuperscript{5+} states and slow but simultaneous formation of Mo\textsuperscript{4+} states.

We measure the decrease in oxygen/metal ratio in the thin film explaining the limited reversibility of hydrogen sensors based on transition metal oxides. The results also enlighten the recent debate on the mechanism of the high temperature hydrogen reduction of bulk molybdenum oxide. The specific mechanism is a result of the balance between the reduction by hydrogen and water formation, desorption of water as well as nucleation and growth of new phases.

With oxygen having a much larger electronegativity than hydrogen, most binary d-metal oxides are much more stable than the corresponding hydrides\textsuperscript{1-3}. Exposed to a gas mixture even at low hydrogen to oxygen ratios of 1:10\textsuperscript{−6}, most transition metals form binary oxides instead of ternary hydrido-oxides or oxy-hydrides. Hydroxides do exist, but tend to decompose into the corresponding oxides as well\textsuperscript{2}. However, due to the small atomic diameter and the ambivalent character of hydrogen, hydrogen can intercalate into oxides and act as a donor or acceptor of electrons\textsuperscript{4-6}, being the origin of various optical and electronic effects with many applications.

The effect is particularly strong in WO\textsubscript{3}\textsuperscript{7,8} and MoO\textsubscript{3}\textsuperscript{9,10}, which have long been known for their gasochromic properties, and can be utilized as hydrogen\textsuperscript{10} and ammonia sensors\textsuperscript{11}. Hydrogen atoms from molecular hydrogen or decomposition of hydrogen containing reducing molecules such as ammonia intercalate into the oxide and form hydrogen molybdenum bronzes H\textsubscript{x}Mo\textsubscript{5−x}O\textsubscript{6+1}O\textsubscript{10}. The phase transformation causes only small crystallographic rearrangements (topotactic reduction): hydrogen atoms occupy sites in the van der Waals gaps between double layers of MoO\textsubscript{3} octahedra as well as intralayer sites on zigzag chains along the channels\textsuperscript{12,13}. This results in a relatively small increase of the cell volume and slight distortion of the lattice changing the overall crystal symmetry from orthorhombic orthorhombic (phase I) to monoclinic (phases II, IV)\textsuperscript{12,14}. Although lattice distortion and hydrogen ordering increase the complexity of the system\textsuperscript{12}, the electronic structure may be described using the semiconductor model with hydrogen as dopant (Fig. 1). In this model, the MoO\textsubscript{3} structure motif (MoO\textsubscript{6} octahedrons) remains unchanged and defines the overall electronic structure, but is perturbed by hydrogen atoms as new band gap states\textsuperscript{10}. These states change the optical and electrical properties: pristine MoO\textsubscript{3} consists of Mo\textsuperscript{6+} forming the conduction bands and O\textsuperscript{2−} forming the valence bands. Pristine MoO\textsubscript{3} is semiconducting (and thus transparent) with a band gap of 3.2 eV\textsuperscript{10}. Hydrogen gives its electron to the conduction band forming protons and...
Figure 1. Left: Simplified crystal structure of MoO₃ and hydrogen bronze(s). Chains of MoO₆ octahedrons are fused together by edge sharing to form corrugated layers. The intercalation of hydrogen into MoO₃ does not markedly modify the structural motif apart from slight increase of the cell volume, lattice distortion and hydrogen ordering¹²–¹⁴. As already suggested by the vicinity of hydrogens to oxygen, water is formed at higher concentrations. In this case, the metal/oxygen ratio is modified leading to MoO₂. The changes of the electronic structure by hydrogen intercalation are depicted in the right panel. Hydrogen forms band gap states (red) and “valence band-like Mo⁵⁺ states” (green-rimmed boxes: grey: occupied, white: empty), as depicted by the width of electronic states. The loss of oxygen at higher hydrogen concentrations is depicted by the smaller width of the blue rimmed boxes, simultaneously, more Mo bands are filled.

“valence band-like Mo⁵⁺ states” (see Fig. 1: green/grey colored states in the band gap). As a result, a hydrogenated MoO₃ film appears blue due to the intercalation–charge transfer from the newly formed Mo⁵⁺ to adjacent Mo⁶⁺ upon optical excitation. The controversy remains, whether the optical properties are sufficiently described by the intercalation charge transfer theory between Mo⁵⁺ and Mo⁶⁺ ions, or by polaron absorption (small-polaron theory)¹⁰, which nonetheless relies on the formation of Mo⁵⁺ states. Simultaneously with the color change, the electrical conductivity increases, supporting the doped semiconductor model. There is a maximum doping level of hydrogen: exceeding x = 1 in HₓMoO₃, leads to formation of Mo⁴⁺ ions (sketched by the width of the electronic states in Fig. 1). However, this situation seems to be unstable. Indeed, at higher concentrations water and hydrogen free MoO₂ consisting of Mo⁴⁺ and O²⁻ states is formed. Every missing oxygen atom is balanced by two more electrons in the Mo 4d bands (see Fig. 1). This picture explains the effect of oxygen defects on the electronic structure of the MoO₃ phase as well. The phase transformation is associated with major structural rearrangements and correspondingly high activation barriers. Thus, it is usually only observed at high temperatures or at very high driving forces [see, e.g., ref. 15, and discussion later]. The precursor of this transformation may be the formation of OH ions as observed for hydrogen concentrations x ≫ 1 by inelastic neutron scattering¹³. The ambivalent character of hydrogen is similar in the related WO₃ system: its electronic structure analogous to the one of MoO₃ sketched in Fig. 1 depends sensitively on the fact whether H-O-H bridge bonds are formed, or whether hydrogen acts as a delocalized dopant in the semiconductor¹⁶.

In addition to the changes observed during exposure to hydrogen gas, MoO₃ is photo- and electrochromic, and thus used for photo- and electrochromic coatings¹⁰. Gasochromism and photo/electrochromism are directly related: optically or electronically excited electrons in the conduction band can decompose water adsorbed at surface and interfaces of MoO₃. The produced hydrogen intercalates into the bulk and changes the optical and electronic properties of MoO₃ as described above¹⁰.

Thin MoO₃ films can be quite simply prepared by physical¹¹ and chemical vapor deposition¹⁷ or via coating-processes using precursor solutions¹⁸ or nanoparticle dispersions¹⁹. Thus, MoO₃ has been proposed as an anode interfacial layer in organic¹⁶,¹⁷–²⁴ and dye-sensitized solar cells²⁴. The low charge injection/extraction barrier at MoO₃/organic interfaces is believed to be due to the favorable energy level alignment between the high work function value of MoO₃ and the highest occupied molecular orbital of an organic molecule¹¹–²². Due to the complex chemistry of this material and the strong impact of external stimuli on the electronic properties, a coherent understanding of the hole extraction process across MoO₃ in OPV cells is still lacking²⁴. For the application as an electron injection/extraction layer, the formation of hydrogen bronzes by photolysis of hydrogen containing molecules is an undesired effect, because it diminishes the favorable electronic properties²⁴.

Hydrogen bronzes of MoO₃ are metastable states²⁴: they can be further reduced via formation of water to lower oxides and thus the oxygen – metal ratio depends on the specific experimental conditions. In gasochromic and related applications, the hydrogen concentration is relatively high, and oxygen (water) can leave the oxide resulting in irreversible reduction of the latter to MoO₂, and eventually to Mo metal. The easy reducibility can thus be hypothesized to be the origin of the limited reversibility of such devices. On the other hand, it is assumed to be the source of the remarkable catalytic properties for oxidation reactions of hydrocarbons and alcohols²⁷.

Because of its evident importance, bulk as well as surface properties of MoO₃ have been carefully studied by surface science methods such as photoemission and electron diffraction and bulk methods (e.g., XRD, EXAFS¹⁵,²⁸). Simplified, the outcome is as follows: at higher temperatures (> 700 K), the surface of MoO₃ is reduced already in vacuum²⁹. Reduction of bulk MoO₃ requires high temperature and hydrogen at several mbars, and is proportional to the hydrogen partial pressure²⁸. The exact decomposition pathway from MoO₃ to
eventually Mo metal, in particular the significance of intermediate phases such as Mo$_6$O$_{17}$, is still controversially debated. This is due to unprecise experimental conditions (hydrogen purity, in particular the water/oxygen contaminations), and the number of possible reaction steps involved: hydrogen dissociation, hydrogen diffusion, water formation and diffusion, phase nucleation and growth$^{35}$. Furthermore, the high temperature results are not directly transferable to room temperature, as the rate limiting step may change.

In this paper, we apply the XPS-membrane approach$^{30}$ to analyze the reduction mechanism of MoO$_3$ thin films at room temperature. X-ray photoelectron spectroscopy (XPS) is an ideal tool to measure the oxidation states of the elements in oxides, see, e.g. ref. 31, and has been successfully used to study MoO$_3$.$^{23,32,33}$ Unlike in UHV-XPS-systems, where only post-mortem analysis of ex-situ treated films is possible, this approach allows an operando study of the hydrogenation of MoO$_3$ at relevant hydrogen pressures$^{35}$. For this, the MoO$_3$ thin film is deposited on a hydrogen permeable Pd-membrane (see Fig. 2). The high selectivity for hydrogen diffusion in Pd guarantees an ultrapure quality of hydrogen entering the MoO$_3$. Furthermore, it is atomic hydrogen interacting with the oxide. The dissociation of hydrogen on oxide surfaces depends on various physico-chemical parameters (among them the oxidation state of the metal). Therefore, the hydrogen flux into the sample of a bare oxide thin film is difficult to control, in contrast to the membrane approach, where it is controlled by adjusting the hydrogen pressure at the back of the membrane. Hydrogen dissociation on Pd is fast as is the subsequent hydrogen diffusion through the Pd-membrane. Possible rate limiting steps of the reduction of MoO$_3$ are now limited to oxygen diffusion (desorption) and nucleation and growth of new phases. Furthermore, the approach mimics the situation in gasochromic sensors, because also here a Pd layer on top of the thin film provides atomic hydrogen interacting with the layer. The same is true for electrochromic and photochromic devices: water splitting by electrons or photons results in atomic hydrogens first. Surface science methods are usually limited to UHV-pressures, the membrane approach allows pressures up to 1 bar hydrogen$^{30}$. In addition, the membrane provides atomic hydrogen, i.e., hydrogenation of catalytically inactive surfaces such as oxides is possible as well.

Results

Figure 2 shows typical XPS-overview spectra of MoO$_3$ deposited on a Pd membrane as prepared and after long term hydrogenation. The film thickness of 10 nm is just thick enough to consider it behaving bulk-like (the interfaces of noble metals to MoO$_3$ are discussed in depth in ref. 21). From the peak intensities of the oxygen 1 s and molybdenum 5d peaks, the metal/oxygen stoichiometry is determined$^{33}$. In good agreement with literature, the oxygen content decreases after hydrogenation. However, the oxygen loss is not directly related to the applied hydrogen pressure. This is indicated by the time dependence of the process. The diffusion through the Pd-membrane is relatively fast: in previous measurements on hydrogen permeation through the 150 µm thick Pd membrane we observed dynamic equilibrium after approximately 500 s (see Methods section, ref. 30) due to the fast hydrogen diffusion in Pd even at room temperature. We do not expect deceleration by hydrogen diffusion through the 10 nm thin MoO$_3$ film (the diffusion parameter of H in MoO$_3$ is of the order of 10$^{-11}$ m$^2$/s$^{29,30}$). However, after an initial hydrogenation at 100 mbar, vacuum was applied. Unexpectedly, a decrease of the oxygen content was measured after hours in vacuum (Fig. 3). The rate limiting step is thus not hydrogen diffusion.

More details are visible after magnifying the spectral regions of the Mo 5d and O 1 s core levels. Figure 3 compares the oxygen 1 s core levels as deposited and after long term exposure to hydrogen. The data is fitted to two lines separated by approximately 1.6 eV. The value of the main peak most prominently visible in the as deposited MoO$_3$ film is in perfect agreement with literature, see, e.g. refs 33,35. The second peak may be attributed to oxygen as OH in MoO$_3$ following the discussion of the electronic structure. However, prior to desorption, water formed by the hydration of MoO$_3$ will accumulate at the surface. The existence of the peak in the as deposited state as well as the observed oxygen loss, which proceeds via the desorption of water, supports the interpretation of this peak as water adsorbed at the surface$^{30}$. A better probe for the evolution of the electronic structure during hydrogenation are the Mo 5d states. Figure 4 shows the evolution of the Mo 5d states during hydrogenation at 100 mbar. The shape and positions of the peaks change drastically indicating the change of the oxidation state of Mo from Mo$^{6+}$ to Mo$^{4+}$.$^{20,23,32,33,35}$.
A fitting of such complex line shapes is error prone if performed on single spectra alone. However, the power of the membrane approach is the possibility to follow the evolution of the electronic structure operando. Starting situation is defined: Mo\textsuperscript{6+} states exhibiting two 5d core excitations (5\textsubscript{2}/2 and 3\textsubscript{2}/2). Low hydrogen dose results in additional peaks assigned to Mo\textsuperscript{5+}. With continued hydrogenation, a shoulder at lowest binding energy develops, which is assigned to Mo\textsuperscript{4+}. To corroborate the formation of Mo\textsuperscript{4+}-states, we compare the reduced MoO\textsubscript{3} spectrum with literature data (see Methods Section). All oxidation states display two peaks\textsuperscript{20,22,33,35}. To resolve the spectra, we fit all 6 peaks to predefined fixed binding energies and widths; and the intensities, i.e., only the concentrations are chosen as free fitting parameters. This causes a slight scattering of the fitting results, because small deviations of the exact binding energies as a function of the hydrogen concentration are not included. However, the outcome is very clear: the growth of the Mo\textsuperscript{4+} states takes place at the expense of the Mo\textsuperscript{6+} states. The corresponding kinetics is much slower than the diffusion of hydrogen (see discussion above, Methods section). The rate limiting step is thus not the hydrogen supply, nor desorption of water (oxygen, see Fig. 2), and is therefore assigned to the nucleation and growth of the new H\textsubscript{x}MoO\textsubscript{3−δ} phase.

Figure 3. Left panel gives the oxygen/metal ratio during and after hydrogenation at 100 mbar. The right panel shows details of the oxygen 1 s core level spectra as deposited and after long term exposure to hydrogen (background subtracted). The data is fitted to two lines centered around 529.6 ± 0.2 eV and 531.2 ± 0.2 eV, assigned as O and OH, respectively. The intensity ratio between OH and O peaks increases from approximately 6% to 50%.

Figure 4. Time resolved XPS-measurements of the Mo 5d states during hydrogen intercalation (hydrogen pressure 100 mbar). The grey-scale image (left top image) is a 2D representation of the time evolution. In the right graph, the starting (S) and final (E) spectra are plotted and the applied fits considering Mo\textsuperscript{6+}, Mo\textsuperscript{5+}, and Mo\textsuperscript{4+} 5d 5\textsubscript{2}/2 and 3\textsubscript{2}/2 states are given in the bottom left image. Their intensities are taken as measure for the molar fraction of the respective phases shown with the grey-scale plot.
Surprisingly, the Mo\(^{4+}\) state develops independently from this behaviour, and linearly increases over time (Fig. 4). This was also confirmed by experiments in which the hydrogen backpressure at the membrane was set to zero, but the evolution of the Mo\(^{4+}\) states and loss of oxygen (see Fig. 2), i.e., the formation of a molybdenum oxide MoO\(_x\) with an oxygen content of \(x \ll 3\), continued. As discussed in the Methods section, the high chemical potential of hydrogen in the MoO\(_3\) films is reached on a much faster time scale than the observed evolution of the Mo\(^{4+}\)-states. Thus, the supply of hydrogen is not the rate-limiting step. The oxygen content of the new phase associated with Mo\(^{4+}\) is lower than in the hydrogen bronze, and thus oxygen removal is rate-limiting for forming this phase. Due to the noise in the data, only the trend of decreasing oxygen content is experimentally verified. Locally higher oxygen content at the surface may also be realized by reshuffling of oxygen by phase separation into oxygen rich and pure phase as suggested in ref. 33. It is worth noting that the reduced state once reached does not reverse back to the original state in vacuum, at least within the measurement time of several days.

Discussion

These results shed light on the kinetic behaviour of the phase formation in non-equilibrium conditions. Numerous studies investigate the occurrence of intermediate phases during (high-temperature) reduction to unravel the decomposition mechanism. In particular the one-step reduction mechanism (MoO\(_3\) directly to MoO\(_2\)) is discussed against multiple step mechanisms with additional intermediates being involved (e.g. Mo\(_4\)O\(_{11}\))\(^{15}\). To simplify the discussion, we have sketched a qualitative potential energy surface (PES) for the reduction reaction of MoO\(_3\) to MoO\(_2\) in Fig. 5. The hydrogen bronze is a thermodynamically unstable state\(^{26}\), which will eventually be further reduced because of the globally lower free energy of MoO\(_2\) and water\(^{1,15,26}\). However, this 2nd reduction step is associated with the removal of oxygen by water. For both steps, an energy barrier has to be overcome. As the systems has a high number \(n\) of degree of freedom (reaction coordinates), the PES is a \(n\)-dimensional hyper surface, simplified as a 2-dimensional surface in Fig. 5. While energy minima can be related to thermodynamic parameters, the barriers and thus the reaction path requires complex calculations of the electronic structure. The potential energy surface displayed here is an educated guess based on empirical figures. We give the enthalpy of formation of the various phases expected to occur to illustrate their location on the energy potential surface\(^{26}\). As a quantitative indicator for the barrier heights, we added the activation energies of reduction at higher temperatures (data from ref. 15). It is worth noting that also the experimentally derived activation energies depend on the pathway.
The results at hand also indicate that the reaction pathway depends on the rate limiting step controlled by the external conditions: in our experiments, the chemical potential of hydrogen supply is very high, and thus the system follows the kinetically favoured path: that is, the intercalation of hydrogen due to the small activation energy \( E_{\text{int}} \) for hydrogen diffusion in MoO₃ (see Fig. 5, ref. 29) and thus formation of hydrogen bronzes. However, the lower reduction state Mo⁴⁺ is simultaneously formed, but at a much slower pace (compare \( E_a \) and \( E_{\text{diff}} \) in Fig. 5). Oxygen deficient MoO₃ surfaces, which can be imagined as MoO₂ inclusions in a MoO₃ matrix, can be formed by heating in UHV without further reductant. As this takes place only at high temperatures (large \( E_a \)) co-existing phases will be observed only during low temperature reduction. Furthermore, the multiple steps may not be consecutive steps. The hydrogen bronze is a meta-stable phase, i.e., hydrogen absorption without water formation is exothermic, but further reduction under formation of water is thermodynamically favoured (Fig. 5). In addition to the transport of atoms, the kinetics of crystalline phase transformations are limited by long-range order effects. Although the change of the character of hydrogen in the oxide from a delocalized proton to a localized atom bridged to oxygen atoms proceeds without major structural reorientations (compare Fig. 1), the corresponding changes of the overall electronic structure affect the whole crystal.

The local energy minimum of \( \text{H}_x\text{MoO}_3 \) explains its practical existence, but bronzes with high hydrogen concentrations are only formed under high chemical hydrogen potentials using atomic hydrogen from chemical reactions (nascent hydrogen), gaseous hydrogen dissociated at Pd overlayers (typical hydrogen sensor setup), or produced electrochemically, where water removal is slow. The formation of further reduced oxide and water is thermodynamically preferred, explaining the observed irreversibility of the membrane-hydrogenated MoO₃ thin films. Catalysts usually consist of MoO₃ particles, which are practically inert at low temperature (Fig. 5). The formation of oxygen deficient surfaces at high temperature enables hydrogen dissociation, and also desorption of water is faster at high temperature. In this case, direct reduction of MoO₃ to MoO₂ without formation of a bronze is possible. Similar qualitative explanations are valid for the existence of the various other crystalline phases observed during reduction.

The analysis gives guidelines for better reversibility of devices made of MoO₃. The reduction of Mo should take place without removal of oxygen. This implies the encapsulation of the MoO₃ by materials, which do not get getter oxygen. In hydrogen sensors, this is less a question of the choice of materials (typical setup: substrate/MoO₃/Pd₁₀, Fig. 5), but of the quality of the thin film structure (roughness, coverage). The conditions in organic solar cells are particularly difficult: here, MoO₃ interfaces organic semiconducting small molecules or polymers, possibly even containing residual organic solvents. Most of the chemicals used are reducing and hygroscopic, and thus add an additional thermodynamic driving force for the reduction of MoO₃ via water formation, which affects the device performance. Finally, we note that the experimental observation of low temperature reduction to Mo⁴⁺ is possible only using the membrane approach guaranteeing high flux of hydrogen atoms into the sample and providing a free surface for water desorption.

To summarize, we demonstrated the operando XPS analysis of the reduction of MoO₃ by hydrogen, from which we derived the reaction pathway of the reduction around room temperature. The low temperature results join the missing link between reaction mechanisms proposed for bulk materials at high temperature hydrogenation and the hydrogen–oxide interactions. We show that several reaction pathways of the hydrogen reduction take place simultaneously. The preference of one of these pathways can be controlled by the experimental conditions (open/closed setup, exposure to atomic/molecular hydrogen, temperature), but the then subdominant pathway may still occur as side reaction with detrimental effects on the performance of the sought application. E.g., in hydrogen sensors, the reversible intercalation in and out of MoO₃ is competing with the unwanted irreversible water formation, which eventually disables the sensor function. This situation is observed in many related materials systems such as WO₃ with a broad range of applications from optically active thin films and chemical sensors, hole extraction layers in PV, catalysis, to solar water splitting. An important factor in these applications, which was addressed here for the MoO₃ system, is the transient nature of the various states of matter during hydrogen exposure. The time constant in hydrogen W/Mo bronzes is relatively long; however, there are indications of short-lived, but highly mobile and reactive hydrogen states in various other meta-stable systems, to be studied using the membrane approach.

**Methods**

10 nm thick MoO₃ thin films were deposited onto 150 μm thick polycrystalline Pd-membranes by thermal evaporation (0.2 Å/s). In situ XPS surface analysis was performed in a modified VG EscaLab spectrometer with a base pressure below 10⁻⁶ mbar. XPS spectra were collected with a SPECS PHOIBOS 100 analyzer using a non-monochromatic X-ray source (Al K alpha: 1486.6 eV).

The membrane approach is based on a relatively simple setup to overcome the so-called pressure gap in photomission. The core idea of the approach is the membrane device, which is exposed to UHV in the analysis chamber on one side and ambient pressure hydrogen on the other. The hydrogen flux from the surface into the vacuum is desorption rather than diffusion limited, leading to the equivalence of ambient pressure conditions at the analysed surface of the membrane (Fig. 6). For details of the membrane approach we refer to ref. 30. Data evaluation was performed using CasaXPS. For fitting of the Mo 5d states, we used the following parameters:

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\begin{align*}
\text{Mo}^{6+}: & \quad E_g(5/2) = 232.5 \text{ eV}; \quad E_g(3/2) = 235.8 \text{ eV} \\
\text{Mo}^{5+}: & \quad E_g(5/2) = 231.1 \text{ eV}; \quad E_g(3/2) = 234.3 \text{ eV} \\
\text{Mo}^{4+}: & \quad E_g(5/2) = 229.7 \text{ eV}; \quad E_g(3/2) = 233.1 \text{ eV}
\end{align*}
\]
in good agreement with literature data\(^{32,33,35,39}\). The intensity ratio of the 5/2 to 3/2 peak was fixed to 5/3, which is also very near to the result obtained from fitting using free parameters of as prepared MoO\(_3\) spectra consisting of only 6\(^+\) states. Figure 7 is a comparison of measurements on membrane-hydrogenated MoO\(_3\) and literature data on MoO\(_2\) (from ref. 39). Although MoO\(_2\) may be described by one Mo\(^{4+}\) and two O\(^2-\) ions, the XPS shows all three states\(^{38}\).

**References**

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Author Contributions
A.B. and R.D., designed and performed the XPS experiments, S.J. prepared the MoO₃ thin films, O.S., R.H. and F.N. contributed to the evaluation and scientific discussion of the results. All the authors commented on the manuscript.

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