Polymorphic expressions of ultrathin oxidic layers of Mo on Au(111)†

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Ultrathin oxidic layers of Mo (i.e. O/Mo) on the Au(111) substrate are investigated using first-principles density-functional theory calculations. Various polymorphic structural models of these O/Mo layers are proposed and compared with previous experimental results – covering both spectroscopic and microscopic approaches of characterization. We find that, through the control of metal–oxygen coordination in these ultrathin oxidic O/Mo films on Au(111), the oxidation state of Mo atoms in the O/Mo layers can be modulated and reduced without intentional creation of oxygen vacancies. This is also assisted by a charge transfer mechanism from the Au substrate to these oxidic films, providing a direct means to tune the surface electronic properties of ultrathinoxide films on metal substrates.

Introduction

The advances of surface science techniques to create and characterize structures at the atomic level provide a foundation for the development of many industrial applications such as heterogeneous catalysts and semiconductor devices.1 In particular, the molecular-level surface characterization methods, such as X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM), make it possible to understand the elementary steps of surface reactions and growth mechanisms, or to monitor the behavior of surface diffusion and the formation of labile surface structures.2 Moreover, the use of these techniques has also enabled the study and control of local atomic structures and stoichiometries in ultrathin oxide films for desired surface properties.3,4

There have been several surface science investigations for the growth and manipulation of molybdenum (Mo) oxide layers on the various supports, such as metal substrate5–8 and metal oxide surface (SiO2, Al2O3, and Fe3O4)9–11 controlling their morphologies for the desired functionality. In particular, to facilitate the growth of the well-ordered α-MoO3 nanostructure (orthorhombic phase with a space group Pnma) is of the interest due to high catalytic activities in partial oxidation reactions with a high selectivity, such as production of formaldehyde from methanol,12,13 and converting propene to acrolein.14

The common strategy to grow and manipulate α-MoO3 oxide layers for the desired applications is to use deposition methods.15,16 However, those experimental techniques lack the precise control of surface structures at the atomic level and a scalable well-ordered thin layer, which is critical to grow highly crystalline MoO3 surfaces.17 Therefore, the preparation of a thin oxide layer using the advanced surface science technique under the ultra-high vacuum (UHV) is regarded as a more rational approach. The augmentation and functionalization of MoO3-like thin films (typically of few monolayers (ML) thick) on Mo facets (e.g., (100), (110), and (112)) have few drawbacks for the preparation of the high crystalline thin MoO3 layers, such as the formation of MoO2-like surface as a thermodynamic product rather than MoO3 surface18–20 and the preparation of highly stepped structures (corrugated surfaces) of thin oxide layers caused by the structural incoherence between the oxidic layers and the Mo substrate.5,8,21,22

As an alternative, ultrathin MoO3-like layers on a surrogate metal substrate, e.g. Au(111) have been considered,7,17,23–27 which were reported as possessing a different surface morphology with previous distributed MoO3 islands.5 The prepared surface structures of thin oxidic layer of Mo are in the high-quality crystallinity where scalable crystalline phase was
difficult to grow.\textsuperscript{5,6,21} In the series of works by Friend’s group from 2004 to 2008, MoO\textsubscript{3} monolayer islands formed on Au(111) were prepared and characterized by STM and XPS, and showed a distinctively different behaviour from the bulk phase of MoO\textsubscript{3}.\textsuperscript{7,23-26} These thin oxide films have been suggested to resemble a \((2 \times 2)\) \(\sigma\)-MoO\textsubscript{3}(010) surface with minimal distortions to fit on the \((4 \times 2)\) Au(111) substrate. This involves a slight modification to the lateral symmetry of the MoO\textsubscript{3} layers from a square to a rectangular surface cell, with approximately 0.5 nm in height.\textsuperscript{25,26}

In a more recent work by Freund et al.,\textsuperscript{17} they have carefully studied the oxidation of Mo on Au(111) via STM and XPS measurements, tracing the structural evolution of ultrathin Mo oxidic layers to the \(\sigma\)-MoO\textsubscript{3}(010) surface as a function of Mo surface concentration. In their observation,\textsuperscript{17} the oxidation of different surface coverages of Mo lead to the formation of different surface structures including those identified as being similar to the monolayer reported in earlier works.\textsuperscript{7,23-25} Also, they have identified thicker oxidic layers (of 0.7 to 1.3 nm in height) as the precursor surface structure for the growth of \(\alpha\)-MoO\textsubscript{3}(010).\textsuperscript{17} They have further investigated and determined the structure of a monolayer of MoO\textsubscript{3} on Au(111) via statistical analysis and optimization algorithms.\textsuperscript{27} Despite these reports, a fundamental understanding of the surface atomic configurations and electronic structure properties of these Mo oxidic layers (beyond 0.5 nm) is still lacking.

In this work, by using first-principles density-functional theory (DFT) calculations and the revised \textit{ab initio} atomistic thermodynamics approach,\textsuperscript{28} the thermodynamic stability of different surface configurations of thin Mo oxidic layers (up to a few ML thick) on Au(111) under various growth conditions is presented and discussed. To characterize these thin oxidic layers of Mo, complementary theoretical spectroscopy and microscopy simulations are performed for various oxidic surface structures of O/Mo/Au(111).

### Methodology

**Density-functional theory calculations**

We perform DFT calculations with the generalized gradient approximation (GGA) to the exchange–correlation (xc) functional, including self-consistent van der Waals (vdW) correction (optB88).\textsuperscript{29} All DFT calculations are performed using the Vienna \textit{Ab initio} Simulation Package (VASP)\textsuperscript{30,31} where the electron–ion interactions are described within the projector augmented-wave (PAW) framework.\textsuperscript{32} The detailed computational setup for the O/Mo/Au(111) slab model calculations is listed in the ESI.\textsuperscript{†}

**\textit{Ab initio} atomistic thermodynamics**

To evaluate the binding strength of oxygen of the Mo oxidic layers on Au(111), the average adsorption energy of oxygen \((E^{ad})\) is computed, using eqn (S1) of the ESI.\textsuperscript{†} The relative stabilities of Mo oxidic layers on Au(111) under a reactive oxygen gas environment are computed, obtaining the Gibbs free energy of adsorption \((\Delta G^{ad})\), based on eqn (S2)\textsuperscript{†} via the revised \textit{ab initio} atomistic thermodynamic approach under the condition of a mildly-doped metal surface.\textsuperscript{28,33} Here, for the realistic chemical reservoir of Mo atoms to form Mo oxidic layers on Au(111) substrate, various Mo/Au surface structures are considered, introducing the change of chemical potential of Mo \((\Delta \mu_{Mo})\) (see eqn (S3)\textsuperscript{†}) of different Mo\textsubscript{5}Au\textsubscript{y} nano-composite structures with reference to the total energy of the Mo atom. Finally, to understand how metastable and/or kinetically-hindered oxidic surface structures may play a role in populating the actual substrate under growth conditions, the surface population (defined as eqn (S4)\textsuperscript{†}) of these O/Mo/Au(111) structures is computed following a Boltzmann distribution-type behaviour.

### Results and discussion

**Structural motifs of Mo oxidic layers on Au(111)**

The experimental procedure for Mo oxidic layer deposition on Au(111) has been conducted as a two-step process. Firstly, Mo atoms are deposited on Au(111) with controlled surface coverages of Mo atoms, which results in the formation of Mo clusters on the substrate. Then, subsequent oxidation \textit{via} NO\textsubscript{2} or O\textsubscript{2}, at specific molecular pressures are performed.\textsuperscript{7,17,24} Interestingly, it has been reported that above 525 K, the deposition of Mo on Au(111) leads to the formation of a Mo–Au surface alloy, although these two elements are known to be bulk immiscible.\textsuperscript{24} However, oxidation of this surface structure brings about Mo–Au dealloying with the formation of single layer MoO\textsubscript{3-x} islands and vacancies on Au(111).\textsuperscript{7,24} Therefore in this work, thin Mo oxide film formation on Mo–Au alloyed substrates are not considered.
As detailed in previous reports,\textsuperscript{25,26} monolayers of $c(2 \times 2)$ \(\text{MoO}_3\) on the \(c(4 \times 2)\) \(\text{Au}(111)\) substrate experience a small lattice mismatch of $-1.37\%$. In Fig. 1(a), the atomic configuration of monolayer \(\text{MoO}_3\) (denoted as 1L in this work) on \(\text{Au}(111)\) bears a resemblance to the surface structure of \(\alpha\)-\(\text{MoO}_3\)(010). The 1L surface structure consists of two distinct O atoms, \(O_a\) (the axial oxygen) and \(O_e\) (the equatorial plane oxygen) denoted in Fig. S2(a) of the ESI.\textsuperscript{†} The bond length between Mo and \(O_a\) is 1.67 Å, which is much shorter than those between Mo and \(O_e\) (2.03 and 2.00 Å).

One of the notable experimental observations that have not been considered fully in the previous theoretical studies\textsuperscript{25,26} is the height (or the number of atomic layers) of the thin oxidic films on the substrate. The measured (apparent) height of the thin Mo oxide layers obtained by STM varied from 0.5 to 1.3 nm,\textsuperscript{17,23,24} as listed in Table S1.\textsuperscript{†} Also, it is commonly accepted that the obtained apparent height \textit{via} the STM probe is dependent on the applied bias and might substantially deviate from the real height. However, the slab models used in previous theoretical studies\textsuperscript{25,26} were solely dedicated to only very thin films with 0.5 nm in real height, which is not well studied in terms of structural configurations.

In the present study, thicker surface structures are considered by varying the surface coverage of Mo atoms, \(\Theta_{\text{Mo}}\) (defined as the number of Mo atoms in the oxidic layer to the number of outermost Au atoms in the substrate slab model) from 0.50 to 1.00 ML using the 1L structural model as the basic growth template (to test for more structural configurations). The real height profiles of the optimized Mo oxidic structures and the apparent heights obtained from the STM experiments are summarized in Table S1 in the ESI.\textsuperscript{†}

The discovery of new polymorphic phases of ultrathin oxide layers on a metal substrate is of high interest\textsuperscript{44} (even if they are metastable) as it expands the utilization of materials for specific target applications.\textsuperscript{45} Therefore, we constructed various structural models, motivated by the structural connectivity of polymorphic phases of bulk \(\text{MoO}_3\) as shown in Fig. 1. The \(sh2L\) surface structure (see Fig. 1(b)) originates from the Mo–O bonding feature in a \(\text{MoO}_3\) bilayer unit of the \(\alpha\)-\(\text{MoO}_3\) phase in the [010] direction. The axial O atom bonded to the Mo atom in the first layer (closest Mo atom to the Au substrate) becomes the equatorial plane oxygen (\(O_e\)) for a Mo atom in the second layer.

The 2L structure possesses a resemblance to the Mo–O bonding character of the \(\beta\)-\(\text{MoO}_3\) phase (one of the polymorphic phases of \(\text{MoO}_3\) with a space group \(P2_1/n\)). The pyramidal \(\text{MoO}_5\) unit is stacked on \(O_a\) in the first layer as shown in Fig. 1(c). The \(\text{MoO}_5\) unit of the \(inv2L\) surface structure (Fig. 1(d)) is stacked with an inverted direction compared to that of the 2L surface. The stacked second layer \(\text{MoO}_5\) unit interacts with the first layer \textit{via} vdW forces which is, in fact, similar in bonding character to that found between bilayers of the \(\alpha\)-\(\text{MoO}_3\) bulk phase in the [010] direction.

![Fig. 1 Various structural motifs of Mo oxidic layers on the c(4 × 2) Au(111) substrate: (a) 1L, (b) sh2L, (c) 2L, and (d) inv2L. The dark gray, light gray, red, pink, and white spheres represent Mo atoms of the first and second layers, O atoms bonded to the Mo atoms in the first and second layers, and Au atoms, respectively. The surface unit cell is denoted by the solid yellow line.](Image)
In addition to these basic surface features, the surface stoichiometries are controlled by introducing O vacancies, since it has been reported that oxygen vacancies are formed easily on MoO$_3$(010) facets in a previous study.$^{46}$ Therefore, we considered a total of 12 structures varying in the height of the Mo oxidic layer from about 0.3 to 0.9 nm (i.e. 3 to 9 Å). The surface coverages of Mo and O ($\Theta_{Mo}$ and $\Theta_{O}$) and the ratio between Mo and O atoms ($N_{O}/N_{Mo}$) of the oxidic layers are listed in Table S2,† and an illustration of the surface atomic structures, with the notation for each Mo and O atoms is shown in Fig. S2.†

### Thermodynamics of Mo oxidic layers on Au(111)

As outlined in our previous work,$^{28}$ under controlled growth conditions where the chemical origin of the deposited atom (here, Mo) may differ, changes to the surface thermodynamics of these oxidic thin films can be expected. That is, the evaporated Mo atoms can lead to the formation of Mo–Au nanocomposites, which can act as the chemical reservoir of Mo atoms for the creation of the thin Mo oxide films on the Au substrate in an oxygen environment. As also discussed, the actual experimental growth process to prepare these Mo oxidic layers on Au involves first deposition of Mo atoms on the Au(111) facet, and then followed by the introduction of a reactive oxygen atmosphere.$^{7,17,24}$

Before we understand how the different formation of Mo–Au nanocomposites vary the surface stabilities, the computed $\Delta\mu_{Mo}$ values obtained via eqn (S3)† are plotted as a function of surface coverage of Mo ($\Theta_{Mo}^{Mo/Au}$) in the Mo/Au surface models with the illustration of surface atomic structures in Fig. 2(a) and (b). In Fig. 2(b), an exponential decrease of $\Delta\mu_{Mo}$ can be seen with increasing Mo coverage in the Mo–Au nanocomposite systems, which is similar to the trend in $\Delta\mu_{Cu}$ for the Cu/Au system.$^{28}$ The calculated $\Delta\mu_{Mo}$ of the Mo/Au nanocomposite when $\Theta_{Mo}^{Mo/Au}$ is 2 ML, approaches that of the bulk Mo. The value of $\Delta\mu_{Mo}$ for the monolayer structure (when $\Theta_{Mo}^{Mo/Au}$ reaches 1 ML) is more negative than that for the Mo–Au alloy surface, reflecting immiscibility between Au and Mo atoms.

To understand the characteristics of oxygen adsorption, $\Delta\mu_{ad}^{O}$ (cf. eqn (S1)†) is computed as a function of oxygen coverage ($\Theta_{O}$) and plotted in the Fig. 3(a). In general, $\Delta\mu_{ad}^{O}$ increases when the surface coverage of Mo (which is correlated to $R_{Mo/Au}$) becomes larger, from 0.50 to 1.00 (denoted as circles with different size), implying that further oxidation beyond a 1L structure ($R_{Mo/Au} = 0.5$) is the energetically preferred process. Also, similarly to our previous observations,$^{47}$ introduction of a minute amount of Mo (or in general, chemically-active transition metal atoms) to the inert Au(111) substrate results in an increase of oxygen binding strength compared with the $\Delta\mu_{ad}^{O/Au}(111)$ system.$^{48,49}$

In Fig. 3(b), we plot the surface phase diagram as a function of the changes of chemical potential of Mo and O species (i.e. $\Delta\mu_{Mo}$ and $\Delta\mu_{O}$, respectively) using eqn (S2).† It is first noted that the stable region for pristine Au(111) (shaded as light blue color) is much smaller than that for the O/Cu/Au case,$^{28}$ which shows the stronger oxidation character of Mo atoms than Cu atoms. Moreover, unlike Cu oxidic layers on Au(111),$^{28}$ the surface phase diagram of Mo oxidic layers on the same substrate possesses less dependency on $\Delta\mu_{Mo}$ values for the surface structure stability, showing almost no phase transition with variation of $\Delta\mu_{Mo}$ values. In our previous work,$^{28}$ we claimed that the stable structures could be determined by the chemical potential of the metal via changing the deposited amount of metal atoms, whereas this is not the case for the O/(Mo/Au)(111) system. The reason is that the Mo surface coverage of these observed structures is almost the same, with values ranging from 0.50 to 1.00 ML as listed in Table S2.† Furthermore, the high formation energy of intrinsic Mo vacancies, compared to oxygen vacancies, in the MoO$_3$ system (n-type conductivity)$^{50}$ causes it to be independent of $\Delta\mu_{Mo}$ as compared to the O/Cu/Au(111) system, which more readily forms Cu defects than O defects.$^{51}$

Therefore, we have chosen the chemical reservoir of Mo as bulk Mo (denoted as a horizontal line in Fig. 3(b)) and have plotted the Gibbs free energy of adsorption, $\Delta G^{ad}$ (cf. eqn (S2)†) in Fig. 4(a). With increasing $\Delta\mu_{Mo}$, surface structural transitions are predicted. At $\Delta\mu_{Mo} = -3.30$ eV, the structural transition from sh2L + $V_{O}$ (with one vacancy of outmost oxygen atoms) to sh2L occurs. Moreover, for $\Delta\mu_{Mo}$ from $-2.81$ to $-2.70$ eV, the 2L + $V_{O}$ structure can be stabilized, and for $\Delta\mu_{Mo}$ over $-2.70$ eV, the 2L structure is predicted to be the thermodynamically stable structure. However, the relative energy difference between the 2L and im2L structures is very small, ±0.01 eV Å$^{-2}$, implying the possibility of the coexistence of the two phases.

Referring to our previous publication for transition points from oxidic layer to bulk oxide (or oxide surface),$^{28}$ due to the
thermodynamic limit on the amount of Mo atoms, the MoO$_3$ oxide structures cannot be formed. Therefore, the Au$_2$O$_3$ bulk oxide starts to form when $\Delta \mu_O$ is $-1.12$ eV. Based on our thermodynamic analysis, the experimentally observed 1L structure might be the kinetically hindered phase or formed by a limited amount of Mo atoms.

In an earlier experimental work by Freund’s group, Mo oxidic layers prepared by oxidation of thicker Mo (denoted as 1.15 ML Mo on Au(111)) at 673 K showed MoO$_3$(010)-like STM images with a greater height (0.7 to 1.3 nm) than the 1L structure via oxidation of 0.46 ML Mo/Au(111). These flat MoO$_3$(010)-like oxidic layers play a critical role for the further growth of the stoichiometric MoO$_3$(010) surface. Freund et al. proposed its structural origin as two oxide monolayers. Our stable surface structures (2L or inv2L) could correspond to the observed surfaces because they indeed are made up of bilayers of MoO$_5$ pyramidal units.

As reported in ref. 17, the intermediate phase with the 11.5 Å × 5 Å rectangular unit cell was obtained with twice the unit cell vector of the 1L structure in one direction and formed by oxidation of a 0.92 ML Mo/Au sample. The STM image showed clear corrugation lines, and it was regarded as the precursor structure between one monolayer and bilayer Mo oxidic layers. In our work, the flat Mo oxidic layers are of interest due to the unique structural properties as the growth template for the MoO$_3$(010) surface.

In Fig. 4(b), we have plotted the surface populations, $P(n, p, T)$ (cf. eqn (S4)). In the graph, the experimental conditions reported in ref. 17 (673 K and partial pressure of oxygen, $p_O_2$ as 50 mbar) are considered. Under these conditions, 2L and inv2L surface structures are statistically the most probable surface phases, giving support that the experimentally measured structures might be either 2L or inv2L. As for the metastable surface phases, oxygen vacancies may be induced in the surface structures, such as 2L + $V_O$ and 2L + 2$V_O$, or the sh2L surface may then be observed.

**Surface characterization of Mo oxidic layers on Au(111)**

**Simulated scanning tunneling microscopy.** To compare with experimental STM images, the constant current approach for theoretical microscopic simulations is employed using a +2.5 V bias voltage probing the unoccupied states of Mo oxidic layers with a blunt W(110) tip model. Here, for further analysis, we focus on the four different surface configurations: the basic template structure (1L), the surface configuration with similar bonding character to the bilayer of bulk $\alpha$-MoO$_3$ (sh2L), and the predicted structures corresponding to the experimental conditions (2L and inv2L). The resulting simulated STM images are shown in Fig. 5.

The experimental STM image of the oxidic layer prepared by oxidation of the 1.15 ML Mo/Au system (which possesses the thickness of 0.7 to 1.3 nm) shows similar structural fea-
These STM features are observable in our simulated images of the sh2L, and 2L structures (shown in Fig. 5(b) and 5(c), respectively) and the brightest spot originates from the axial oxygen (Oa) atoms of the outmost layers. It is due to the dominance of 2p states of the Oa atom (cf. Fig. 8(b) and (c)) with its topological location at the outmost layer. However, the STM image of the inv2L structure (Fig. 5(d)) exhibits different features compared to the others shown in Fig. 5. As shown in Fig. S4,† the STM image of the inv2L structure displays significant sensitivity to the bias voltage (+0.5 to +2.5 V) probing the unoccupied states, whereas the STM images of the other three surface structures are less sensitive to the bias voltage (not shown here). This different behaviour is attributed to the surface structural framework of inv2L, i.e. in its outermost layer, there are no structural corrugations, being composed of flat rectangular Mo–O networks. Therefore, the simulated STM images of inv2L are much more sensitive to electronic effects than the other phases. The STM contrasts are determined by the surface electronic structure which depends sensitively on the bias voltage rather than the geometric topography. This is commonly observed in STM measurements.53

In previous work of theoretical STM studies on magnetite (Fe3O4), the simulated images obtained by using an O terminated tip provided similar images to experiment when generated by Tersoff–Hamann calculations.54 Thus, the good agreement between the experimental and theoretical STM images using the Tersoff–Hamann approach might be the consequence of functionalization of the tip by oxygen molecules. In this work, when we functionalize the STM tip with an oxygen atom, the resulting STM simulations exhibit an interesting feature for the inv2L structure, as shown in Fig. S4(c).†

Fig. 4 (a) Gibbs free energy of adsorption, $\Delta G^\text{ad}$ (cf. eqn (S2)) for Mo oxidic layers on Au(111) as a function of the change in oxygen chemical potential with $\Delta \mu_{O_2}$ from bulk Mo (−6.87 eV). The bulk oxide formation energies of $\text{Au}_2\text{O}_3$ and α-MoO3 are denoted as gray arrows and dotted vertical lines. (b) Surface population, $P(n, p, T)$ (cf. eqn (S4)) of various Mo oxidic layers as a function of temperature (T). The results are obtained for $p_{O_2} = 50$ mbar and the typical experimental temperature is indicated by the vertical dotted line (experimental conditions, 673 K and $p_{O_2} = 50$ mbar).

Fig. 5 Simulated constant-current STM images for thin oxidic layers of Mo at +2.5 V (bias voltage) with the tip model (W adatom on W(110)); (a) 1L, (b) sh2L, (c) 2L, and (d) inv2L. The outmost atomic position (Mo–O rectangular network) is shown superimposed on the STM images, with the top-view of the atomic slab models used shown at the far left (labels for the atoms follow Fig. 1).
For +2.5 V bias voltage, the simulated image at a low current value, i.e. at a typical tip–sample distance of about 5 Å in our case (see the STM image at the right-hand side in Fig. S4(c)†) resembles those of sh2L and 2L as generated by the blunt W(110) tip. This presents the possibility that the experimental structures could correspond to the inv2L structures imaged with an O-functionalized tungsten STM tip. Henceforth, the STM simulations alone cannot be conclusive regarding the actual surface structures identified in the STM experiments. In the following section, the surface core-level shifts for the various O/Mo/Au systems are computed to assist in the identification of these surface structures.

**Theoretical core-level spectroscopy.** In general, the experimental oxygen binding energy ($E_B$) spectrum of a surface structure is expressed by the superposition of the Gaussian functions for $E_B$ of each oxygen species. To make a comparison with experimental XPS spectra, we generate the theoretical $E_B$ spectra using the DFT-computed core-level binding energy ($E_{CLS}$) values of O 1s state for the various Mo oxidic surfaces. The systematic procedure of plotting $E_B$ spectra is listed in the ESI (cf., Fig. S1†).

We have successfully generated the $E_{CLS}$ spectrum from the discrete values for the O/Mo/Au surface structures. However, the absolute values of $E_{CLS}$ from DFT calculations are known to be in poor agreement with experiments. The comparison of energy differences between the calculated $E_{CLS}$ and a well-defined reference system (hence, $E_{CLS} - E_{CLS}$ the surface core-level shift and tabulated in Table S3†) is regarded as the best possible strategy to afford a better comparison with experiments. In our case, the generated $E_{CLS}$ spectra have to be shifted horizontally with the proper reference value. The reference point (i.e. the well defined reference system) for $E_{CLS}$ of the O 1s state is conventionally taken to be that of the bulk oxide (here, $\alpha$-MoO$_3$).42,43

However, the $\alpha$-MoO$_3$ phase has three different oxygen atoms in the unit cell and the computed $E_{CLS}$ values vary by 0.5 eV. Also the center values of XPS peaks of $\alpha$-MoO$_3$, which is equivalent to $E_{CLS}$, are different depending on the literature references (530.3,57 529.6,58 530.4,50 and 530.6 eV (ref. 59)). This is most likely due to the fact that XPS measurements are very sensitive to the immediate chemical environment, such as local atomic defects/distortions and the interfacial structures with the underlying substrate. Thus, we have decided to use the $E_{CLS}$ values for the O 1s state of the 1L structure as the reference state, given that the structural model of the 1L phase has been demonstrated in previous literature.17,23–26 This includes the recent work by Freund et al.17 that reports the distinctive O 1s XPS peak for the 1L structures (via oxidation of the 0.46 ML Mo/Au system) as being 530.0 eV.

Fig. 6 shows the theoretical $E_B$ of the oxygen 1s state for the Mo oxidic layers plotted and convoluted by the Gaussian function method detailed above, with respected to the 1L structure aligned to the experimental $E_B$ value (530.0 eV (ref. 17)). The $E_B$ plot for each Mo oxidic layer shows one characteristic peak fitted to a Gaussian function. The obtained $E_{CLS}$ (taken with respect to that of the 1L oxidic structure) for sh2L, 2L, and inv2L are −0.11, −0.57, and +1.10 eV, respectively. The corresponding full width at half maximum (FWHM) values for the fitted plots of the 1L, sh2L, and inv2L structures are +1.12, +1.11, and +1.12 eV, implying the variation of the $E_{CLS}$ values for the oxygen component is smaller than that of the 2L structure (1.34 eV).

The variation of $E_B$ was also reported for Mo oxidation of Mo/Au nanocomposites for a range of Mo coverages. It was found that increasing the coverage of Mo atoms in the oxidic layers from 0.45 to 1.15 ML results in the saturation of $E_B$ to the values of thicker films (530.65 eV), obtained by the oxidation of 3.45 ML of Mo/Au precursor. Also, as the thickness of the films increased, the XPS peaks converged to their bulk values.

Our calculated $E_B$ results show that the sh2L structure possesses an almost identical value of $E_B$ to that of the 1L structure, manifesting the $E_{CLS}$ value as −0.11 eV with respect to the $E_B$ of the 1L structure. This is highly indicative that both phases possess very similar bonding character. However, the 2L structure shows a negative shift with respect to that of the 1L structure. This is mainly attributed to the oxygen atoms in the second layer as observed from the absolute $E_{CLS}$ values (listed in Table S3†). Interestingly, the $E_B$ of the inv2L structure shows a positive shift relative to the 1L structure of about 1.10 eV. Although the degree of shift with respect to the 1L structure is larger than that of experiments (0.65 eV), amongst our considered surface structures, the inv2L structure shows...
the only positive shift. The DFT computed $E_h$ have a larger error bar (from 0.10 to 0.30 eV), which was also discussed in several earlier theoretical works when compared to known experiments. Considering this aspect, the $im2l$ may be the experimentally observed surface structure, in view of both our thermodynamic and STM analysis.

Projected density-of-states. To compare the electronic structures of our surface structure models with Mo–O reference systems, such as bulk $\alpha$-MoO$_3$ and the $\alpha$-MoO$_{3.1}$[010] surface, we first consider the projected density-of-states (PDOS) of those systems as plotted in Fig. S3† and Fig. 7, respectively, along with their atomic structures.

The bulk $\alpha$-MoO$_3$ phase is composed of edge-shared bilayers of MoO$_6$ octahedron with severe distortion of the central Mo atom. It brings three types of oxygen: (1) the outmost oxygen atoms of bilayers of MoO$_6$ octahedron interacting with the other bilayer via van der Waals forces in the $b$ direction (O$_{avw}$), (2) the oxygen atoms sharing with lateral MoO$_6$ octahedron (O$_{edge}$), and (3) the oxygen atoms bonded to the other MoO$_6$ unit in the bilayer (O$_{corner}$). Referring to Fig. S3† the PDOS of bulk $\alpha$-MoO$_3$ demonstrates the semiconducting character with a band gap ($\epsilon_{\text{gap}}$) of 1.75 eV. In this work, because we have employed the semi-local optB88 xc functional, $\epsilon_{\text{gap}}$ is underestimated when compared to that calculated by a hybrid xc functional (2.95 eV). The 2p state of O$_{edge}$ is strongly hybridized with the Mo 4d state in the low energy range from $-7$ to $-5$ eV, implying a strong interaction between Mo and O$_{edge}$ compared to the other oxygen atoms.

The PDOS of the stoichiometric MoO$_3$[010] surface (in Fig. 7[a]) possesses similar characteristics to that of the bulk phase, e.g., the 2p state of O$_{outmost}$ which is exposed to the vacuum region, has an almost identical form to that of O$_{avw}$.

To understand the chemical interactions between the Mo oxidic layer and the Au substrate, as well as the chemical bonding properties of the Mo and O atoms, we turn now to the electronic structure of the Mo oxidic layers (see Fig. 8). Here, we have plotted the PDOS for Mo 4d and O 2p states of the outmost oxidic layer atoms, and the averaged 5d states of interfacial Au atoms interacting with the Mo oxidic layers. In most of the oxidic layers, semi-metallic properties are obtained due to the presence of Mo 4d states near the Fermi level. These changes may be induced by the charge transfer from the Au substrate to the oxidic layers. In addition, in the oxidic layers, the Mo 4d state of the second layer Mo atoms (Mo$_{L2}$) exhibits different electronic properties depending on the oxidic polymorphic models.

In Fig. 8(a), the O 2p states of the 1L structure are hybridized with 5d states of the Au substrate in the low energy window ($-6$ to $-1$ eV), implying chemical interaction between the first layer oxygen atom and the Au substrate. Interestingly, the 2p states of the outmost oxygen atom (O$_{L1e}$) in the 1L surface structure have a dominant peak in the range $-6$ to $-4$ eV, which is quite different from that of the O$_{outmost}$ atom in stoichiometric MoO$_3$[010]. The dominant peak near $-6$ to $-4$ eV of O$_{L1a}$ in the 1L structure implies stronger binding of oxygen on the oxidic layer than on the oxide surface. This feature of the oxidic layer could be the reason for lower defect concentrations in the thin oxidic layer (when compared to the further oxidized MoO$_3$[010] surfaces) in previous experiments.

When the second MoO$_3$ building unit is stacked in the diagonal direction (as in the $sh2l$ structure), the 4d states of the Mo atom in the first layer (Mo$_{L1}$) exhibit significant differences compared to that of the 1L structure (see Fig. 8[a]), i.e., the 4d states of Mo$_{L1}$ are occupied near the Fermi level. Like the oxygen atoms (O$_{L1e}$) in the first layer, the 2p states of second layer oxygen atoms (O$_{L2a}$ and O$_{L2c}$) are strongly hybridized with Au 5d states. The PDOS of the 2L structure in Fig. 8(c) shows that the O 2p states and Mo 4d states are up-shifted by about 2.0 eV, which may lead to an increase in chemical reactivity when molecular species interact with surface oxygen atoms.

In summary, the electronic structures of Mo$_{L1}$ and Mo$_{L2}$ atoms are significantly influenced by the Au substrate, which gives rise to different electronic properties compared to the MoO$_3$[010] surface.

Effective Bader charge analysis

Thin MoO$_3$ layers on an Au substrate have been previously investigated using ultraviolet photoelectron spectroscopy (UPS). Greiner et al. observed a reduction in the oxidation state of Mo atoms, i.e. from Mo$^{6+}$ to Mo$^{5+}$, occurs without the presence of oxygen vacancies when thin MoO$_3$ films were formed on an Au substrate (of less than 2 nm). The mechanism of reduction of the Mo oxidation states was attributed to charge (or electron) transfer from the Fermi level of the Au substrate to the MoO$_3$ layers. The authors concluded that lowering the oxidation state of Mo can be capitalized to tune the work function of this oxide system from about 6 to 7 eV in the presence of an Au substrate.

To verify the origin of the charge transfer mechanism between the oxidic layers and the Au substrate, we have calcul-
lated the effective Bader charges ($q_{\text{eff}}$) as defined by the difference between the number of considered valence electrons and the DFT-computed Bader charges for the oxidic layers, bulk α-MoO$_3$ and pristine Au(111). The resulting values are listed in Table 1.

The computed $q_{\text{eff}}$ values of Mo atoms in the oxidic layer and bulk α-MoO$_3$ indicate changes in the oxidation states of Mo occur via charge transfer from the Au substrate. The $q_{\text{eff}}$ values of Mo atoms in the oxidic layer, maintaining the chemical stoichiometry of MoO$_3$ (for 1L, 2L, and inv2L) range from +2.55 to +2.64e, however Mo atoms of the bulk oxide possess a $q_{\text{eff}}$ of +2.68e. The origin of the transferred charges to the Mo atoms is from the Au substrate because the $q_{\text{eff}}$ of Au atoms in the Au substrate becomes positive (+0.02) when compared to the negative values (−0.02) for pristine Au(111). This implies that electron depletion occurs at the Au substrate when the oxidic layer interacts with the Au substrate, and these excess electrons are accumulated on the Mo atoms of the oxidic layers. This charge transfer mainly occurs between the Au and Mo atoms since the $q_{\text{eff}}$ of oxygens atoms in the oxidic layers are almost identical to that of oxygen atoms in bulk α-MoO$_3$.

The second layer of Mo atoms also display some degree of charge accumulation due to the Au substrate, showing the reduction of oxidation states as compared with that of the bulk. However, for the case of the O deficient oxidic layer (in sh2L), the charge transfer (or charge redistribution) mechanism is considerably different. First, the reduction of the oxidation states of Mo (from +2.68 to +2.26e) is more significant than the considered stoichiometric models. Also, the degree of the charge accumulation to O atoms (−0.94e) is more enhanced in comparison with that of the others (−0.88e). Unlike, the Au substrate in sh2L undergoes a charge accumu-

![Fig. 8 Projected density-of-states (PDOS) for various oxidic layers of Mo: (a) 1L, (b) sh2L (c) 2L and (d) inv2L. For each of the surface structures, oxygen 2p states of the outermost Mo oxidic layer (O$_a$ and O$_e$) and Mo 4d states of the first and second layers are plotted. The Fermi energy is denoted by the vertical dashed line at 0 eV. The corresponding surface atomic structures, with polyhedron, are illustrated in (e) with gray and red circles indicating Mo and O atoms, respectively.](image-url)
loration with respect to clean Au(111), which is clearly shown by the $q_{\text{eff}}$ of Au atoms ($-0.06e$).

The reason for the more distinguished charge accumulation to Mo, O, and Au atoms is because of the under saturated bonding character of one of the equatorial O atoms ($O_{1,2e1}$ which is also the axial O atom bonded to the Mo atoms in the first layer, cf. Fig. 1(b)). The $O_{1,2e1}$ atom maintains different coordination number (CN = 3) with Mo atoms in contrast to the O atoms of stoichiometric models (CN = 2), resulting in a reduction in chemical stoichiometry (MoO$_{2.5}$). This feature can be explained by the total Bader charge of O atoms in the formula unit ($-2.36e$) of $sh2L$ which is less negatively charged in comparison with other oxidic layers ($\sim-2.63e$ on the average).

Finally, due to the reduced chemical stoichiometry of Mo–O, it demonstrates that the total charge depletion in the oxygen atoms can account for the charge accumulation in the Mo atoms and the Au(111) substrate, resulting in the change of the oxidation state of the Mo atoms.

**Work function analysis.** The $\alpha$-MoO$_3$(010) surface has a large electron affinity (6.2 eV) and a high work function, ranging from 6.20 to 6.90 eV due to the large dipole created by the vdW interaction region between MoO$_3$ bilayers. These properties of the MoO$_3$ system make it very useful as a hole-injection or hole-transport layer in organic optoelectronic devices. Also, it was reported that controlling the thickness of ultrathin MoO$_2$ layers on metal substrates (e.g. on Au, Ni, V, and Cu) to a few angstroms in height can be used to lower the work function of the heterostructure, via altering the oxidation state of the Mo atoms.

We have investigated the work function ($\Phi$) and surface dipole moment ($\mu$) which is defined as a function of oxygen surface coverage ($\theta_O$) of ultrathin Mo oxidic layers on the Au substrate, stoichiometric MoO$_3$(010), and pristine Au(111) as listed in Table 2. Here, the work function is determined as the energy difference between the Fermi and vacuum levels. For the case of the stoichiometric MoO$_3$(010) surface, the difference between the valence band maximum and the vacuum level is taken instead (i.e. the ionization potential (IP)).

The computed IP for the stoichiometric $\alpha$-MoO$_3$(010) surface is 8.83 eV which is considerably larger than that of experimental measurements (6.20 to 6.90 eV). A possible reason for this discrepancy could be attributed to the choice of our surface structural model (i.e. an ideal defect-free surface). Experimentally, oxygen-deficient MoO$_2$(010) surfaces are commonly observed, and in a previous theoretical study, the IP of MoO$_3$(010) with oxygen (O$_{\text{corner}}$) vacancies, was indeed found to be of a lower value (6.25 eV). In comparing our calculated IP value to that reported in a previous theoretical study of stoichiometric $\alpha$-MoO$_3$(010) (9.66 eV), it is in reasonable agreement considering different functionals were employed (i.e. the semi-local optB88 xc functional in this work and the hybrid HSE06 xc functional in ref. 69).

Turning now to the surface work function of Mo oxidic layers on Au(111), our surface structures show reduced values ranging from 5.51 to 8.38 eV, as compared to stoichiometric MoO$_3$(010). However, these oxidic layers have increased work function values compared to that of the clean Au(111) substrate (5.43 eV). The $sh2L$ surface has a lower work function than that of the 1L structure as a consequence of possessing lower oxidation states of Mo (cf. see Table 2). More interestingly, the work function of the 2L structure (8.38 eV) is significantly higher than that of the other surface structures considered, which is attributed to the large surface dipole created by stacked MoO$_3$ pyramidal-like units (as referenced to the type-three polar surfaces in the classification by Tasker). The $inv2L$ structure shows the lowest work function (5.51 eV), since the surface termination of $inv2L$ is composed of Mo and O atoms, thus reducing the polarity of the surface. These trends are captured by the calculated surface dipole values listed in Table 2.

Our observations demonstrate clear evidence that the surface work functions are governed by the oxidation state of Mo atoms and the local atomic configuration which affects the surface electrostatic potential. Finally, our results show that the different structural connectivities (or polymorphic expressions of the oxidic layer) can significantly alter the surface electronic properties, which affords the tunability of the surface work function, even though the relative stabilities are similar.

**Summary**

To determine the stable structural configuration of Mo oxidic layers on Au(111), we performed DFT calculations within the framework of $ab$ initio thermodynamic considerations. Our results present the $inv2L$ (or 2L) surface models as the experimentally observed oxidic structure with the underlying metal substrate from first-principles theoretical microscopic and spectroscopic calculations. Regarding the surface electronic structure, a unique charge transfer mechanism between the oxidic layer and the metal substrate is proposed, which alters the charge state of Mo atoms. Finally, it is proposed that the polymorphic connectivity of oxidic layers on the Au(111) can be used to tune the functionality of the system such as altering its work function. These findings provide a guide to the formation and associated surface properties of ultrathin Mo oxidic layers for various electronic applications, and will stimulate further investigations and structural discovery of new Mo oxidic polymorphic phases.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\Phi$ (eV)</th>
<th>$\Delta \Phi$ (eV)</th>
<th>$\mu^{SD}$ (Debye)</th>
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<tbody>
<tr>
<td>$\alpha$-MoO$_3$(010)</td>
<td>8.83</td>
<td>1.42</td>
<td>0.19</td>
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<tr>
<td>Au(111)</td>
<td>5.43</td>
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<td></td>
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<tr>
<td>1L</td>
<td>6.85</td>
<td>1.18</td>
<td>0.08</td>
</tr>
<tr>
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<td>6.61</td>
<td>2.95</td>
<td>0.23</td>
</tr>
<tr>
<td>2L</td>
<td>8.38</td>
<td>1.98</td>
<td>0.01</td>
</tr>
<tr>
<td>$inv2L$</td>
<td>5.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Supporting Information:

Polymorphic Expressions of Ultrathin Oxidic Layers of Mo on Au(111)

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Methodology

Computational setup for the slab model calculation

We use a supercell slab approach for the O/Mo/Au(111) system, consisting of a total of 7 to 10 atomic layers with a vacuum region of 15 Å. The Mo oxidic layers are constructed on one side of a 4 atomic layered Au(111) substrate. For atomic geometry relaxation, the bottom 2 layers of Au(111) are kept at their bulk positions and a dipole correction is applied. The Brillouin zone integrations are performed using a Γ-centered 12×12×1 grid for p(1×1) Au(111) substrate and equivalent k-point grids for the larger surface supercells. The valence configuration for the Mo, Au, and O PAW potentials are 4s^24p^64d^55s^1, 5d^{10}6s^1, and 2s^22p^4, respectively.

We note that the convergences of the Bader charges, surface work function, and the $E_{SCLS}$ have been tested by increasing the number of grid points for the charge density integration, by varying vacuum region from 15 Å to 20 Å, and also by changing the size of the surface supercells (up to a maximum to 288 atoms in the supercell). The convergence criteria for the Bader charges, surface work function, and the $E_{SCLS}$ is set to 0.005 e, 5 meV and 0.1 eV, respectively.

Ab initio atomistic thermodynamics

The average adsorption energy of oxygen atom (as taken with respect to the O₂ molecule), $E^{\text{ad}}$ of the Mo oxidic layer on Au(111) is defined as,

$$E^{\text{ad}} = \frac{1}{N_O} \left( E_{O/Mo/Au} - E_{Au(111)} - N_{Mo} E_{Mo} - \frac{N_O}{2} E_{O_2} \right),$$

(1)

where $E_{O/Mo/Au}$ and $E_{Au(111)}$ are the DFT-calculated total energies for O/Mo/Au(111) and pristine Au(111), respectively. $N_{Mo}$ and $N_O$ are taken as the number of Mo and O atoms in O/Mo/Au(111), while $E_{Mo}$ and $E_{O_2}$ are then the DFT-calculated total energies of a Mo
atom in bulk Mo and the oxygen molecule, respectively. Here, $E_{O_2}$ is corrected using the experimental binding energy of the $O_2$ molecule\(^1\) to overcome the large errors as reported for GGA calculations of $O_2$ binding energies.\(^2\)

To evaluate the thermodynamic stability of Mo oxidic layers on Au(111) under a reactive oxygen gas environment, the revised \textit{ab initio} atomistic thermodynamic approach for a mildly-doped metal surface\(^3,4\) is employed. The Gibbs free energy of adsorption ($\Delta G^{\text{ad}}$) is defined as,

$$\Delta G^{\text{ad}}(T,p) = \frac{1}{A} \left( G_{O/Mo/Au} - G_{Au(111)} - \Delta N_{Au} \mu_{Au} - N_{Mo} \mu_{Mo} - N_{O} \mu_{O} \right), \quad (S2)$$

where $G_{O/Mo/Au}$ and $G_{Au(111)}$ are the Gibbs free energies of O/Mo/Au(111) and pristine Au(111) with a surface area of $A$, respectively. $\mu_{Au}$, $\mu_{O}$, and $\mu_{Mo}$ are the chemical potentials of the Au, O, and Mo atoms, correspondingly. $\mu_{Au}$ is taken as the total energy of bulk Au ($E_{\text{Au}}^{\text{bulk}}$), since the number of Au atoms in the simulated system is assumed to be infinite in the equilibrium state with bulk Au. $\mu_{O}$ is computed with reference to half of the total energy of the $O_2$ molecule. $\Delta N_{Au}$ is taken as the change in the number of Au atomic species to form oxidic layers. $N_{O}$ and $N_{Mo}$ are then the number of O and Mo atoms in the oxidic layers, respectively.

In this spirit, various Mo/Au surface structures are considered to compute $\Delta \mu_{Mo}$ with reference to the total energy of the Mo atom as,

$$\Delta \mu_{Mo} = \frac{1}{N_x} \left( G_{Mo_x Au_y} - N_{y} \mu_{Au} - N_{x} E_{\text{atom}}^{\text{Mo}} \right), \quad (S3)$$

where $N_x$ and $N_y$ are the number of atoms of Mo and Au in the Mo$_x$Au$_y$ nanocomposite system, respectively. Since the amount of Au is infinite to reach the equilibrium of the bulk phase, the assumption of $\mu_{Au}$ taken as the total energy of bulk Au ($E_{\text{Au}}^{\text{bulk}}$) is well-grounded.

Finally, to understand how metastable and/or kinetically-hindered oxidic surface structures may play a role in populating the actual substrate under growth conditions, the surface
population, \( P(n, p, T) \) of these O/Mo/Au(111) structures is computed following a Boltzmann distribution-type behaviour:

\[
P(n, p, T) = \frac{\exp\left(-\frac{G_n(T,p)}{k_B T}\right)}{\sum_{n=1}^{N} \exp\left(-\frac{G_n(p,T)}{k_B T}\right)},
\]

(S4)

where \( G_n(p, T) \) is the Gibbs free energy of adsorption for each surface structure, \( n \), and it can be interpreted as a function of partial pressure \( (p) \) and temperature \( (T) \) of the \( O_2 \) molecule, and \( k_B \) is the Boltzmann constant. We refer readers to our previous publications for details on this approach.\(^{2,3}\)

**Theoretical framework to plot \( E_B \) spectra**

To make a comparison with experimental XPS spectra, we calculate the theoretical \( E_B \) spectra within the DFT framework following the procedure (as illustrated in Figure S1 below):

1. For each surface structure (1L, \( sh2L \), 2L, and \( inv2L \)), the unique oxygen atoms \( (O_i) \) which possess different chemical bonding characters, are chosen for the core-level binding energy \( (E_{CL}) \) calculations.

2. Using a Gaussian function centered on each \( O_i \) core-level binding energy, the \( E_{CL} \) curve is generated with a full width at half maximum (FWHM) of 1.00 eV to simulate the experimental XPS spectrum.

3. The relative intensity of the Gaussian function for each \( O_i \) is then set proportional to the relative surface oxygen density within the considered surface structure.

4. Lastly, to obtain the \( E_{CL} \) spectrum for the surface structure, the Gaussian function for \( O_i \) is then superimposed for a given surface structure.
Figure S1: Procedure to plot $E_B$ spectra

$$f(E_{CL}^O) \propto \rho_{O_i}$$

$$f(E_{Surface}^B) = \sum f(E_{CL}^O)$$
Figure S2: The various structural motifs of Mo oxidic layer on c(4 × 2) Au support. (a) 1L, (b) sh2L, (c) 2L, (d) inv2L. The dark gray, light gray, red, pink, and white spheres represent Mo atoms of the first and second layers, O atoms bonded to the Mo atoms in the first and second layers, and Au atoms, respectively. The surface unit cell is denoted as yellow solid line. The ‘L’, ‘a’, ‘e’ stand for the layer, axial and equatorial oxygen, e.g., O_{L2a} is the axial oxygen of second layer.
Figure S3: (a) Projected density-of-states (PDOS) for bulk $\alpha$-MoO$_3$ of Mo 4$d$ and O 2$p$ states and (b) its atomic structures. The structural models are denoted with dark gray and red circles for Mo and O atoms including MoO$_6$ octahedron as light gray. The Fermi energy is denoted by the vertical dashed line at 0 eV.
Figure S4: Simulated constant-current STM images of the inv2L structure for various bias voltages (+0.5, +1.5, +2.0, and +2.5 from left to right) using two types of tip model: (a) using a blunt W(110) tip with W adatom on its surface, and (b)-(c) using a blunt W(110) tip functionalized with O atom on the W adatom, at relatively high current (b) and low current (c). We refer the readers to Reference 5 for the details of the simulation.
# Tables

Table S1: The real height profiles of various Mo oxidic layers of optimized structural models in this work and the apparent heights obtained in STM experiments in the cited references.

<table>
<thead>
<tr>
<th>Structure</th>
<th>From support to top oxide layer (Å)</th>
<th>From bottom oxide layer to top oxide layer (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L</td>
<td>4.68</td>
<td>2.23</td>
</tr>
<tr>
<td>1L+V\textsubscript{O}</td>
<td>4.76</td>
<td>2.23</td>
</tr>
<tr>
<td>1L+2V\textsubscript{O}</td>
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<td>0.27</td>
</tr>
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<td>sh1.5L</td>
<td>6.29</td>
<td>3.98</td>
</tr>
<tr>
<td>sh1.5L+V\textsubscript{O}</td>
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<td>2.40</td>
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<td>7.04</td>
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<tr>
<td>2L</td>
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</tr>
<tr>
<td>inv2L</td>
<td>7.68</td>
<td>5.21</td>
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Reference 6 5.0
References 7,8 5.0 – 7.0
Reference 9 0.5, 7.0 – 13.0
Table S2: The surface coverage of Mo ($\Theta_{\text{Mo}}$) and O ($\Theta_{\text{O}}$) as defined as ratio of the numbers of Mo and O atoms to the number of Au atom and the ratio of O to Mo ($N_{\text{O}}/N_{\text{Mo}}$) of oxidic layers.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\Theta_{\text{Mo}}$ (ML)</th>
<th>$\Theta_{\text{O}}$ (ML)</th>
<th>$N_{\text{O}}/N_{\text{Mo}}$</th>
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<tr>
<td>1L</td>
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<td>1.50</td>
<td>2.00</td>
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Table S3: The computed surface core-level shift ($E_{\text{SCLS}}$, unit in eV) and theoretical binding energy ($E_{\text{B}}$, unit in eV) values using O 1 s state for various oxygen atoms for oxidic layer of Mo. Each $E_{\text{SCLS}}$ and $E_{\text{B}}$ values are calculated with respect to (w.r.t.) the different reference states. The references states of $E_{\text{SCLS}}$ w.r.t. $E_{\text{CL}}^{\alpha-\text{MoO}_3}$, $E_{\text{SCLS}}$ w.r.t. $E_{\text{CL}}^{\text{O}_1\text{L}}$, and $E_{\text{B}}$ w.r.t. $E_{\text{B}}^{\text{O}_1\text{L}}$ are averaged $E_{\text{CL}}$ values of O 1 s state in the bulk $\alpha$-MoO$_3$ (in Figure S3(b)), namely, $O_{\text{corner}}$, $O_{\text{vdW}}$, and $O_{\text{edge}}$, computed O 1 s state of $E_{\text{CL}}$ value of 2L surface structure, and the experimental binding energy of 1L surface structure.\(^9\) We note that for convenience, the labels used for the oxygen species as shown in Figure 6 of the main manuscript are tabulated in the very first column.

<table>
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<th>#</th>
<th>Structure</th>
<th>Species</th>
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References


