Supporting Information: Theoretical methods.

As outlined in the introduction, a number of periodic DFT studies have recently provided detailed information on the structures and electronic properties of unpromoted and promoted MoS$_2$ (100) surfaces [1-8]. All of them were carried out using similar theoretical methodologies but led sometimes to quite different results, which evidently has to be related to differences in the parameters affecting energy convergence or in the size of the supercell used to model the surface. In order to get more insight in these differences, we have systematically studied the influence of key parameters affecting the accuracy and computational demand of these calculations. We briefly discuss this issue in this section.

Comparative study: test calculations on MoS$_2$ surfaces. For our calculations, we have used the Vienna Ab-initio Simulation Program (VASP) [9] based on the Density Functional Theory. Exchange-correlation was treated using the functional of Perdew and Zunger[10] and corrected of non-local effects using the generalized gradient approximation (GGA) of Perdew et al. [11]. The wave functions were expanded in plane waves and the ionic cores were modeled by Ultra-Soft Pseudo-Potentials (US-PP) [12]. The solution of the Kohn-Sham equations was improved self-consistently until a difference lower than $10^{-4}$ eV was obtained between successive iterations. The fastest convergences were obtained using an initial linear mixing of the density followed by a Pulay mixing [13] keeping up to twenty of the last charge dielectric functions. All the ions were fully relaxed using a conjugate gradient algorithm until all exact Hellman-Feynman forces acting on ions are smaller than $2 \times 10^{-2}$ eV Å$^{-1}$.

Most of the previous settings are either similar to the ones used in the previous studies [1-8] or do not strongly influence the relative convergence of energies and surface geometries. We come now to the main differences. In order to make the comparison easier, we have reported in Table 1 the calculation settings used by each group.
A crucial point of these calculations is the unit cell (or supercell) that is used to represent the actual surface one intends to study. Figure 1 of the article shows a supercell that contains two MoS$_2$ layers along the x direction (stacking), three Mo rows along the y direction and three rows along the z direction. In this axis system, the (100) MoS$_2$ active surface is represented by the upper layers parallel to the xy plane and it exhibits alternative rows of exposed molybdenum atoms and sulfur atoms which are commonly called molybdenum edges (or Mo edges) and sulfur edges (or S edges). Since the supercell is repeated periodically in the three directions of space, one has to ascertain that the cell is sufficiently large to avoid unwanted interactions between neighboring cells. In respect of the x direction, two MoS$_2$ sheets are required to correctly represent the actual AB stacking of bulk MoS$_2$. Except if one intends to study the adsorption of very large molecules, this is enough to model (100) surfaces since the distance between two subsequent molybdenum (sulfur) edges is ca. 9.4 Å between S atoms. Inspection of Table 1 shows that most of all recent studies have indeed used this setting, except Byskov et al. who used only one MoS$_2$ sheet repeated periodically with a vacuum layer of ca. 9 Å between S atoms. Within this model, the interactions between A and B MoS$_2$ sheets are neglected. Along the y direction, most of previous studies have used a cell containing 3 Mo atoms and have shown that this avoids unwanted interactions in the case of thiophene [3], benzothiophene [6] and 4-methylbenzothiophene [6].

An important point, which has raised some debate, is the way the z direction is modeled. First, artificial interactions between the (100) ‘active surface’ and the ‘bottom’ layer of bulk are easily avoidable by the use of vacuum layers sufficiently large: using layers of 7 Å and 13 Å in the z direction, we found energy differences lower than 0.01 eV. The crucial point is the number of Mo rows that is used to model both surface and ‘bulk’ MoS$_2$. Thus, Byskov et al. have used two fully relaxed rows in total, so that all Mo atoms of the system belong to a surface, either the ‘active’ one or the ‘bottom’ one. On the other hand,
other groups, after Raybaud et al. have used two fully relaxed rows to represent the 'surface' and two rows frozen at the computed MoS$_2$ bulk geometry for the 'bulk' part of the model. These four layer models have led to huge differences in the computed S binding energy as well as on the resulting surface structures[3]. Evidently, latter models have to be considered superior but are much more computational demanding. For these reasons, we have considered an intermediate possibility in which 'surface' and 'bulk' parts are modeled as a whole by three fully relaxed Mo rows: it is hoped that the truncation of the last frozen row of the four-layer model would be somehow compensated by full relaxation of the structure. Clearly, in such a model, no frontier distinguishes 'surface' from 'bulk' but these notions are admittedly vague when one deals with nanosized particles like those we intend to model in the present study. In order to validate this model, we have carried out calculations of the (100) molybdenum and sulfur edges at various surface coverages for three and four fully relaxed Mo layers in the z direction. In order to limit the total computation time, we have modified the as-cleaved (100) surface presented on Fig. 1 by transferring exposed sulfur atoms from the sulfur edge to the molybdenum edge. Following Cristol et al. [6-8], we will denote the surfaces obtained by this way by a pair of integers [nm] where n corresponds to the number of sulfur atoms of the S edge and m to the number of sulfur atoms of the Mo edge (in this series of calculations, n+m = 6). The relative energies of these surfaces, the as-cleaved [6-0] surface taken as reference, are reported in Table 2 and compared, whenever it is possible, with the data reported by Raybaud et al. [4] and Cristol et al.[7]. Before going further on, it is important to note that our calculations were carried out with a cut-off energy of 250 eV to be compared with the cutoff energies of 200 eV used by Raybaud et al. [4] and 210 eV used by Cristol et al. [6]. Calculations carried out to check the convergence of the relative energies with respect to the basis set did not show differences higher than 0.1 eV for cutoff energies of 200 and 250 eV. Secondly, we have to take into account that in the former studies, the sulfur
edge and molybdenum edge surfaces were modified independently, the energy of a [nm]
surface being estimated from the energies of the [n-0] and [6-m] surfaces. Therefore,
comparison with our results should take into account the possible interactions between
different Mo and S edges.

Table 2 clearly shows that all the models lead to the similar trends for the relative energies of
the six surfaces. The most important differences (ca. 0.4 eV) are observed for the [42] and
[3-3] surfaces optimized with symmetry constraints – mirrors in the Mo planes – that are
irrelevant for our present study. As for the other surfaces, no striking differences in relative
energies are observed: the most important differences are ca.0.2 eV for the fully relaxed [33]
surface, but do not change whether three or four layers are used. From this, we conclude that
three Mo layers in the z direction are sufficient considering the precision of these calculations.
On the other hand, although modifying both MoS₂ slabs together does not significantly
change the relative energies of the resulting surfaces within 0.2 eV, it should be noted that
slight differences might appear in some bondlengths within both edges, in the order of few
picometers.

Finally, other calculation parameters may have a strong influence on the convergence of the
relative energies. The sampling of kpoints at which the wavefunctions are computed is of
particular importance. As shown in Table 1, most of the previous studies have used the
Γ point only, in the center of the Brillouin zone. To check a possible effect of adding
supplementary k-points in the calculation, we have computed the relative energies of some of
the previous surfaces with different kpoint samplings (Table 2). In this table, the sampling is
denoted by three integers, ixjxk, corresponding respectively to the number of kpoints used
in the x, y and z directions of the direct lattice. The case of the [4-2] surface with symmetry
constraints is particularly informative. Increasing the number of k-points in the y direction
leads to differences in the relative energy of this surface as high as 0.7 eV for two k-points
whereas adding a third k-point in this direction or one k-point in the x direction do not significantly change the relative energies, at least within 0.2 eV. It should be noted, moreover, that such differences are not systematic, since in the case of the fully relaxed [33] surface, the differences in relative energies are in the order of 0.3 eV, all other settings taken equal. From this, we conclude that using a single k-point (Γ) may be insufficient for some surfaces. In order to model accurately such surfaces, one should either use two k-points in the y direction or extend the supercell by using more than three Mo atoms in this direction.
Table 1: Comparison of calculation parameters

<table>
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<tr>
<th></th>
<th>This study</th>
<th>Cristol et al⁶⁻⁸</th>
<th>Raybaud et al⁹⁻⁴</th>
<th>Byskov et al¹⁻²</th>
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<td>3</td>
<td>3</td>
<td>2</td>
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<tr>
<td>(110) rows</td>
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<td>4</td>
<td>2</td>
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<td>~ 7</td>
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<td>Cutoff Energy (eV)</td>
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Table 2. Relative energies of modified MoS₂ (100) surfaces (eV).

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³ geometry optimization with mirror symmetry in the Mo planes.
References


(c) http://cms.mpi.univie.ac.at/vasp/


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