Closed-Loop Defect States in 2D Materials with Honeycomb Lattice Structure: Molybdenum Disulfide

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Platelets and ribbons of monolayer molybdenum disulfide (MoS$_2$) exhibit characteristic electronic states along the edges, which tend to decouple from the extended states in the interior of the 2D extended structure. Under sulfur excess specifically triangular platelets are formed, which exhibit 1D extended electronic states with a pronounced catalytic activity along the edges. The present density-functional-based investigation shows that very similar electronic states occur also along the edges of holes inside an otherwise perfect, extended MoS$_2$ monolayer. For triangular defects, the edge states can delocalize around the hole. Density functional molecular dynamics simulations on 150 different nanoscale defect geometries and termination variants prove the high structural stability of hole defects in MoS$_2$ against further reconstructions and a thermodynamic propensity to participate in sulfur exchange reactions.

1. Introduction

1D confined electronic states along the edges of 2D materials have been observed both in electronic structure calculations\cite{1,2} and experimentally by scanning probe techniques such as scanning tunneling microscopy and spectroscopy\cite{3,4} or tip-enhanced Raman mapping.\cite{5} Like its 2D counterpart, the surface of bulk solids, the edge termination of 2D materials differs from the extended material in its local composition and the atom arrangement. This, in turn, leads to the formation of termination-specific electronic states, which are confined to the atoms along the edge and in its close vicinity. They may split off the electronic states of the extended 2D layer and possess distinctly different physical and chemical properties, for instance, even exhibit chiral features.\cite{6,7} For holes, which are inner boundaries in 2D materials, such states have been addressed less frequently, but results from high-resolution transmission electron microscopy,\cite{8} electron holography,\cite{9} and model calculations with the density-functional theory\cite{10} indicate their presence.

For elemental 2D materials such as graphene, local bonding changes along the edge and well-defined reconstructions of the honeycomb lattice occur, which may open a bandgap in armchair-terminated structures\cite{11,12} and lead to chiral and spin-split states along the zigzag edges.\cite{13,14} Along armchair edges temperature-dependent reconstructions occur and may lead to alternating five- and seven-membered rings of Stone-Wales type,\cite{15} which are electronically localized\cite{16} or to more extended reconstructions with metallic superlattice modes.\cite{17} For binary 2D compounds, the composition along the edges is another key property, which influences the electronic edge states. Electron holography and electronic structure calculations give evidence that large bandgap materials such as hexagonal boron nitride (h-BN) form mostly stoichiometric, straight, and unreconstructed edges without distinct electronic states along the edges.\cite{18,19,20} Ribbons and platelets of 2D transition metal dichalcogenides (TMDCs), on the contrary, form 1D extended electronic states\cite{21,22} and may even show Luttinger-liquid characteristics\cite{23,24} along sulfur-rich zigzag edges, whereas states at metal-rich edges may spread further into the 2D bulk\cite{25} and be spin polarized.\cite{26} In addition to the high potential of TMDCs for (opto)electronic applications (cf. recent reviews\cite{27}) they also exhibit significant catalytic activity and high turn-over numbers in sulfur-transfer or water-splitting reactions.\cite{28,29} As the rim is the growth front of the ribbon or platelet, the different terminations and also composition variations are accessible in a controlled manner by the growth conditions.\cite{30,31}

More recently, also vacancy clusters and holes in the interior of TMDCs have been established as sites, which are catalytically very active\cite{32,33} and may be used to tune the optoelectronic\cite{34} and thermoelectric properties.\cite{35} Those defects, however, also act as localized scattering centers and potentially deteriorate, e.g., the electronic transport properties.\cite{36,37,38} Such structural defects in...
2D materials are typically induced by the irradiation of extended 2D layers with electrons or ions, but with little control over the shapes and the precise atomistic structure and bonding properties along the circumference of the hole. In particular, the high kinetic and potential energies involved in ion-beam irradiation open up pathways for both electronic and nuclear knock-on damage, which lead to several damage scenarios simultaneously.

In contrast, in situ experiments in the high-resolution transmission electron microscopy revealed that the size of irradiation-induced holes in 2D materials can be influenced by the properties of the electron beam, whereas the shape is material- and thickness-dependent. Comparative numerical studies by time-dependent density-functional theory (DFT) and Ehrenfest dynamics elucidated that defects can occur already below the energy threshold required for purely knock-on damage, because charging by the electron beam assists the vacancy formation process. Monolayers of the insulating h-BN tend to form ideally triangular holes, holes in perfectly stacked h-BN bilayers are hexagonal, and circular holes with irregular coordinations along the edge are only found for holes in rotated h-BN bilayers. Graphene is the other extreme case, in which already the conductive monolayer forms irregularly shaped holes which may be annealed in the electron beam. For semi-conducting TMDCs such as MoS2, which has a larger variability of the local composition and formal oxidation states at the metal centers, various catalytically active defects have been summarized, among them sulfur vacancies within the 2D plane and larger, both regular triangular and irregularly shaped holes. Upon annealing in a suitably reducing environment, plasma-treated MoS2 sheets turn into 2D networks of triangular holes similar to the ones studied theoretically and investigated further here. For MoS2 DFT calculations indicate that localized electronic states are formed at point defects such as sulfur or molybdenum vacancies, but 1D extended states may be formed along the edges of ribbons, platelets, and triangular holes.

This study focuses on the evolution of 1D extended electronic states along the edges of holes in the MoS2 monolayer as a prototypical TMDC, their interplay with extended 2D and localized defects and the relative thermodinamic stability. Section 2 briefly describes the model systems used in the study: sulfur-terminated triangular platelets with the composition MoS2, sulfur-poor and sulfur-rich terminations of triangular holes in the extended MoS2 layer and a more general pore with hexagonal shape, that combines both termination types. Section 3 first analyzes the size-dependence of the stability and the electronic properties of those nanostructures. It further elaborates the differences between edge states at outer and inner triangular boundaries of MoS2 in dependence on the termination and the composition. Finally, it extends these observations to the mixed termination situation in a hexagonal hole. This work concludes with implications for the catalytic activity, other chalcogenide material systems, and more generally for 2D materials with a honeycomb lattice.

2. Model Systems

In the first step, two complementary sets of test structures were investigated and compared: Nonperiodic triangular platelets and triangular holes in an otherwise perfectly periodic MoS2 sheet. For both test series, the size and termination of the structures were systematically varied, and the thermodynamic stability and the evolution of the electronic properties were evaluated as a function of increasing system sizes.

In the upper part, Figure 1 shows representative structures for triangular platelets with \( n = 4 \) Mo atoms long the edges. The structure in Figure 1a is \( \text{Mo}_{10}\text{S}_{30} \) and represents platelets of the stoichiometry \( \text{Mo}_n\text{S}_{(n-2)(n+1)} \) with \( N = n(n+1)/2 \), which corresponds to the termination with a sulfur surplus of \( 2n+2 \) atoms, corresponding to a low sulfur excess of \( 2/n \) per formula unit. Figure 1b shows \( \text{Mo}_{28}\text{S}_{66} \), a member of the more sulfur-rich platelet family with the composition \( \text{Mo}_{n}\text{S}_{n(n+5)/2} \). Here, the sulfur surplus amounts to \( 4n \) atoms per platelet, which leads to a larger sulfur excess of \( 4/(n+1) \).

The complementary triangular holes are obtained by cutting platelets with an edge length \( n \) from the pristine MoS2 monolayer as visualized in the lower part of Figure 1. Figure 1c shows the situation with the low sulfur surplus of \( 2n \) atoms per hole, Figure 1d shows the case with the higher sulfur surplus of \( 4n-2 \) sulfur atoms per hole. As the holes are formed in a formally infinitely extended MoS2 monolayer, the value of the sulfur excess depends also on the amount of perfectly stoichiometric MoS2 between adjacent holes. For the reference structures, symmetric simulation cells with \( m \times m = m^2 \) MoS2 unit cells are chosen. When a trigonal platelet with edge length \( n \) is cut out, a stoichiometric supercell contains \( M = m^2 - N \) formula units of MoS2, and is denoted by the indices \( (m,n) \) in the following. For \( m > n \), a continuous layer of evenly spaced, separate holes is created, which has a sulfur excess of \( 2n/M \) and \( (4n-2)/M \) for the low and high sulfur excess cases. For the depicted hole size, \( n = 4 \), the maximum values of the sulfur excess are obtained for \( m = 5 \). For that specific case, the periodically repeated motifs have the compositions \( \text{Mo}_{10}\text{S}_{18} \) and \( \text{Mo}_{15}\text{S}_{44} \) for the terminations with low and high sulfur contents, and the values of the highest possible sulfur excess for that hole size amount to 4/15 and 7/15, respectively. Hence, with decreasing hole size and increasing distance between adjacent holes the overall composition converges toward the stoichiometric case for both termination types.
to the termination with the lower sulfur excess, and the right panels to the one with higher sulfur excess. The periodic bulk calculation (b) exhibits the reduced bandgap of 1.52 eV typical for modeling at the local density level used in this study\(^\text{[30]}\); it appears slightly reduced by a Gaussian broadening of 0.5 eV. For both termination types, the DOS curves of the very small clusters exhibit the pronounced confinement effects discussed in the study by Seifert et al.\(^\text{[19]}\) and differ significantly from the bulk curve.

For small platelets below \(n = 5\), both termination variants exhibit a distinct closed-shell electronic structure with considerable energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In this size range, the center of the HOMO–LUMO gap (indicated by dashed lines in Figure 3) is lower for the platelets with low sulfur excess (left panels) than for the ones with high excess (right panels). This finding correlates with the experimentally observed preference for the low-excess termination in the limit of very small platelet sizes.\(^\text{[27,31,51]}\) The crossover occurs in the range \(5 \leq n \leq 7\), for which both termination types coexist in experiments\(^\text{[20–27]}\) and may be structurally converted to hexagonal platelets with both termination types by cycling between the sulfur- and hydrogen-rich reaction conditions encountered also in catalysis.\(^\text{[52,53]}\) The recently observed full interconversion between both triangle shapes via the hexagon\(^\text{[53]}\) in the presence of hydrogen occurs only upon substitution of Mo by the more electron-rich Co atoms. Adding hypothetically an equal amount of negative charge to the binary structures of this study would shift the dashed line to energy values of about −2.5 eV. There, the HOMO–LUMO gaps are tiny. They are smeared out by the broadening in Figure 3 for larger platelets. The DOS curves of both terminations become electronically quite similar. This could be the electronic basis for the reversibility of the hydrogen-based structure interconversion of very small Co-promoted MoS\(_2\) catalyst platelets.\(^\text{[53,54]}\)

Beyond platelet edge lengths of eight unit cells in the low-sulfur and 13 unit cells in the high-sulfur excess cases the DOS curves in the valence and conduction band regions gradually evolve toward the features of the unperturbed MoS\(_2\) monolayer. However, in all clusters, the gap is filled by additional states, which are not present in the pristine bulk, and in all those platelets, the transition from the HOMO to LUMO levels occurs within a single peak in the DOS curves. Concomitant with earlier DFT results on the optical spectra\(^\text{[30]}\) and on scanning probe investigations\(^\text{[31]}\) of platelets with low sulfur excess, the additional peaks on the conduction-band side of the energy gap can be assigned to 1D delocalized states around the circumference of the platelet. For the platelets with the higher sulfur content, additional sulfur-based states occur on the valence-band side of the gap.

As a consequence, an energy gap starts evolving from the valence band side for the platelets with the lower sulfur content and from the conduction band side for the sulfur-rich termination, visible as a dip between the midgap levels in Figure 3. To enhance the activity of such midgap levels for catalyzing the hydrodesulfurization or the hydrogen evolution reaction would require the addition of electrons, e.g., by the well-established Co-doping scheme.\(^\text{[54–57]}\) Within the investigated platelet size range, the center of the HOMO–LUMO gap converges to about

### 3. Results and Discussion

#### 3.1. Edge States of Triangular TMDC Platelets and Holes

First, the evolution of the density of electronic states (DOS) is systematically analyzed for the triangular platelets as a function of the platelet size in Figure 3. As indicated, the left panels refer
from below for both terminations with increasing platelet size. Therefore, for all platelet sizes and terminations the frontier orbitals are considerably below the Fermi level of the unperturbed MoS2 monolayer at \( E_F \approx 2.75 \) and still \( 0.3 \) eV below its valence band maximum. Hence, already MoS2 platelets adsorbed on extended 2D MoS2 films are able to polarize the uppermost MoS2 layer(s) locally and facilitate the interaction with polar or polarizable molecular species during catalytic reactions even without the need to involve other substrates. Other activation mechanisms, e.g., by sulfur vacancies in otherwise unperturbed MoS2 areas\[48,58\] have been analyzed in detail\[38\] and are beyond the scope here.

In contrast to platelets and isolated point defects, only few theoretical studies have been devoted to holes in TMDC layers\[8,41,44,47\]. Our preliminary investigations for two selected hole geometries with different lateral spacing analyzed the local atom relaxations and the atom- and orbital-resolved electron density distribution with particular focus on the localization of edge states within the same computational setting as in this study\[8\]. A very small structural relaxation of 0.16 Å occurs for the atoms located in the corners of the holes; all other relaxations are 60% of this value or smaller and limited to the atoms in the next nearest vicinity of the edges and corners. For comparing the localization of different orbitals quantitatively a participation ratio was defined in the study by Niebur et al.\[8\]. It indicates the percentage of all atoms within the structure model that contribute to a specific orbital. The frontier orbitals of the perfect MoS2 sheet are delocalized and separated by the energy gap discussed earlier. Triangular holes have additional defect states within that energy gap, for which the preliminary studies suggest specific trends: (a) midgap states reside on the atoms located along the edges and in the corners, (b) states within few tenths of an eV of the valence and conduction band edges delocalize in the unperturbed bulk regions between the holes, and (c) the localization of midgap states on the atoms along the edge increases with increasing spatial distance between adjacent holes. As the localized midgap states are unoccupied, the partial charges on the single atoms do not differ significantly between defective and pristine areas of the MoS2 monolayer\[8\].

As experimental results indicate that the (electro-)catalytic properties of defective MoS2 depend on the size and density of the triangular holes, this study investigates the evolution of the densities of electronic states of triangular pores in MoS2 as a function of the hole size and the hole distance, which both affect the average density of potentially catalytic defects. The obtained results for the densities of electronic states as a function of the energy are shown in Figure 4 for holes with low sulfur excess along the edges and in Figure 5 for holes terminated with high sulfur excess.

As a general trend, the Fermi levels of the defective layers are below the Fermi level of pristine MoS2. For hole sizes \( n \leq 2 \), they converge toward the valence band maximum of the unperturbed MoS2 sheet in the limit of large distance between adjacent holes, when the major part of the system is built from unperturbed MoS2. For this reason, the properties of hole-containing MoS2 monolayers vary more smoothly with the defect sizes and defect.
densities than the quite pronounced changes discussed for the small platelet geometries with comparable edge length. This makes the window for tuning catalytic properties for nanoporous thin films with respect to pristine MoS$_2$ smaller than the one for platelets, but the hole-related defect states are closer to the Fermi level of bulk MoS$_2$ and thus more readily accessible without further activation. Only for the smallest holes with $n = 1$, the Fermi level of the defective layer crosses the valence band maximum of MoS$_2$.  

Figure 4. Densities of states calculated for triangular holes with low sulfur excess along the circumference of the hole with the DFTB + code. A systematic comparison of model systems with increasing supercell size $n+1 \leq m \leq 10$ and hole sizes $1 \leq n \leq 8$ is presented in comparison with the bulk curve. The dotted line indicates the Fermi level.

Figure 5. Densities of states calculated for triangular holes with high sulfur excess along the circumference of the hole with the DFTB + code. A systematic comparison of model systems with increasing supercell size $n+1 \leq m \leq 10$ and hole sizes $2 \leq n \leq 9$ is presented in comparison with the bulk curve. The dotted line indicates the Fermi level.
the pure MoS$_2$ monolayer from below once the distance between the holes is larger than four lateral unit cells, i.e., in the limit of low defect numbers and little interactions between adjacent defects.

In more detail, Figure 4 shows an overview of the DOS curves obtained for triangular holes terminated by the edges with a low sulfur excess. Each panel displays the evolution of the DOS curves for a specific hole size $n$ as a function of the supercell size $m$ and along with the DOS of the pristine bulk. For the smallest hole size, $(m, 1)$, one can observe a clear transition from the defect-dominated regime for values of $m \leq 3$ over defect states in the gap that still couple to the conduction band up to $m \leq 6$ and further to localized defect states around the hole, which are split off the band structure of the surrounding bulk from $m = 7$ on. These findings imply that this smallest possible defect state affects a rim with width of about two unit cells adjacent to the edge. Slightly larger holes with edge lengths $n \leq 3$ show very similar features. For larger triangular pores from $n = 4$ on, the same lateral extension of the edge state can be concluded from the evolution of the DOS curves. A pronounced difference occurs for larger supercell sizes beyond $m = 9$, which do no longer exhibit a series of localized defect states in the bulk band gap, but rather an extended feature at the lower conduction band edge. This trend is continued for hole sizes $n = 5$ and above, which do not exhibit localized defect states in any supercell size, but immediately develop the 1D extended defect state around the circumference of the hole.

Figure 5 shows the analogous analysis for the triangular holes terminated with the higher sulfur excess. For steric reasons, the smallest possible hole size is $n = 2$, thus the series starts with the $(m, 2)$ pore structures. For that smallest pore, very similar transitions from the completely defect-dominated scenario to the case of interacting local defects and further to well separated, localized defect states are obtained, which have been discussed earlier. One subtle difference is that the edge-specific states occur at the upper edge of the valence band for this type of the termination, such that the gap starts to open from the side of the conduction band edge. As for the comparatively sulfur-poor holes of Figure 4 also the sulfur-rich platelets exhibit localized defect states in the bandgap only for hole sizes of up to $n = 4$, whereas for larger holes the Fermi level is within the DOS of the defect states for any supercell size. In both cases, the DOS for systems with larger holes exhibits the same trends with respect to their electronic structure as the DOS for the platelets of the same termination. This confirms the assumption made in very early DFT-based studies and reconfirmed recently for activated structures that the edge of larger platelets may be approximated by a 1D extended ribbon model, whereas the edges of few nm large structures are better represented by modeling the complete structure.

3.2. Combination of Edge States in a Hexagonal Pore

As outlined in Section 1, holes in 2D materials need not necessarily be triangular in shape. In particular, molybdenum as an element of the middle of the transition metal series supports several large formal oxidation states and can stabilize sulfur contents of up to three sulfur atoms per molybdenum atom in the case of high sulfur excess during the synthesis. From the aforementioned discussion, it is evident that this allows molybdenum atoms at the edge of MoS$_2$ platelets or holes to accommodate a variable sulfur content that depends on the local partial pressure and is at the heart of the high catalytic potential of MoS$_2$. Standard DFT calculations account neither for variations of the overall stoichiometry nor for changes of local composition, but extensions have been devised to access the chemical potential in general and for the Mo:S material system in particular. The atomization energy, i.e., the total energy per atom of a compound can be used to compare relative stabilities of model structures with different size but similar composition. If resolved as a function of the composition such atomization energies can, thus, be utilized to rate the stabilities of multinary structures qualitatively as a function of the partial pressures of the components. This concept has successfully been applied to rationalize the amazing structural wealth of molybdenum sulfide nanostructures in the limit of low atom numbers. In a catalytic context it is, however, more common to analyze relative stabilities of differently composed small structures with the help of the energy of their formation from reference compounds, $E_f$. In accordance with our earlier calculations, $E_f$ is calculated from the total energies of the relaxed structures of the repeat unit with the hole, $E_t$(Mo$_x$S$_y$), the unperturbed MoS$_2$ monolayer, $E_t$(MoS$_2$), and $\alpha$-sulfur, $E_t$(S$_\alpha$), which has the S$_8$ crown structure, where $x$ and $y$ are the numbers of Mo and S atoms in the supercell with the hole

$$E_f = \frac{1}{x + y} \left( E_t(\text{Mo}_x\text{S}_y) - xE_t(\text{MoS}_2) - \frac{y - 2x}{8} E_t(\text{S}_\alpha) \right)$$

This approach is equivalent to the recent discussion of the catalytic activity of edges in molybdenum sulfide-based nanostructures in a simplified way without additional hydrogen in the reaction sphere. Figure 6 shows an overview of these formation energies $E_f$ as a function of the composition for all model structures investigated in this study and from earlier reference calculations on selected triangular platelets terminated by the low sulfur excess variant (green squares in Figure 6).

Figure 6. Formation energy $E_f$ relative to body-centered cubic Mo, $\alpha$-type S (S$_8$) and the 2D-extended MoS$_2$ monolayer (in H/atom) as a measure for the relative stability of all investigated structures as a function of the stoichiometry. The green open squares are reference values compiled in the study by Joswig et al. and stem from studies with an earlier version of the DFTB code employed here and from full DFT calculations.

$$E_f = \frac{1}{x + y} \left( E_t(\text{Mo}_x\text{S}_y) - xE_t(\text{MoS}_2) - \frac{y - 2x}{8} E_t(\text{S}_\alpha) \right)$$
The values for the optimized platelet structures (filled triangles) reach up to very high Mo:S ratios of 1:3 for the smallest platelets with the highest sulfur excess along the edge and reach a lower limit slightly above Mo:S = 1:2 for the largest platelets with low sulfur excess. The hole structures (red triangles) have lower overall sulfur excess and occur closer to the lower limit of Mo:S = 1:2. The short dashed line is a guide to the eye which envelopes the formation energies from below and underlines that sulfur-terminated platelets remain the most stable structures at larger sulfur excess. The difference between structures with high and low sulfur content is within few meV per atom, which means that both termination types are present under thermodynamic equilibrium conditions. This thermodynamic propensity for the coexistence of different terminations is the second prerequisite for exploiting the catalytic activity discussed above. The open triangles denote formation energies obtained from the average total energies of DFT-based molecular dynamics simulations. The values, in particular also the ones for the hole structures, are within the same energy range per atom as for the ground-state structures and support this interpretation.

The green hexagons denote the formation energy of the fully stoichiometric platelet (filled symbol) and three different termination variants of the hexagonal hole. The higher energy of the hexagonal platelet shows that the combination of two different termination variants in a single structure is less favorable than the presence of only one type. As the additional edges are sulfur-deficient this finding suggests that such edges are energetically less stable and will be the reactive spots of hexagonal platelets. This finding is corroborated by the results obtained for the hexagonal holes, where the most stable structure is the fully sulfur-terminated one with an overall sulfur excess of 11% with respect to pristine MoS2, followed by the sulfur-deficient hole with a sulfur excess of ~8% and the fully stoichiometric variant. Nevertheless, also the most stable hexagonal hole is less stable than the trigonal ones.

Closer inspection of representative orbitals for the defect states within the bandgap for the most stable structure in Figure 7 rationalizes that finding. The small triangular (10,4) hole in Figure 7a shows a 1D extended defect state which encircles the hole completely, extends from one to two unit cells into the adjacent perfect MoS2 and hybridizes with the respective defect state of the neighboring hole. This extension of the defect state is very similar to earlier results calculated for trigonal platelets,[63] which exhibit a brim state that extends about two units cells into the interior of the platelet. The defect state of the fully sulfur-saturated hexagonal hole in Figure 7b also ranges from one to two unit cells into the surrounding bulk, but resides mostly along the sulfur-rich edges of the hole. Thus, a stabilizing 1D delocalization around the whole hole is not feasible for the hexagonal case.

4. Conclusions

In conclusion, DFT-based structure optimizations and molecular dynamics simulations for MoS2 defects and hole structures in an otherwise perfect MoS2 monolayer indicate that both structure elements are thermodynamically stable. Both form very similar 1D extended electronic edge states, which support the catalytic activity of MoS2 defect states. Catalysis with holey MoS2 layers may have several advantages over the standard platelet-based process: holey MoS2 is intrinsically heterogeneous and easy to separate from the reaction mixture. In contrast to supported platelets leaching of the catalyst particles is less likely. Second, the electronic states involved in the catalysis are closer to the valence band and the Fermi level of pure MoS2 and may require less additional effort for activation. And, finally, the design of the pore size and termination may be used to fine tune the catalytic potential and further to act as a membrane, which selects specific educt or product sizes.

5. Computational Methods

The calculations for the defect properties of MoS2 platelets and holes in the continuous MoS2 layer were carried out using the DFTB method[64] as implemented in the program DFTB+. The tolerance during the geometry optimizations amounted to 10−4 Hartree Å−1. Molecular-dynamics simulations were carried out with a time step of 1 fs over a period of 10 ps; the temperature was set to 300 K by a Berendsen thermostat[85] with a coupling constant of 0.1 ps.

All 2D structures are aligned parallel to the (x,y) plane. Triangular clusters are validated against the atom arrangement and electronic structure of small MoS2 platelets and related clusters investigated earlier with full DFT.[19,51,68] For the pore structures, the starting point was the optimized...
unit cell of the MoS$_2$ monolayer, which was infinitely repeated by periodic boundary conditions in the $(x, y)$ plane. Along the $z$ direction, the supercell size was set to 100 Å, in order to avoid interactions between the periodic replicas. For triangular interior defects, the atom arrangement of the termination with low sulfur excess was included in the calculation of the formation energies, because experimental evidence and theoretical modeling consistently show that beyond edge lengths of six unit cells triangular platelets of MoS$_2$ prefer that termination thermodynamically for the sulfur partial pressure during the platelet synthesis.$^{[16,20,27,30]}$

The validation of the periodic DFTB calculations was carried out against DFT calculations using the SIESTA code$^{[67]}$ for the defect-free (5,0) MoS$_2$ monolayer and the sulfur-poor (6,2) triangular defect structure. The density of states around the Fermi level as well as structural parameters were compared. The DFT calculations were carried out with a generalized-gradient approximation exchange-correlation functional, a pseudo atomic-orbital energy shift of 0.005 H, and a mesh-cutoff energy of 125 H.

For the sulfur-poor triangular platelets, the presently calculated formation energies per atom as a function of the composition (full yellow triangles) match earlier data obtained by full DFT calculations on small structures$^{[51,59]}$ with the deMon code$^{[68]}$ using gradient corrections and DFTB calculations$^{[10,62]}$ (hollow green squares in Figure 6).

Figure SI1, Supporting Information, embeds the formation energies calculated in this study in the broader context of the molybdenum sulfide nanostructures, which have been observed so far: small clusters, 1D tubes and wires with different structural motifs, larger hollow octahedra and fullerene-like structures, and 2D extended platelets and layers, where also gradient-corrected DFT calculations with the ABINIT code$^{[69,70]}$ were carried out for periodic structures and selected sulfur-poor platelets.$^{[30,59]}$

The triangular and hexagonal holes were close to the ideal stoichiometry MoS$_2$, and with growing size the stoichiometry of the platelets deviated less and less from the ideal 2D MoS$_2$ monolayer. Hence, the comparison was limited to the S:Mo composition range 1.5–3.0 and formation energies of up to 0.05 H/at.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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