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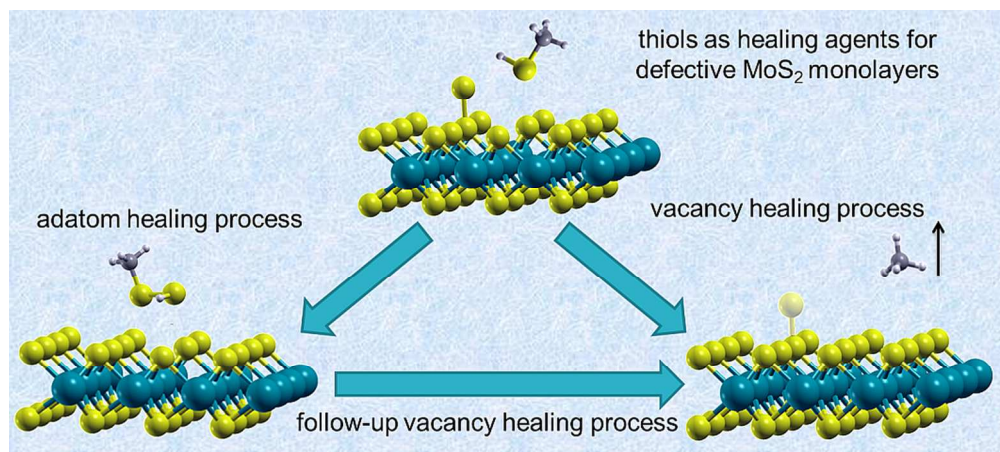
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Chemical and Electronic Repair Mechanism of Defects in MoS₂ Monolayers

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Abstract

Using *ab initio* density functional theory calculations, we characterize changes in the electronic structure of MoS₂ monolayers introduced by missing or additional adsorbed sulfur atoms. We furthermore identify the chemical and electronic function of substances that have been reported to reduce the adverse effect of sulfur vacancies in quenching photoluminescence and reducing electronic conductance. We find that thiol-group containing molecules adsorbed at vacancy sites may re-insert missing sulfur atoms. In presence of additional adsorbed sulfur atoms, thiols may form disulfides on the MoS₂ surface to mitigate the adverse effect of defects.

Keywords

transition metal dichalcogenides, 2D materials, *ab initio* calculations, electronic structure, defects

There is growing interest in two-dimensional (2D) transition metal dichalcogenide (TMD)

semiconductors, both for fundamental reasons and as potential components in flexible, low-power electronic circuitry and for sensor applications.^{1–3} Molybdenum disulfide, MoS₂, is a prominent representative of this class of TMDs. A free-standing, perfect 2D MoS₂ monolayer possesses a direct band gap of 1.88 eV at the *K*-point in the Brillouin zone.^{4,5} Most commonly used production methods for MoS₂ monolayers are chemical vapor deposition (CVD) and mechanical exfoliation of the layered bulk material,^{6–8} as well as sputter growth atomic layer deposition⁹ (ALD) of the precursor MoO₃ and subsequent conversion to the disulfide under reducing conditions and at high temperatures.^{10,11} A direct ALD process using H₂S and MoCl₅¹² or Mo(CO)₆¹³ is another possibility to obtain MoS₂ monolayers. The CVD technique is probably best suited for mass production, but the synthesized MoS₂ layers lack in atomic perfection. The most common defects in these layers are sulfur and molybdenum vacancies, as well as additional adsorbed sulfur atoms.^{14–19} Eliminating or at least reducing the adverse effect of such defects is imperative to improve the optoelectronic and transport properties of TMDs.

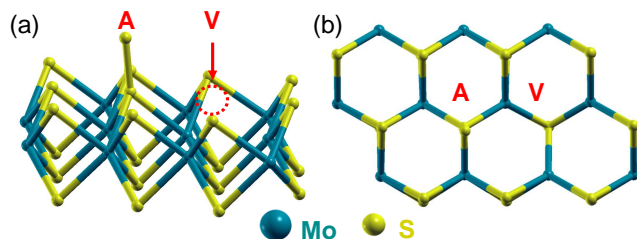


Figure 1: (Color online) (a) Perspective and (b) top view of the optimized geometry of an MoS₂ monolayer containing a sulfur monovacancy (V) and a sulfur adatom (A).

In search of ways to mitigate the adverse effect of defects, different methods have been suggested, including exposure of MoS₂ to superacids²⁰ or thiols.^{21,22} In the related MoSe₂ system, Se vacancies could be filled by S atoms from an adjacent MoS₂ layer.²³ In the present study, we focus on the reactions of thiols with defective MoS₂ monolayers.

First, we characterize changes in the electronic structure of MoS₂ monolayers introduced by missing or additional adsorbed sulfur atoms using *ab initio* density functional theory (DFT) calculations. We provide microscopic information about the chemical and electronic function of thiols as a theoretical background for the understanding of the successful use of thiols, which have been reported to reduce the adverse effect of sulfur vacancies in quenching photoluminescence and to improve the electronic conductance of defective MoS₂. We found that adsorbed thiols may re-insert missing sulfur atoms at vacancy sites. We also found that in presence of sulfur adatoms, thiols will form disulfides on the MoS₂ surface, which both mitigate the adverse effect of defects.

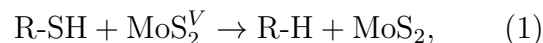
In Figure 1 we display the structure of a defective MoS₂ monolayer with a sulfur monovacancy (V) and an additional sulfur adatom (A), since these defects are known to significantly affect the electronic properties of MoS₂.²⁴ The formation energy of the sulfur vacancy is 2.71 eV and that of the sulfur adatom is 1.07 eV. Consequently, the recombination energy of a sulfur vacancy and a sulfur adatom is -1.89 eV. In spite of the large energy gain, no spontaneous healing will occur in a system with

both defect types present due to the high activation barrier of ≈ 1.5 eV for this reaction. The listed defect formation energies are in agreement with a study reporting the effect of various defect types on the electronic structure of MoS₂,²⁵ and also with a study of vacancy defects.²⁶

Defects affect drastically the electronic structure in the vicinity of the Fermi level. Setting apart the inadequacy of DFT-PBE calculations for quantitative predictions of band gaps, we should note that in our computational approach with (large) supercells and periodic boundary conditions, also defects form a periodic array. In spite of their large separation, defect states evolve into narrow bands that may affect the band structure of a pristine MoS₂ monolayer. The effect of a sulfur monovacancy, as well as that of a sulfur adatom, on the density of states (DOS) of an MoS₂ monolayer around the band gap region is shown in Figure 2.

As seen in Figure 2c, sulfur monovacancies introduce defect states within the band gap and their superlattice shifts the DOS down by 0.16 eV with respect to the pristine lattice. The defect states are localized around the vacancy as seen in Figure 2a. The effect of a superlattice of sulfur adatoms, addressed in Figure 2b and 2d, is to reduce the DFT band gap from 1.88 eV to 1.72 eV, in agreement with published results.^{24,25}

Defect sites play an important role as catalytically active centers¹³ and as sites for functionalization reactions of 2D MoS₂.²⁷ Sulfur vacancies in particular are considered to be important nucleation sites for a functionalization with thiol molecules R-SH. The likely possibility of an adsorbed thiol group transferring a sulfur atom to the vacancy and thus repairing the defect is particularly appealing. In this case, the detached hydrogen atom may reconnect with the remaining R to form R-H and fill vacancy site of MoS₂ with sulfur, as



where MoS₂^V denotes the MoS₂ layer with a sulfur vacancy.

An alternative reaction has been proposed to

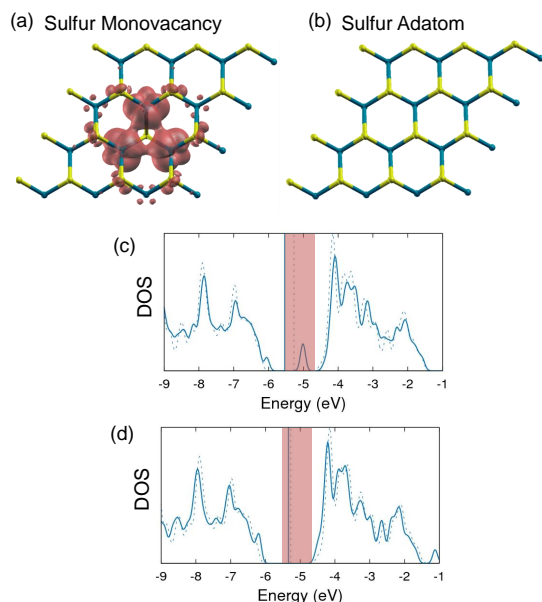
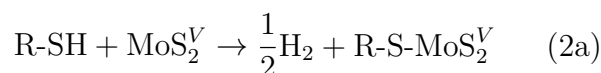


Figure 2: (Color online) Ball-and-stick models of (a) a sulfur vacancy defect and (b) a sulfur adatom defect in an MoS₂ monolayer. Density of states (DOS) of MoS₂ with (b) a vacancy and (d) an adatom defect. The DOS and the position of the Fermi level are shown by solid blue lines in defective lattices and by dotted blue lines in the corresponding pristine lattices in (c) and (d). The DOS has been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV. The energy range of interest in the gap of the pristine lattice is highlighted in red. The local density of states (LDOS), representing the charge density associated with this highlighted energy range, is represented by an isosurface and superposed to the structure of a vacancy defect in (a) and an adatom defect in (b). The isosurface value in the LDOS plots is 0.003 e/bohr³.

benefit from the STM tip current in an STM study.²² In the first step of reaction (2), similar to reaction (1), a hydrogen atom is removed from the thiol as its sulfur atom fills the previous vacancy, determining the reaction barrier for both reactions (1) and (2a). The removed hydrogen atom will then form H₂ and desorb from the MoS₂ surface. The rest R is still bound to the sulfur atom, adsorbed at the sulfur vacancy site. The final assumption of the proposed mechanism²² is that the R-groups are removed with the support of the STM tip, as

represented in reaction (2b).



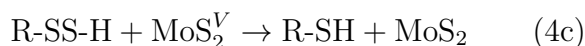
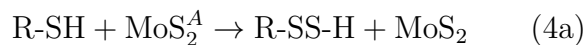
There is evidence in the literature supporting both reaction (1) (References [21], [28], [29]) and reaction (2) (Reference [22]).

The authors of Reference [30] propose yet another reaction (3a). Instead of the thiol molecules repairing the sulfur vacancy, they form an adsorbed R-SS-R disulfide at the surface of MoS₂ while releasing a hydrogen molecule. We also considered the possibility that instead of desorbing, the hydrogen molecule will fill the vacancy defect as described in reaction (3b),



Based on a previous study³¹ and the observation of H₂S as well as H₃C=CH₃ during the reaction of C₂H₅SH with bulk MoS₂ in Reference [28], we also considered a sulfur atom adsorbed on the MoS₂ surface, identified as MoS₂^A, as the driving force for the observed disulfide formation.

In this case, the reaction to form the disulfide R-SS-R is divided into the following two steps. In reaction (4a), one thiol reacts with the adatom to R-S-S-H and, in the follow-up reaction (4b) with a second thiol, to R-S-S-R. An alternative reaction with a sulfur vacancy following reaction (4a) is also possible. Similar to reaction (1), the SH-group of R-S-S-H can cure the vacancy defect, leading to the reduction of R-S-S-H to the thiol R-S-H in Reaction (4c),



To better understand the above reaction mechanisms (1) – (4), we performed DFT calculations to compare the energy associated with the pathways of these reactions. For the sake

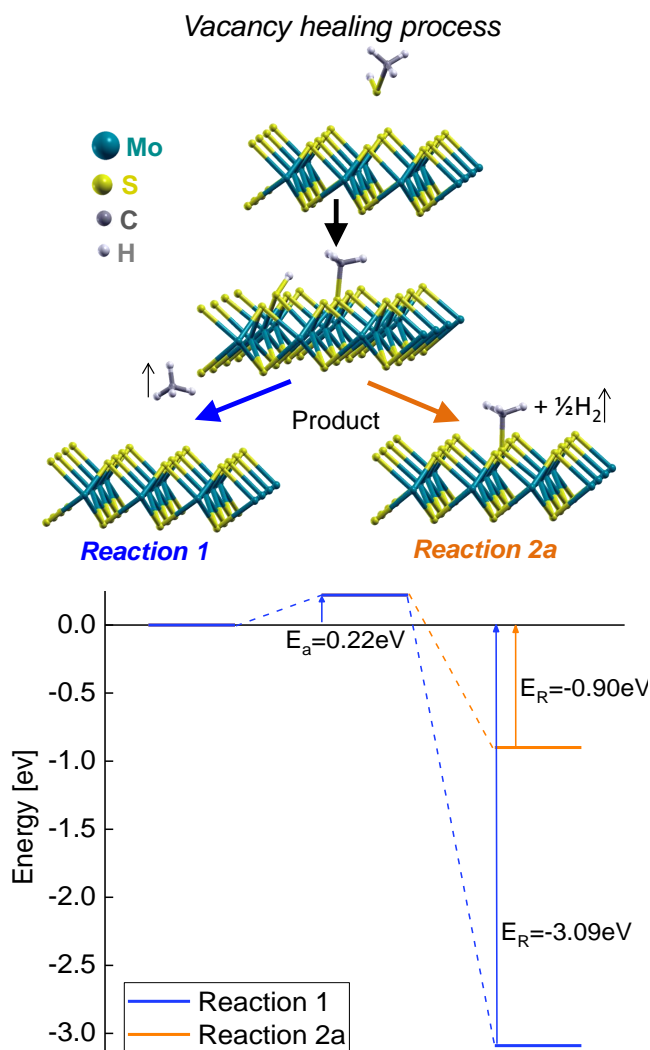


Figure 3: (Color online) Reaction scheme for the sulfur vacancy healing process caused by exposure of MoS₂ with vacancies to CH₃SH. E_R denotes the reaction energy and E_a the activation barrier. The same initial state can lead to two different final states *via* the same transition state. The favorable reaction (1), shown in dark blue, leads to a free CH₄ molecule. The energetics of reaction (2a) is displayed in light orange.

of easy understanding, we consider the small methanethiol molecule CH₃SH as a representative of thiols.

We limit our study of vacancy repair processes to reactions with MoS₂ monolayers that contain one sulfur monovacancy per unit cell. We analyze which reactions with thiols are favorable to repair vacancy and adatom defects. Our results also unveil the likely cause of apparent contra-

dictions in the interpretation of experimental results obtained by different researchers.

Results/Discussion

Vacancy Repair

The majority of published results indicate that thiol molecules interacting with sulfur-deficient MoS₂ may fill in sulfur atoms at the vacancy defect sites. Reaction pathways for the two vacancy-healing reactions (1) and (2a), which have been proposed in the literature,^{22,28,29} are sketched in Figure 3. We note that reaction (1) has been studied in greater detail for a different thiol²¹ and agrees with our findings for the model compound H₃C-SH.

We find that reactions (1) and (2a) are both exothermic and require crossing only a low activation barrier of 0.22 eV, since they share the same transition state shown in Figure 3. The larger energy gain $E_R = -3.09$ eV in reaction (1) in comparison to -0.90 eV in reaction (2a) suggests that the former reaction is thermodynamically preferred.

Figure 4a shows the DOS and partial densities of states (PDOS), projected on individual atoms, of the product of reaction (1). Figure 4b provides the corresponding information for reaction (2a), and Figure 4c provides a detailed view of the PDOS for the CH₃-group and the connected sulfur atom. In both cases, the defect states associated with sulfur monovacancies have been removed. In the final state of reaction (1) the DOS is completely restored to the undamaged state of the semiconductor. For reaction (2a), on the other hand, the Fermi level is shifted to the lower edge of the conduction band due to the CH₃-group. Therefore, only the preferred repair reaction (1) leads to both an electronic and a chemical repair of MoS₂.

Disulfide Formation

A different reaction scenario (3a) has been proposed in Reference [30], suggesting that disulfides are formed when thiols interact with MoS₂. We investigated the MoS₂ surface both in its pristine state and in presence of sulfur

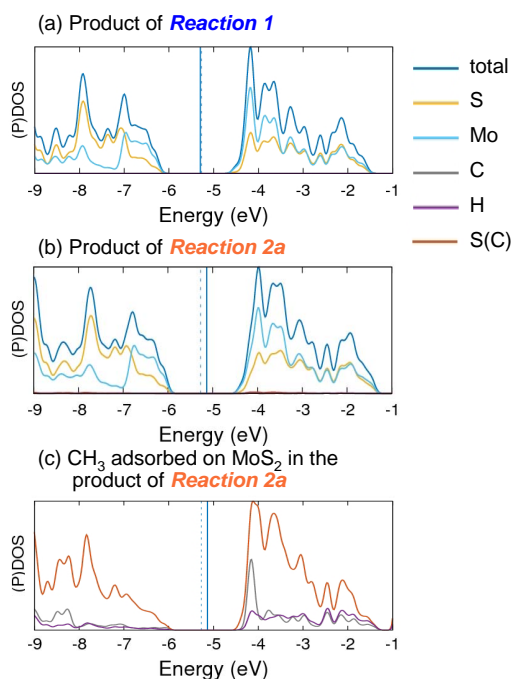


Figure 4: (Color online) Electronic structure of products of the vacancy healing process shown in Figure 3. The total density of states (DOS) and partial densities of states (PDOS) of the products of reactions (a) (1) and (b) (2a). (c) PDOS of the CH_3 -molecule bonded to a sulfur atom in an MoS_2 monolayer. The PDOS of the sulfur atom connected to C in CH_3 , S(C), is shown by the brown line. All DOS and PDOS functions have been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV. The position of the Fermi level is shown by solid blue lines in defective lattices and by dotted blue lines in the corresponding pristine lattices.

vacancies to clarify the differences in the catalytic potential for disulfide formation. Figure 5 illustrates reaction (3a) on pristine MoS_2 and reaction (3b) on a sulfur-deficient MoS_2 substrate. The schematic reaction profile indicates that both reactions involve significant activation barriers. As seen in Figure 5, reaction (3a) is endothermic with a reaction energy of $E_R=0.39$ eV and involves a high activation barrier of 2.91 eV. Reaction (3b) near a sulfur monovacancy is only slightly endothermic, with a reaction energy $E_R=0.02$ eV, and involves a somewhat lower activation barrier of 2.13 eV. Thus, reaction (3b) is energetically more favor-

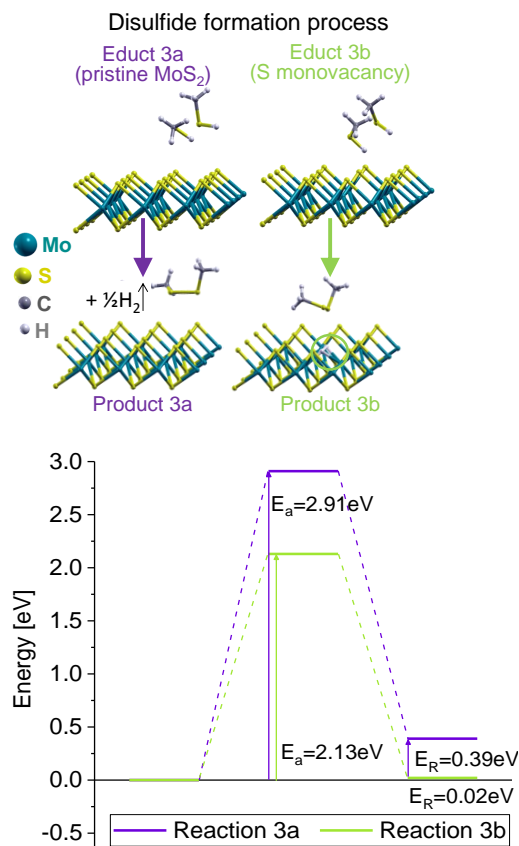


Figure 5: (Color online) Reaction scheme of the disulfide formation process involving exposure of an MoS_2 monolayer to two CH_3SH molecules. E_R denotes the reaction energy and E_a the activation barrier. Reaction (3a), shown in dark purple, occurs on pristine MoS_2 . Reaction (3b), shown in light green, occurs on a sulfur-deficient MoS_2 substrate.

able than reaction (3a).

The near-neutral reaction energy of reaction (3b) can be explained by the Kubas interaction of transition metal $\eta^2\text{-H}_2$ -complexes.^{32,33} It means that the excess H_2 molecule in the product of reaction (3b), which is attached to an Mo atom at the sulfur vacancy site and indicated by a circle in Figure 5, still retains the H-H bond character. According to Reference [34], the Kubas interaction energy is in the range of 0.2 – 0.4 eV, in agreement with the reaction energy difference of 0.37 eV between reactions (3a) and (3b).

The Kubas interaction also reduces the reaction barrier and degree of endothermicity considerably. Nevertheless, reactions (3a) and (3b) are not competitive in comparison with the

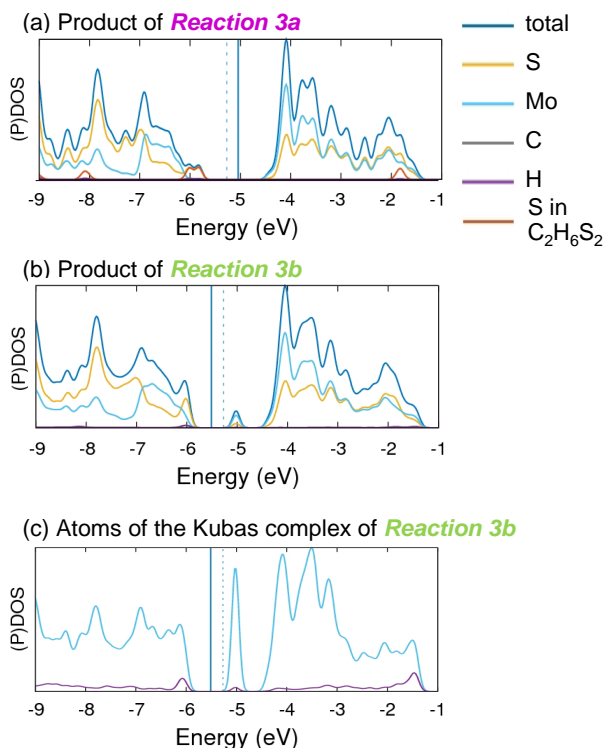


Figure 6: (Color online) Electronic structure of products of the disulfide formation process shown in Figure 5. The total density of states (DOS) and partial densities of states (PDOS) of the products of reactions (a) (3a) and (b) (3b). (c) PDOS of the 3 Mo atoms and the H₂ molecule attached to the vacancy that form the Kubas complex in the product of reaction (3b). All DOS and PDOS functions have been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV. The position of the Fermi level is shown by solid blue lines in defective lattices and by dotted blue lines in the corresponding pristine lattices.

strongly exothermic reaction (1) with $E_R = -3.09$ eV in thermodynamic equilibrium.

The PDOS functions characterizing the products of reactions (3a) and (3b), visualized in Figure 5, are shown in Figure 6. The product of reaction (3b) still contains a defect state in the gap region, indicating that the chemisorbed H₂ molecule is incapable of electronically repairing the effect of the sulfur vacancy. This is seen in the PDOS of the Mo atoms of the Kubas complex surrounding the vacancy defect in Figure 6c. The product of reaction (3a), on the other hand, shows no indication of a defect

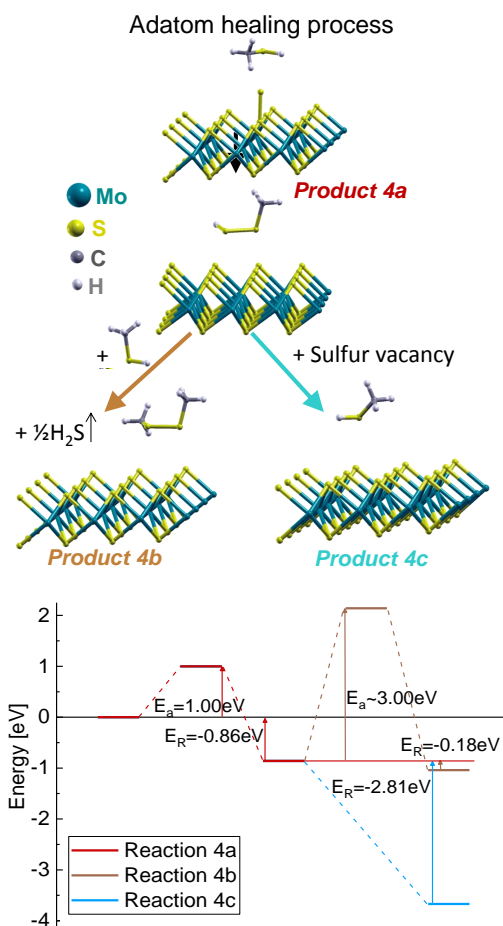


Figure 7: (Color online) Reaction scheme of the adatom healing process that starts with reaction (4a) and leads to disulfide formation in presence of extra sulfur atoms on MoS₂, shown in dark red. Subsequent ligand exchange reaction (4b) is shown in brown. Alternative subsequent vacancy repair reaction (4c) is shown in light blue. E_R denotes the reaction energy and E_a the activation barrier.

state, since the vacancy-free MoS₂ monolayer is not affected much by the physisorbed disulfide, as seen in the PDOS of Figure 6a.

We can thus conclude that the disulfide formation reaction (3a), suggested in Reference [30], is endothermic. The alternative reaction (3b) on a sulfur-deficient MoS₂ substrate displays a lower activation barrier and an end-product stabilized by the Kubas interaction, but is still weakly endothermic and thus unlikely. In the following, we propose an alternative pathway towards disulfide formation.

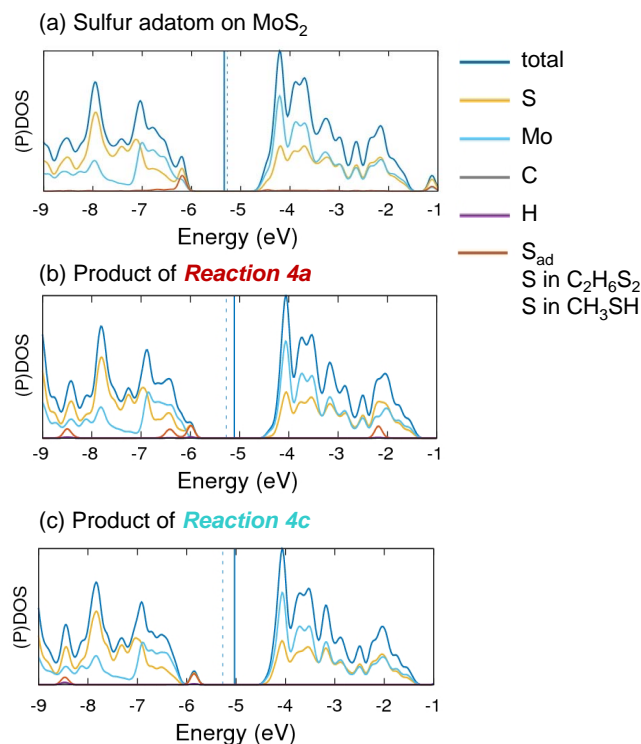


Figure 8: (Color online) Electronic structure of products of the adatom healing process shown in Figure 7. The total density of states (DOS) and partial densities of states (PDOS) of (a) MoS₂ with a sulfur adatom (without CH₃SH), (b) the product of reaction (4a), and (c) the product of reaction (4c). All DOS and PDOS functions have been convoluted by a Gaussian with a full-width at half maximum of 0.1 eV. The position of the Fermi level is shown by solid blue lines in defective lattices and by dotted blue lines in the corresponding pristine lattices.

Adatom Repair

The postulated alternative reaction requires extra sulfur atoms adsorbed on the MoS₂ surface, which act as nucleation sites for the disulfide formation. The reaction leading to the formation of disulfide R-SS-R in presence of sulfur adatoms consists of two steps, described by reactions (4a) and (4b), as well as the alternative reaction (4c) following reaction (4a), as shown in Figure 7.

In reaction (4a), a CH₃SH molecule interacts with the reactive sulfur adatom to methylhydro-disulfide (CH₃SSH), releasing -0.86 eV due to the formation of a stable

disulfide bond. The estimated activation barrier for this reaction is close to 1 eV, which is considerably lower than the values for the corresponding reactions (3a) and (3b) in absence of an extra sulfur adatom.

Electronic structure changes during the adatom healing process are displayed in Figure 8. The DOS of the product of reaction (4a), shown in Figure 8b, shows no defect-related states in the band gap, indicating chemical and electronic repair of the sulfur adatom defect that is seen in Figure 8a.

In the subsequent reaction (4b), shown in Figure 7, a second CH₃SH molecule interacts with the methylhydro-disulfide CH₃SSH, leading to the exchange of the hydrogen atom with a methyl group and formation of hydrogen sulfide (H₂S) as a side product. This reaction is mildly exothermic, with an overall reaction energy of -0.18 eV. Even though the combined reaction (4a) and (4b) for the formation of CH₃SSCH₃ is strongly exothermic with a net energy gain of -1.05 eV, the activation barrier for the ligand exchange in reaction (4b) is prohibitively high with $E_a \approx +3$ eV, which essentially suppresses the formation of CH₃SSCH₃ following reaction (4a).

Therefore, we investigated reaction (4c) as an alternative follow-up process to reaction (4a). In reaction (4c), the CH₃SSH molecule interacts with a nearby sulfur vacancy defect. This reaction is similar to the vacancy healing reaction (1) and consequently is strongly exothermic with a reaction energy of -2.81 eV. Reaction (4c) is barrier-free and thus occurs spontaneously. As seen in in Figure 8c, describing the product of reaction (4c), the defect-related state above E_F has been removed from the DOS. This means that following the adatom repair and disulfide formation reaction (4a), reaction (4c) will take place in case that also sulfur vacancies are present. The two reactions will thus heal both vacancy and adatom defects.

Our above considerations offer an attractive explanation why disulfide formation was observed in Reference [30], but not in References [21], [22], [28] and [29]. Initially, reactions (1) and (4a) plus (4c) have taken place in all samples that contained vacancies.

Vacancy healing as primary outcome of reactions reported in References [21], [22], [28] and [29] could likely be achieved due to an abundance of vacancies in the samples used. We may speculate that the MoS₂ sample of Reference [30] contained more sulfur adatoms than sulfur vacancies. In that case, all vacancy defects could be repaired, but some adatom defects were left unrepaired in the sample of Reference [30]. At this point, lack of vacancy defects would block reactions (1) and (4c). The only viable reaction was (4a), which repaired adatom defects, leaving a pristine MoS₂ surface behind with disulfide as a by-product. This speculative assumption is also consistent with the observation that the electronic structure of MoS₂ has remained unaffected by the reaction leading to the formation of disulfide.³⁰

Conclusions

We studied three different reaction paths of thiols, represented by methanethiol (CH₃SH), with a defective 2D MoS₂ monolayer. We showed that the repair of sulfur monovacancies by adsorbed CH₃SH is an exothermic reaction releasing up to 3 eV. In another possible reaction between CH₃SH and MoS₂, leading to the formation of disulfide, we found that presence of sulfur vacancies lowers the reaction barrier due to the Kubas interaction at the defect site. The corresponding reaction involving MoS₂ with sulfur adatoms instead of vacancies, on the other hand, leads to disulfide formation and releases about 0.9 eV. In the presence of sulfur vacancies, the formed disulfides will immediately reduce to thiols while simultaneously healing the vacancy defect. We can therefore conclude that, regardless of interim disulfide formation, thiols always lead to a chemical repair of available sulfur vacancies by filling-in the missing sulfur atoms and consequently eliminating vacancy-related defect states in the gap.

Methods/Theoretical

To obtain insight into the reaction processes, we performed DFT calculations using the

SIESTA code.³⁵ We used *ab initio* Troullier-Martins pseudopotentials³⁸ and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³⁶ throughout the study. Except for sulfur, all pseudopotentials used were obtained from the on-line resource in Reference [39]. The pseudopotential of sulfur has been generated without core corrections using the ATM code in the SIESTA suite and the parameters listed in Reference [39]. All pseudopotentials were tested against atomic all-electron calculations. We used a double- ζ basis set including polarization orbitals (DZP) to represent atoms in crystal lattices, 140 Ry as the mesh cutoff energy for the Fourier transform of the charge density, and 0 K for the electronic temperature. We used periodic boundary conditions with large supercells spanned by the lattice vectors $\vec{a}_1 = (12.84, 0.00, 0.00)$ Å, $\vec{a}_2 = (6.42, 11.12, 0.00)$ Å, $\vec{a}_3 = (0.00, 0.00, 22.23)$ Å to represent pristine and defective 2D MoS₂ lattices. The unit cells of defect-free MoS₂ contained 16 molybdenum and 32 sulfur atoms, and were separated by a vacuum region of ≈ 15 Å normal to the layers. The Brillouin zone was sampled by a $4 \times 4 \times 1$ k -point grid³⁷ and its equivalent in larger supercells.

The above input parameters were found to guarantee convergence. In particular, we found that using the larger triple- ζ polarized (TZP) instead of the DZP basis and increasing the mesh cutoff energy affected our total energy differences by typically less than 0.01 eV. We furthermore validated the *ab initio* pseudopotential approach used in the SIESTA code by comparing to results of the all-electron SCM-Band code⁴¹ and found that energy differences obtained using the two approaches differed typically by less than 0.3 eV.

All geometries have been optimized using the conjugate gradient method,⁴⁰ until none of the residual Hellmann-Feynman forces exceeded 10^{-2} eV/Å. In addition to the default density matrix convergence, we also demanded that the total energy should reach the tolerance of $\lesssim 10^{-4}$ eV. To eliminate possible artifacts associated with local minima, we verified initial and final state geometries by performing canonical molecular dynamics (MD) sim-

ulations using the NVT-Nosé thermostat with $T = 273.15$ K and 1 fs time steps.

Due to the complexity of the reaction energy hypersurface and the large number of relevant degrees of freedom, approaches such as the nudged elastic band, which are commonly used to determine the reaction path including transition states, turned out to be extremely demanding on computer resources. We focused on transition states only and initiated our search by running canonical MD simulations starting from a set of educated guesses for the geometry. Following the atomic trajectories, we could identify a saddle point in the energy hypersurface, where all forces acting on atoms vanished, and postulated this point in configurational space as a transition state. To confirm this postulate, we ran MD simulations starting at a slightly altered geometry of the postulated transition state. We concluded that the postulated transition state is indeed the real transition state once all trajectories reached either the initial (educt) or the final (product) state. The activation barrier was determined by the energy difference between the initial and the transition state.

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Notes

The authors declare no competing financial interest.

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