Covalent photofunctionalization and electronic repair of $2H-MoS_2$

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1 Computational details

1.1 LDA+GdW/BSE

1.1.1 Gaussian basis set

For the DFT-LDA calculations, which are the starting point of the LDA+GdWprocedure, we employed an atom-centered Gaussian basis set including 4 shells for each carbon or nitrogen atom, and 3 shells for hydrogen atoms (angular momentum $l \leq 2$, 40 or 30 basis functions). The decay constants for N and C were optimized with respect to the total LDA energy of azobenzene. The final values are $\alpha_{\rm C} = [0.12, 0.41, 1.12, 4.01]a_B^{-2}$ for carbon, $\alpha_{\rm N} = [0.29, 0.81, 2.07, 6.27]a_B^{-2}$ for nitrogen, and $\alpha_{\rm H} = [0.16, 0.69, 3.58]a_B^{-2}$ for hydrogen. In Ref.¹ the BSE results for polythiophene are insensitive to small basis set errors. For Mo and S atoms the decay constants are : $\alpha_{\rm S} = [0.16, 0.56, 2.5]a_B^{-2}$ and $\alpha_{\rm Mo} = [0.18, 0.49, 1.39]a_B^{-2}$.

For the Gaussian basis for the exchange part of the electron-hole interaction kernel the following decay parameters were chosen:

$$\begin{split} &\alpha_{\rm C} = [0.12(2), 0.41(3), 1.12(3), 4.01(3)] a_B^{-2}, \\ &\alpha_{\rm N} = [0.29(2), 0.81(3), 2.07(3), 6.27(3)] a_B^{-2}, \\ &\alpha_{\rm H} = [0.16(2), 0.69(3), 3.58(3)] a_B^{-2}, \\ &\alpha_{\rm S} = [0.16(2), 0.56(3), 6.25(3)] a_B^{-2}, \\ &\alpha_{\rm Mo} = [0.18(2), 0.49(3), 1.93(3)] a_B^{-2}, \end{split}$$

where the number in brackets gives the maximal angular momentum of the shell.

1.1.2 GWA band summation

At least 72 empty bands (and its equivalent for larger supercells) were used in the summation for the self-energy in LDA+GdW calculations of monolayer MoS_2 .

In Ref.² the LDA+GdW quasiparticle gap is better converged than $\approx 0.01 \text{ eV}$ for only 90 unoccupied bands summation for the self-energy. The difference between 72 and 90 unoccupied bands is smaller than 0.01 eV in the BSE results. For isolated azobenzene the difference in LDA+GdW band gap is smaller than 0.02 eV for 296 conduction bands (valence bands times 4) instead of all DFT bands (1860). The energy difference in the first excited state is smaller than 0.01 eV.

The band gap of aminoazobenzene-functionalized MoS_2 differs by less than 0.01 eV if only 912 instead of all 3300 DFT bands are used. The largest differences in the band structure are smaller than 0.02 eV.



Fig. S1: Band structures for 3×3 supercells pristine ML (left) and ML+transaminoazobenzene (right) using $\psi_{n\mathbf{k}}^{QP} = \psi_{n\mathbf{k}}^{DFT}$ (blue) and $\psi_{n\mathbf{k}}^{QP} = \sum_{m} D_{n\mathbf{k}}^{m} \psi_{m\mathbf{k}}^{DFT}$ (black).

1.1.3 Off-diagonal GdW-Hamiltonian elements

For pristine MoS_2 and isolated azobenzene it is approximately

$$\psi_{n\boldsymbol{k}}^{QP} \approx \psi_{n\boldsymbol{k}}^{DFT}.$$
 (1)

Therefore the errors are small, if only the diagonal elements of the Hamiltonian are evaluated in GdW/BSE calculations (similar to so-called one-shot GdW). Yet, for functionalized MoS₂, the LDA states of the monolayer and the molecule are strongly hybridized. As the quasiparticle corrections are larger for molecular states, the LDA+GdW Hamiltonian has to be self-consistently diagonalized.

1.1.4 BSE calculations of isolated aminoazobenzene

Experimentally the lowest excitation of trans-aminoazobenzene (trans-AAB) in ethanol was measured at around 2.68 eV - 2.81 eV (i.e. 442 nm - 462 nm).³ For trans-azobenzene (trans-AB) 2.82 eV (i.e. 440 nm) were measured in ethanol.⁴ The lowest excitation of cis-AAB in diethyl ether was measured at 2.67 eV (i.e. 465 nm)⁵, and for cis-AB in ethanol at 2.82 eV (i.e. 440 nm).⁴

Non-periodic GW/BSE calculations with iteratively updated 6 G give 2.43 eV for the first excitation of trans-AAB. The periodic calculations of MoS₂+molecule

Table 1: 1st excitation of AAB from BSE calculations using different methods, unit cells, and numbers of spin-degenerated valence/conduction bands in the active space

method	unit cell	active space	$\operatorname{trans}\left(\mathrm{eV}\right)$	cis(eV)
$\exp^{3,5}$			≈ 2.7	2.67
GW	non-periodic	37/37	2.43	2.44
GW	non-periodic	5/1	2.29	2.50
GdW	24 Å \times 24 Å \times 32 Å	5/1	2.20	2.17
GdW	$9.48\mathrm{\AA} imes 9.48\mathrm{\AA} imes 29\mathrm{\AA}$	5/1	2.14	1.87

require approximations to be computationally feasible: LDA+GdW, a very small unit cell, and a small active space¹ of 5 valence and 1 conduction bands. The results for different sets of parameters are compared in table 1.

1.2 TDDFT

The spectrum of pristine ML was calculated at the Γ point for different super cell sizes. The position of the first peak is well converged for 3×3 , but higher excitations change significantly when going to 6×6 . Due to the high computational cost, it was not possible to converge these peaks, too.² They have energies larger than 2.7 eV (for the 6×6 super cell), which is in good agreement with experiments.⁷



Fig. S2: Convergence of the energy of the first excitation with super cell size of monolayer MoS_2 calculated at the Γ point.

 $^{^1\}mathrm{For}$ the full system (MoS₂+AAB; 3×3 supercell) the active space of 42 occupied and 60 unoccupied bands approximately covers an quasiparticle energy range 2.7 eV for both valence and conduction bands (1.8 eV and 2.0 eV of DFT energies, respectively). In this range there are 5 occupied and 1 unoccupied spin-degenerated AAB states.

 $^{^2 \}rm For$ the 12×12 super cell only 100 excited states were considered.

2 Results and discussion

2.1 Reaction energies



Fig. S3: Functionalization with methanethiol: $E_b = -1.57 \,\mathrm{eV}$



Fig. S4: Functionalization with p-thioazobenzene: $E_b = -1.46 \,\mathrm{eV}$



Fig. S5: Functionalization with p-hydroxyazobenzene: $E_b = -0.24 \,\mathrm{eV}$



Fig. S6: Functionalization with ammonia: $E_b = -1.73 \text{ eV}$



Fig. S7: Functionalization with methylamine: $E_b = -2.03 \text{ eV}$



Fig. S8: Functionalization with p-aminoazobenzene (AAB): $E_b = -1.13 \text{ eV}$



Fig. S9: Functionalization with glycine: $E_b = -1.12 \text{ eV}$



Fig. S10: Repair using methanethiol: $E_r = -1.99 \text{ eV}$



Fig. S11: Repair with p-thioazobenzene: $E_r = -1.80 \text{ eV}$



Fig. S12: Repair using p-hydroxyazobenzene: $E_r = -2.09 \,\text{eV}$

$2.2 MoS_2 + AB C-S bond$

Attaching AB to the ML via C-S bond gives a hypervalent structure with an odd number of electrons. In the bandstructure one occupied and three unoccupied states can be found right below the conduction bands of the ML (Fig. S13). The valence band maximum (VBM) and the conduction band minimum (CBM) are located at the C-S bond and the Mo atoms below as presented in the density isosurface plotted in Fig. S14. The flat bands right above the MoS_2 valence bands and below the conduction bands can be identified as HOMO and LUMO of AB.

The Gaussian basis code⁸ with PBE+D3 was used to optimize the geometry of the 3×3 MoS₂ supercell with C-S bond azobenzene, which was the chosen for the bandstructure calculation. To avoid metallic screening due to the in-gap states, only LDA bands with a minimum gap of 1 eV were considered in the calculation of the parameters for the model dielectric function. As shown in figure S13 LDA+GdW keeps metallic bands in the small supercell. A detailed examination of this effect requires larger supercells to avoid interactions between neighboring defects.



Fig. S13: LDA band structures for 3×3 supercells (optimized using PBE+D3 and Gaussian basis) of pristine ML (blue) and C-S bond azobenzene (black). The valence band maximum of the ML is set to 0 eV to allow for better comparison. The dotted line indicates the Fermi energy of the functionalized system.



Fig. S14: Highest occupied (top) and lowest unoccupied (bottom) state (calculated at the Γ point) of a $5 \times 5 \text{ MoS}_2$ supercell with azobenzene (C-S bond).

2.3 Nitrogen incorporation: N vs. NH vs. NH₃

 NH_3 chemisorbs at a sulfur vacancy with only 0.407 eV adsorption energy.⁹ The weak bonding to the surface is reflected by the large Mo-N bond lengths (Fig. S15a) and the charge density difference

$$\Delta \rho = \rho_{\text{MoS}_2 + \text{NH}_3} - \rho_{\text{NH}_3} - \rho_{\text{MoS}_2(vac)} \tag{2}$$

as shown in Fig. S16 where the optimized coordinates of NH₃ physisorbed at a sulfur vacancy ($\rho_{MoS_2+NH_3}$) are split into two subsystems to calculate ρ_{NH_3} and $\rho_{MoS_2(vac)}$. There are two occupied and four unoccupied bands within the MoS₂ band gap (Fig. S17a).

Filling the sulfur vacancy by a nitrogen atom gives an odd number of electrons. The two almost degenerated bands (one occupied, one unoccupied) within the band gap of the monolayer (Fig. S17c) correspond to the p-type doping behavior of N. $^{10-12}$

The dangling bond can be saturated by addition of a hydrogen atom. This does elongate the Mo-N bonds only slightly from 2.07 Å to 2.10 Å (Fig. S15b,c) and restores the band gap of pristine MoS_2 (Fig. 3d, main paper).



Fig. S15: Optimized geometries of a) NH₃, b) NH, and c) N filling a sulfur vacancy.



Fig. S16: PBE charge density differences between MoS₂ functionalized with a) NH₃, b) NH, c) N and the isolated subsystems. Isosurfaces at $+0.004 e/a_{Bohr}^3$ (blue) and $-0.004 e/a_{Bohr}^3$ (red).



Fig. S17: LDA band structure for 3×3 supercells (optimized using PBE+D3 and Gaussian basis) with a) NH₃ and b) N in sulfur vacancy (black) compared to pristine ML (blue). The valence band maximum of the ML is set to 0 eV to allow for better comparison. Note that the 3×3 supercell is not big enough to allow for completely independent defects, i.e. dispersionless defect bands.

Fig. S18: LDA band structure of isolated trans-aminoazobenzene (trans-AAB) and 3×3 supercells MoS with N-bond trans-AAB are shown in black. The size of the orange points is proportional to the part of the wave function stemming from a) the nitrogen atom inserted into the monolayer, b) the nitrogen atoms of the azo bond, c) the carbon atoms, d) the hydrogen atoms, e) the molybdenum, f) the sulfur atoms. For better visibility in e) and f) the points are scaled by a factor 0.5. For the isolated molecule only the population at the Γ -point is shown. The valence band maximum of the ML is set to 0 eV to allow for better comparison. The highest occupied (occ) band of the functionalized system is labeled.

In the following the Mulliken population analysis¹³ as presented in Fig. 4 (main paper) is shown in more detail. In figure S18 the contributions from different groups of atoms for the states of isolated trans-AAB and the functionalized ML are plotted. Figure S19 demonstrates that the inserted nitrogen atom contributes to the MoS_2 bands in a similar way as a sulfur atom in pristine MoS_2 does.

Fig. S19: In a) the orange points of Fig. S18 a) are enlarged by a factor 10. In b) the bandstrucute of pristine MoS_2 with the fractional contribution of one sulfur atom (also $\times 10$) is shown for comparison.

$2.5 MoS_2 + cisAAB$

The results of the LDA+GdW/BSE calculations for MoS₂+AAB in cis form are shown in figures S20, S21, and S22. The LDA+GdW band gap is 2.52 eV which is smaller than for pristine MoS₂.

Fig. S20: Band structure for 3×3 supercells with N-bond cis-aminoazobenzene (cis-AAB) compared to pristine ML (a) in blue and to cis-AAB (b). The size of the orange points is proportional to the part of the wave function stemming from C/N/H atoms. The valence band maximum of the ML is set to 0 eV to allow for better comparison. The highest occupied (occ) band of the functionalized system is labeled.

Fig. S21: LDA+GdW band structure for 3×3 supercells with N-bond cisaminoazobenzene (cis-AAB) compared to pristine ML (a) in blue. The valence band maximum of the ML is set to 0 eV to allow for better comparison.

Fig. S22: Exciton absorption spectrum (GdW/BSE) of MoS₂ functionalized AAB in trans (red) and cis (blue) form, and of cis-AAB (blue, dotted). Trans-AAB is not shown, as the excitation at 2.14 eV has very small oscillator strength. All calculations in a 3×3 super cell (i.e. $9.48 \text{ Å} \times 9.48 \text{ Å} \times 9.48 \text{ Å}$).

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