# Designing Two-dimensional Materials by Molecular Functionalization and Defect Engineering

# First principle investigation of functionalized transition metal dichalcogenides

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## In Short

- Determination of the favorite adsorbate structures on transition metal dichalcogenides for several inorganic and organic molecules
- Computation of band structures using the GW approximation for improved description of electronelectron correlation
- Calculation of optical spectra using the Bethe-Salpeter-Equation to account for the creation of excitons
- Investigation of the combined effects arising from molecular functionalization and surface imperfections on the binding energy of excitons in transition metal dichalcogenides

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have been receiving tremendous attention because of their outstanding performance as nanoscale devices. Monolayer molybdenum disulfide (MoS<sub>2</sub>) is a very promising candidate for applications such as field effect transistors, chemical sensors and ultrasensitive photodetectors due to its adjustable direct band gap. It is known that structural defects, which can not be avoided during the fabrication of the material, influence drastically its optical and electronic properties<sup>[1,2]</sup>. Most of the defects are due to a lack of Sulfur atoms (S-defect) which have been identified as a primary reason for the observed low performance of MoS<sub>2</sub>-based photoelectric devices. However, the S-defect can also be used in a positive manner, for example, to promote the hydrogen evolution reaction<sup>[3]</sup> and to vary the properties of the material for the adsorption of molecules<sup>[4]</sup> by changing the coordination number of Mo atoms.

Also optical properties of 2D materials play a crucial role for their applicability. The key parameter here is the binding energy of the excitons which are created after electronic excitation. An exciton is a bound electron-hole pair and its binding energy is determined by the electronic and the optical band gaps of the 2D material. The binding energy of an exciton dictates the optoelectronic properties. Other than Frenkel excitons, excitons in semiconductors are spatially delocalized and therefore sensitive to the



**Figure 1:** The exciton, bound electron-hole pair, delocalized in semiconductor. The red and blue balls indicate electron-hole pair; green balls indicate the adsorbed molecule.

chemical surroundings. This has motivated current studies on the effect of molecular functionalization on the exciton binding energy. We also note that the attractive Coloumb interaction in excitons decreases with the number of surface layers, because screening effects occur between the different layers, as shown in Figure 1. For comparison, the exciton binding energy of bulk  $MoS_2$  is  $\sim 0.08 \text{ eV}^{[5]}$  and that of monolayer  $MoS_2$  is  $\sim 0.57 \text{ eV}^{[6]}$ . However, it is still not fully understood how adsorbed molecules influence the optical properties of 2D materials and how changes of the exciton binding energy can be controlled by functionalizing their surfaces.



**Figure 2:** The most stable geometry of  $C_3H_3N_3$  molecule on a S-defective (3×3) MoS<sub>2</sub> supercell.

In this project, we study the electronic and optical properties of perfect and defective monolayer  $MoS_2$  functionalized by  $H_2O$ , NO and 1,3,5-triazine  $(C_3H_3N_3)$  at low coverage. From the theoretical point of view, it is difficult to accurately model the electronic structure of semiconductors and insulators using density functional theory (DFT) because electronelectron correlations are only approximately take into account and excitonic contributions are neglected. In order to accurately compute photoemisson spectra of the systems of interest, we combine the GW approach with the Bethe-Salpeter equation using GPAW<sup>[7]</sup>.



**Figure 3:** Computed quasiparticle band structure and projected density of states for triazine on a S-defective  $(3 \times 3)$  MoS<sub>2</sub>.

Before an accurate electronic structure can be determined, we optimize the molecular geometries on MoS<sub>2</sub> using DFT with van der Waals correction. In Fig. 2, the optimal geometry of  $C_3H_3N_3$  is shown on S-defective MoS<sub>2</sub>. The molecule adsorbes parallel to the surface and the molecular center is located over an undercoordinated Mo atom. The moleculesurface distance is about 3 Å. The computed electronic band structure and the spin-resolved density of states are plotted in Fig. 3. Adsorbed triazine shows features of a non-magnetic semiconductor and the band structures and DOS are similar for both spin states. We also find that exposure of  $MoS_2$ with triazine has small influence on the band gap which remains unchanged at about 2.6 eV. In Fig. 4, we show the optical absorption spectra for pure pristine and defective MoS<sub>2</sub>, and for C<sub>3</sub>H<sub>3</sub>N<sub>3</sub> adsorbed on defective MoS<sub>2</sub>. In comparison to the pristine surface, S-defects lead to a red shift of the optical spectrum. As a consequence, the exciton



**Figure 4:** Optical absorption spectra for pristine, defective  $MoS_2$  and defective  $MoS_2$  doped by  $C_3H_3N_3$  molecule. Blue lines indicate the optical absorption intensity; red lines indicate the optical band gap; red dashed lines indicate the electronic band gap. Exciton binding energies are indicated in each case.

binding energy reduces slightly. Although adsorption of  $C_3H_3N_3$  had little effect on the electronic band gap, the optical band gap is dramatically affected, and the exciton is strongly stabilized. This suggests a high sensitivity of  $MoS_2$  for triazine adsorption which can be used for its detection.

We will now expand our work by studying the influence of the coverage of the adsorbed molecules, concentrating here on water as adsorbed molecule. Our goal is to provide an effective method for the controlled modulating of excitons in 2D materials via special intermoleculer interaction, which have not been studied by experiment and theory

#### WWW

http://www.bcp.fu-berlin.de/chemie/

## More Information

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