Designing two-dimensional materials by chemical functionalization

Engineering Electronic and Optical Properties of transition metal dichalcogenides Monolayer via Covalent Functionalization

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In Short

- Determination of the favorite functionalized structures on transition metal dichalcogenides with varying functional groups
- Computation of band structures using the GW approximation for improved description of electron-electron correlation
- Calculation of optical spectra using the Bethe-Salpeter-Equation to account for the creation of excitons
- Investigation of the effects arising from covalent functionalization on the binding energy of excitons in transition metal dichalcogenides

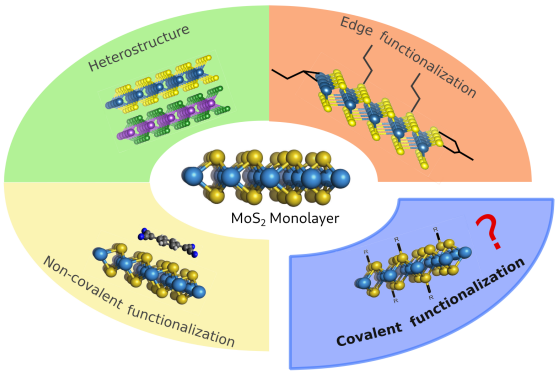

***Figure 1:** Different methods to tune the properties of MoS_2 monolayer.*

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have received much attention due to its outstanding performance as a nanoscale device. Among them, the monolayer MoS_2 is the most readily accessible and chemically stable 2D material. MoS_2 monolayer has different phases characterized by different coordination structures (trigonal, octahedral and distorted octahedral), forming 2H, 1T and 1T'-phases. To further extend the range of properties of MoS_2 monolayer, the pristine MoS_2 monolayer may be modified by edge functionalization[1] or molecular non-covalent functionalization[2], and also by modifying the layer stacking[3] as shown in Figure 1. In general, covalent functionalization is an important route for tailoring the properties of MoS_2 monolayer. However, the MoS_2 monolayer lacks of dangling bond on its basal planes, which greatly reduces its reactivity, thus limiting its application.

Recently, Pérez et al.[4] reported a new method for direct covalent functionalization of 2H-MoS_2 with maleimide derivatives under mild conditions using the soft nucleophilicity of sulfur. Besides, De et al.[5] exploited thiolated ligands to chemically functionalize 2H-MoS_2. These experiments inspire us to further investigate the properties of chemically functionalized 2H-MoS_2. Except for functionalized 2H-MoS_2 monolayer, Miller et al.[6] exfoliated chemically functionalized 1T'-MoS_2 in phenyldiazonium salts, which was measured to have a higher stability when compared with pure 1T-MoS_2. Therefore, a deep theoretical understanding on the changing properties of covalently functionalized 2H- and 1T'-MoS_2, including electronic, optical and excitonic properties, is desired. From the theoretical point of view, it is difficult to accurately model electronic structure and optical absorption spectrum in semiconductors and insulators using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) because they ignore electron-electron correlation and excitonic contributions, respectively. A successful method is GW[7] approximation combined with Bethe-Salpeter Equation[8] on top of DFT calculation (DFT-GW-BSE). The DFT-GW-BSE method based on many-body theory, can accurately calculate the band structure and optical absorption spectrum, which is in good agreement with the experiment and has been applied to a wide variety of systems[9].

Motivated by the success of experiments and the high accuracy of DFT-GW-BSE theoretical method, in this work, we are planning to present theoretical predictions on how the chemical functionalization of the MoS_2 monolayer tunes the electronic, optical and excitonic properties. As shown in Figure 2, the band structure, optical absorption spectrum and exciton binding energy will be investigated in this work. In particular, to gain further insights on the excitonic properties, the spin-orbital coupling induced by the interaction between electron's spin and its orbital motion will be considered to obtain the dark (optical forbidden) and bright (optical allowed) exciton binding energy (see Figure 2). The obtained results will be compared with pure 2H-, 1T- and 1T'-MoS_2 monolayer.

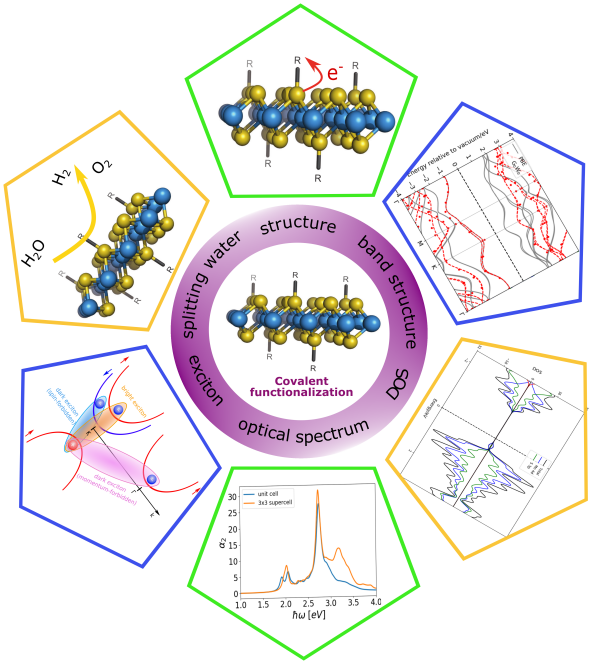

Figure 2: *The properties of covalently functionalized 2H- and 1T'-MoS_2 monolayer to be studied in this work.*

In this work, two main objectives driving this project are as follows: (1) to study the effect of different functional groups on the properties of the MoS_2 monolayer; (2) to explore the effect of different coverages of functional groups on the properties of 2H- and 1T'-MoS_2 monolayer.

Given the dramatic change of band gap from bulk MoS_2 to its monolayer and the sensitivity of exciton in MoS_2 monolayer, we expect that the covalent functionalization with different functional groups at different coverages can provide an effective method to tune the electronic, optical and excitonic properties of the MoS_2 monolayer. In addition, our theoretical study of covalently functionalized MoS_2 monolayer will provide guidance and experience for covalent functionalzation of other TMDs. We believe that our theoretical investigations can stimulate further development and extend the application in the engineering of TMDs.

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More Information

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