Engineering Electronic and Optical Properties of 2D transition metal trichalcogenides

First principle investigation of adsorptions on pristine and defective $MnPX_3$ (X=S, Se) monolayers.

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In Short

- 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 defects on the binding energy of exciton in transition metal trichalcogenides

2D materials have stimulated enormous interests owing to their unique electronic structures and interesting physical and chemical properties (such as 2D magnetic order, superconductivity, and exciting optical properties). Since the discovery of the fascinating properties of graphene, scientists have succeeded in the synthesis or exfoliation from bulk of different 2D materials, like h-BN, silicene, black phosphorene, transition-medal dichalcogenides and many others.

Currently, a series of 2D transition metal trichalcogenides (TMTs) MPX_3 (M = V, Cr, Mn, Fe, Co, Ni and Zn; X = Se and Se) has gained many investigations over their synthesis and optical and electrical properties connected with weak interlayer van der Waals interactions. The crystal of MPX_3 can be easily exfoliated into monolayers, where a single 2D unit consisting of the transition metal atoms shows honeycomb lattice structure similar to that of graphene. It was proposed that they can be used as lowdimensional spin-polarized conductors whose spin character can be tuned by the applied bias, in photocatalysis for the efficient water splitting and hydrogen production as efficient materials for the Li storage, and, for example, the tuning of the vacancy state can lead to the low-dimensional ferromagnetic state.[1]

According to density functional theory (DFT) calculations, the 2D MPX_3 exhibit a variety of magnetic behaviors, which can be modulated through doping or lattice strain effects. These various magnetic functionalities of 2D MPX_3 can be employed for low dimensional spintronic and magnetoelectronic applications. Meanwhile, the wide range of band gaps indicate that 2D MPX_3 compounds can also be considered as promising candidates for clean energy generation, optoelectronic and related water splitting applications.

It is well known that defects (dopants, vacancies, interstitial atoms, etc.) play a significant role in tailoring of 2D materials and controllable modifications can lead to drastic changes of their electronic, magnetic, optical and transport properties.[3] For example, the work in our group shows that great tunability of the excitonic properties of the MoS_2 monolayer by molecular functionalization and defective doping. Also in MPX_3 strongly bound excitations are expected.[4] Although many density functional theory (DFT) calculations have been carried out on the electronic and magnetic properties, the optical properties of pristine and defective 2D MPX_3 and their molecules adsorption and dissociation performance have rarely investigated. According to our results, the band structures calculated by PBE+U+D2 with a value of 2.47 eV for 2D $MnPS_3$ and 1.82 eV for 2D $MnPSe_3$ monolayers both demonstrate semiconductor behaviour and are in the same range as the 3D counterparts. A S/Se defect is not changing the band structure significantly, only lowering the band gap by a small amount of 0.11 eV for $MnPS_3$ and 0.15 eV for $MnPSe_3$, respectively.

Meanwhile, we have performed systematic DFT studies of the initial steps of water adsorption on pristine and chalcogen-defective 2D $MnPX_3$ (X: S, Se)[2], which are shown to be narrow gap semiconductors with a Mott-Hubbard-type conductivity. On pristine monolayers, a molecular adsorption is detected unless the chalcogen vacancy is created and the results obtained for S and Se are almost identical. In the presence of chalcogen vacancies the water splitting is possible. Meanwhile, molecular adsorption is also energetically more favorable in this case. The dissociation pathway is strongly promoted only upon removal of two X atoms from the same chalcogen layer. This can be explained by formation of the strongly localized (in space and in energy) defect state in the density of states of the defective monolayers under study. Furthermore, the MPX_3 monolayers with the vacancy of this type show the improved catalytic activity for the hydrogen evolution reaction.

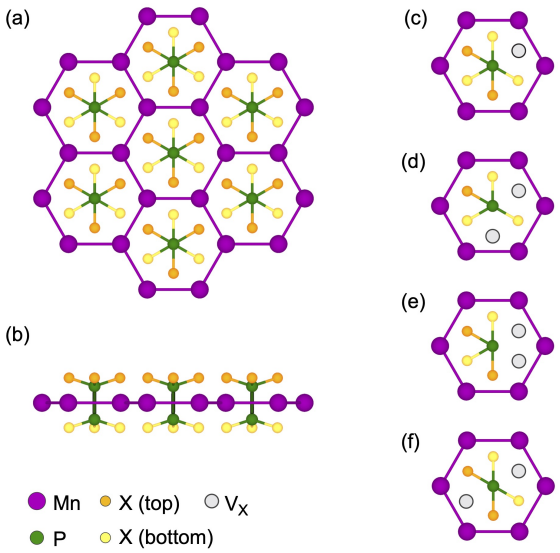

Figure 1: *(a) Top and (b) side views of a single layer of MPX_3. (c-f) Structure of the considered chalcogen defects: c) V_X@1L; d) V_{X2}@1L; e) V_{X2a}@2L; f) V_{X2b}@2L. Spheres of different size/color represent ions of different type.*

Motivated by the success of experimentsand the high accuracy of DFT-GW-BSE theoretical method, we are planning to present theoretical predictions on how the defect and molecules adsorption on the MPX_3 monolayer tunes the electronic, optical and excitonic properties. 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 exciton binding energy.

In conclusion, the unique MPX_3 materials possess exceptional physicochemical characteristics, making them highly suitable for energy conversion and storage applications. Reliable band gap calculations are essential for these applications. In this work, will perform GW calculation to calculate the band structure and use GW-BSE to calculating the optical spectra for the $MnPX_3$ system. Furthermore, we will extend our calculation to encompass the entire MPX_3family,.

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More Information

[1] Samal R, Sanyal G, Chakraborty B, *Journal of Materials Chemistry A* **9**(5), 2560-2591. doi:10.1039/d0ta09752g

[2] Dai, Jiajun, Kangli Wang, Elena Voloshina, Yuriy Dedkov, and Beate Paulus, *ACS Omega* **,** no. 37, 33920–33927, 2023. doi:10.1021/acsomega.3c04677

Project Partners

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