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

- Determination of molecules adsorption on the defective transition metal trichalcogenides
- Investigation of hydrogen evolution reaction (HER) on the defective transition metal trichalcogenides
- 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 and molecules adsorption on the binding energy of excitons 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).[1] 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.[2]

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.

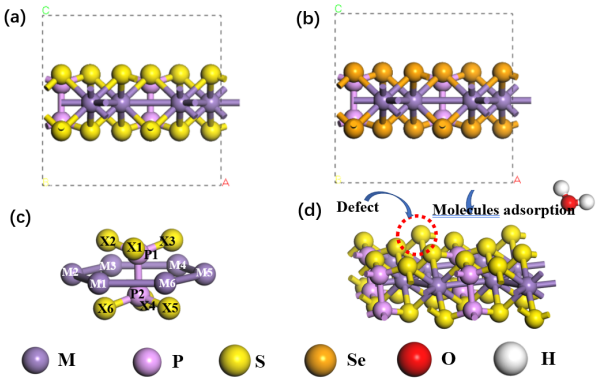

***Figure 1:** structures of (a) MPS_3 and (b) $MPSe_3$. (c) Structure of the M-ion honeycomb lattice and centering bipyramid. (d) Schematic illustration of surface defect and molecules adsorption on MPX_3*

According to our calculation results, the three-dimensional (3D) bulk $MnPS_3$ is in the C2/m space group, while $MnPSe_3$ in $R\bar{3}$. The antiferromagnetic states of $MnPS_3$ and $MnPSe_3$ are apparently more stable compared to their ferromagnetic and nonmagnetic counterparts. The in-plane lattice constant a of the optimized structure highly agreed with the experimental results whereas the interaction between the planes is overestimated by the calculations and results in a slightly underestimated c lattice constant. For 2D $MnPX_3$ monolayere, AFM-Neel state is most stable.

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. Considering various high-symmetry adsorption sites and adsorption orientations, the adsorption and dissociative behavior of water molecules on prinstine and defective $MnPX_3$ (X= S or Se) monolayers were investigated. According to our calculation results, water molecules prefer to bond with the defective monolayers at the defect site. With the introduction of defect on monolayer, the adsorption of water molecule become significantly stronger, with -0.645 eV for $MnPS_3$ and -0.344 eV for $MnPSe_3$, respectively. After finishing the caluclation of water adsorption and dissociation on different monolaye,we want to apply our system as electrocatalysts in the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). We will start with HER in this funding period. This would reveal the underlying mechanism and pave the way for more exciting experimental investigations on these promising materials.

Meanwhile, Motivated by the success of experimentsand the high accuracy of DFT-GW-BSE theoretical method,[5] 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 this work, three main objectives driving this project are as follows: (1) to study the effect of defect on the properties of the MPX_3 monolayer; (2) to explore the effect of molecules adsorption on the properties of MPX_3 monolayer; (3) to investigate the HER on pristine and defective monolayer. We believe that our investigations can stimulate further development and extend the application in the engineering of MPX_3.

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More Information

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