Band Structure Engineering of Monolayer MoS₂ by Surface Ligand Functionalization

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Monolayer transition metal dicalcogenide (TMDC) materials are currently attracting extensive attention due to their distinctive electronic, transport, and optical properties. For example, monolayer MoS₂ exhibits a direct band gap in the visible frequency range, which makes it an attractive candidate for the photocatalytic water splitting. For the photoelectrochemical water splitting, the appropriate band edge positions that overlap with the water redox potential are necessary. Similarly, appropriate band edge alignments will be crucial for the light emitting diode and photovoltaic applications utilizing heterojunctions between two TMDC materials. Carrying out first-principles calculations, we here investigate how the band edges of MoS₂ can be adjusted by surface ligand functionalization. This study will provide useful information for the realization of ligand-based band engineering of monolayer MoS₂ for various electronic, energy, and bio device applications.

INTRODUCTION

Monolayer transition metal dicalcogenide (TMDC) materials are currently attracting extensive attention. Therefore, searching for and engineering efficient and TMDC is still a hot research topic. Recently, molybdenum disulfide (MoS2) has been extensively investigated. It is a layered hexagonal structure with a weak van der Waals interaction between individual sandwiched S-Mo-S layers. Bulk MoS₂ has an indirect band gap of 1.2eV. Monolayer MoS₂ (ML-MoS₂) has a direct band gap of ~1.8eV, which is ideal for solar energy absorption. It was reported that the mobility of MoS2 can even be as large as 200cm²V⁻¹s⁻¹ at room temperature, although much lower values were obtained in other experiments which might originate from the existence of short-range surface defects. Moreover ML-MoS₂ exhibits high electrocatalytic activity and stability for the hydrogen evolution reaction (HER) in acidic environments. These advantages make ML-MoS₂ a potential candidate for PEC water splitting. Similarly, appropriate band level alignments will be crucial for the light emitting diode and photovoltaic applications utilizing heterojunctions between two TMDC materials. In this article, I investigate how the band edges of MoS₂ can be adjusted by surface ligand functionalization. My calculations show that useful information for the realization of ligand-based band engineering of ML-MoS₂ for various electronic, energy, and bio device applications.

CALCULATION METHODS

Using the LCAODFTLab of EDISON Nanophysics, density functional theory (DFT) calculations were performed. All atomic positions and lattice constants were optimized until the Hellmann-Feynman...
Forces acting on each atom and the total energy change were less than 0.02eV and 0.0001eV, respectively. The calculated lattice constants ($a = b = 3.13 \text{ Å}$) of monolayer MoS$_2$ are in fair agreement with the experimental values ($a = b = 3.16 \text{ Å}$). ML-MoS$_2$ was formed by cleaving the surface of bulk MoS$_2$ and incorporating a vacuum larger than 15 Å to ensure decoupling between neighboring slabs. As shown in Figure 1, a 2 X 2 super cell was used to select suitable ligands for surface functionalization. The local density approximation (LDA) was implemented for the exchange correlation functional. The Monkhorst-Pack $k$-point was used for integration over the first Brillouin zone. 10 X 10 X 1 k-point meshes were adopted for geometry optimization and electronic structure calculations, respectively.

**RESULTS AND DISCUSSION**

As shown in Figure 2(a), the calculated band gap of ML-MoS$_2$ is 1.85 eV. Both VBM and CBM are composed mainly of Mo 4d and slightly of S 3p states, and the VBM is below the water oxidation level, whereas the CBM is located below the hydrogen redox potential. The calculation details of the average electrostatic potential and band edge positions of ML-MoS$_2$ are given in the ESI. These results are all in good agreement with the experimental values. We first consider the surface...
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CONCLUSION

In this paper, based on electronic structure calculations and analysis of band edge alignments, we have demonstrated that ML-MoS$_2$ functionalized with ligand is an effective strategy
for engineering the band gap of MoS$_2$ to TMDC materials. I found that the ligand functionalization slightly influences the band gap of MoS$_2$ but greatly affects its band edge positions.

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