Band Structure Engineering of Monolayer MoS_2 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 MoS_2 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 level alignments will be crucial for the light emitting diode and photovoltaic applications utlizing heterojunctions between two TMDC materials. Carrying out first-principles calculations, we here investigate how the band edges of MoS_2 can be adjusted by surface ligand functionalization. This study will provide useful information for the realization of ligand-based band engineering of monolayer MoS_2 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 MoS_2 has an indirect band gap of 1.2eV. Monolayer MoS_2 (ML-MoS_2) 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 $200cm^2V^{-1}s^{-1}$ 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-MoS_2 exhibits high electrocatalytic activity and stability for the hydrogen evolution reaction (HER) in acidic environments. These advantages make ML-MoS_2 a potential candidate for PEC water splitting. Similarly, appropriate band level alignments will be crucial for the light emitting diode and photovoltaic applications utlizing heterojunctions between two TMDC materials. In this article, I investigate how the band edges of MoS_2 can be adjusted by surface ligand functionalization. My calculations show that useful information for the realization of ligand-based band engineering of ML-MoS_2 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 consta nts were optimized until the Hellmann-Feynman

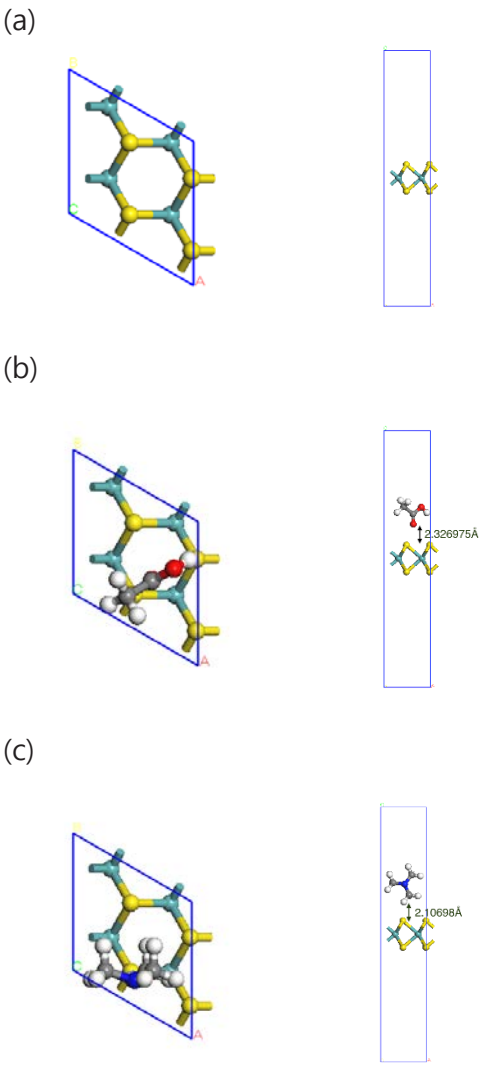


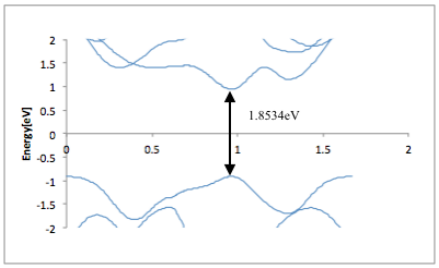
Fig. 33. Top and side views of (a) MoS_2, (b) CA on a 2 X 2 ML-MoS_2, (c) NMe_3 on a 2 X 2 ML-MoS_2, (d) PA on a 2 X 2 ML-MoS_2 , (e) PO on 2 X 2 ML-MoS_2

forces acting on each atom and the total energy c hange were less than 0.02eV and 0.0001eV, respec tively. The calculated lattice constants (a = b= 3.13 Å) of monolayer MoS_2 are in fair agreement with the experimental values (a = b = 3.16 Å). ML-MoS_2 was formed by cleaving form 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 functio nalization. The local density approximation (LDA) was implemented for the exchange correlation fun ctional. The Monkhorst-Pack k-point was used for integration over the first Brillou in zone. 10 X 10 X 1 k-point meshes were adopted for geometry optimiz ation and electronic structure calculations, respecti vely.

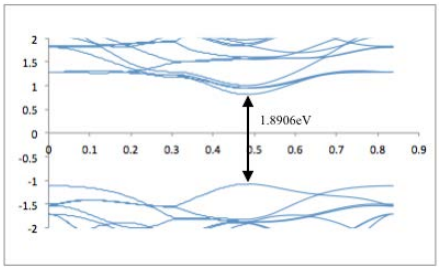
RESULTS AND DISCUSSION

As shown in Figure 2(a), the calculated band gap of ML-MoS2 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

(a)



(b)



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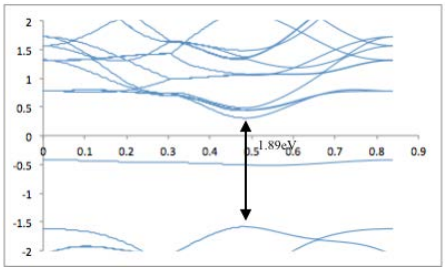

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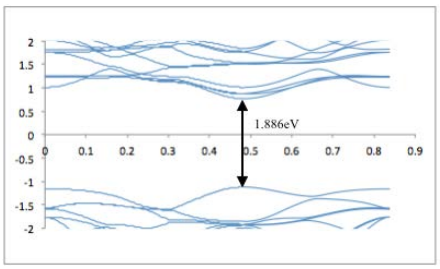

(e)

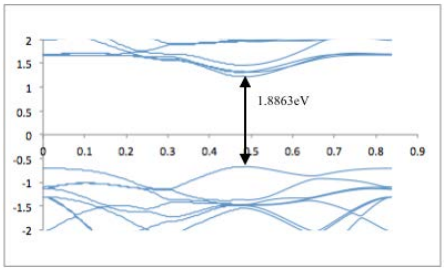

Fig. 2. Top and side views of (a) MoS_2, (b) CA on a 2 X 2 ML- MoS_2, (c) NMe_3 on a 2 X 2 ML-MoS_2, (d) PA on a 2 X 2 ML-MoS_2, (e) PO on 2 X 2 ML-MoS_2

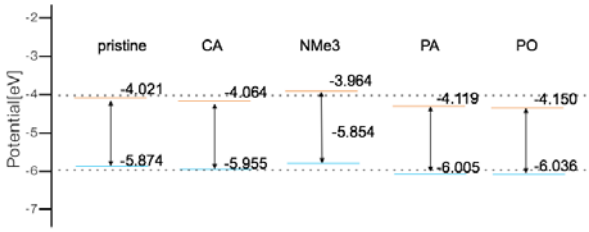

Fig. 3. Calculated band edge positions of MoS2, CA, NMe3, PA and PO-functionalized MoS2

functionalization of ML-MoS2 by various ligand groups, including CA, NMe3, PA, PO, to determine the most suitable surface functionalization ligand. For CA, NMe_3, PA, PO, no chemical bond is formed between the ligand and the surface and distance between them is about 2 Å. The band structure of MoS_2 are displayed in Figure 2. Figure 3 displays the band edge positions of these ligand-funcionalized MoS_2. As is clearly seen from the figure, no overlapping is observed between the ligands and MoS_2, reflecting the weak interaction between ligand and MoS_2. Interestingly, although the charge transfer between the ligands and the surface is very small, we observe charge transfer from MoS_2 to CA and from PA and PO to MoS_2.

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.

ACKNOWLEDGEMENT

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