

Theoretical Study on Tuning Band Gap and Electronic Properties of Atomically Thin Nanostructured MoS₂/Metal Cluster Heterostructures

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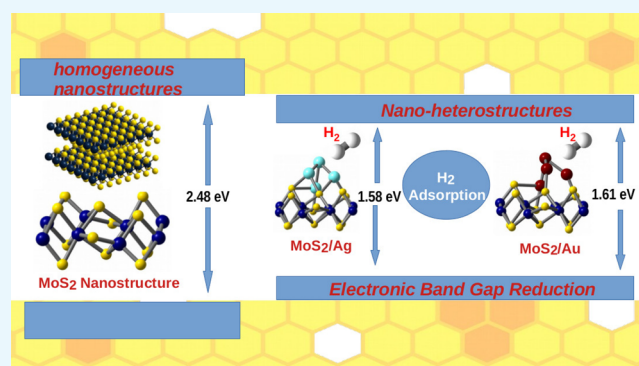


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Supporting Information

ABSTRACT: Nano-heterostructures have attracted immense attention recently due to their remarkable interfacial properties determined by the heterointerface of different nanostructures. Here, using first-principles density functional theory (DFT) calculations, we examine what range the variable electronic properties such as the electronic band gap can be tuned by combining two dissimilar nanostructures consisting of atomically thin nanostructured MoS₂ clusters with small silver and gold nanoparticles (Ag/Au NPs). Most interestingly, our calculations show that the electronic band gap of the nanostructured MoS₂ cluster can be tuned from 2.48 to 1.58 and 1.61 eV, by the formation of heterostructures with silver and gold metal nano-clusters, respectively. This band gap is ideal for various applications ranging from flexible nanoelectronics to nanophotonics applications. Furthermore, the adsorption of H₂ molecules on both nano-heterostructures is investigated, and the computed binding energies are found to be within the desirable range. The reported theoretical results provide inspiration for engineering various optoelectronic applications for nanostructured MoS₂-based heterostructures.



1. INTRODUCTION

Among the various tunable band gap transition metal dichalcogenides (TMDs), monolayer and nanostructured molybdenum disulfides (MoS₂) are promising materials and attracted increasing attention recently because of its excellent physical, chemical, and optical properties.^{1–3} These advantageous properties have provided a solid basis for the fabrication of various MoS₂-based nanoscale electronics and optoelectronic applications.^{4–6} In contrast to multilayer MoS₂, monolayer or nanostructured MoS₂ has tunable band structures with band gaps about 1–2 eV.^{7–10} The modulation of the band gap of monolayer and nanostructured MoS₂ could be beneficial for a wide variety of applications. These include high catalytic activity,¹¹ water splitting reactions,¹² hydrogen evolution reaction catalysts,¹³ energy-efficient optoelectronic devices,¹⁴ photovoltaics,¹⁵ and heterogeneous catalysis.¹⁶

Recently, numerous studies have demonstrated that the electronic structure, the band gap, the energy levels, and the associated optoelectronic properties of monolayer and nanostructured MoS₂ can be well tuned (e.g., range from 1.0 to 2.0 eV) by a variety of physical and chemical parameters,¹⁷ e.g., via chemical doping,¹⁸ chemical modification,¹⁹ defect engineering,²⁰ foreigner species intercalation,²¹ strain engineering,²² and heterostructure construction.²³ Among the various

approaches mentioned, nano-heterostructures have attracted great attention due to significant interest in fundamental research as well as many practical applications because of their unique chemical and physical properties.^{23,24} Combining different nanomaterials in intelligent and effective ways into a single structure results in nano-heterostructures. Further, more nano-heterostructures of diverse nanomaterials are specifically designed^{25,26} for smart optoelectronic device applications. In recent years, to tune the band gap and realign the energy levels in MoS₂-based nano-heterostructures and to enhance optoelectronic and photocatalytic device performances have been intensively investigated both experimentally and theoretically.^{27–30} The interfacial interactions in atomically thin nanostructured MoS₂-based heterostructures dominate the chemical, physical, and interfacial properties.³¹ However, such interfacial properties are not yet understood very well and

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need further theoretical and experimental study for designing new nano-heterostructures.

In the present study, with the goal of understanding the electronic and interfacial properties of nanostructured MoS₂ and the interfacial properties of MoS₂-Ag/Au nano-heterostructures, we have carried out first-principles density functional theory (DFT) calculations. We reported the DFT-optimized ground-state structures, electronic properties, the HOMO-LUMO (highest-occupied molecular orbital to lowest-unoccupied molecular orbital) gap (E_g), and binding energy of MoS₂-based respective heterostructures. Herein, we are particularly interested in exploring how the HOMO-LUMO gap changes with the formation of different nano-heterostructures, leading to applications in the tunable HOMO-LUMO band gap, which allows great flexibility and novel opportunities in design and optimization of nanoelectronic and optoelectronic properties beyond those of homogeneous materials. Most interestingly, our theoretical calculations indicated that the band gap and interfacial properties of the studied atomically thin nanostructured MoS₂-based heterostructures can be well tuned by even 0.9 eV with small silver and gold nanoparticles. Subsequently, we have investigated H₂ adsorption on both nano-heterostructures in terms of adsorption energy. It is found that the calculated adsorption energies are close to the energies required for H₂ storage applications. The present results are beneficial to supply theoretical guidance on synthesizing efficient MoS₂-Ag/Au nano-heterostructures for the use of future various nanoscale optoelectronic applications.

2. COMPUTATIONAL METHODS

In common practices, theoretical modeling of the homogeneous nanostructures involves constructing a super cell and performing periodic boundary condition (PBC) calculations with LDA or GGA DFT functionals, which can reproduce the results of experimental analysis with reasonable accuracy. However, nano-heterostructures, which consist of multiple materials, result in non periodic structures often, and hence, performing PBC calculations became a difficult task. Herein, the theoretical analysis of geometries and energies of atomically thin nanostructured MoS₂ clusters and both nano-heterostructures MoS₂-Au and MoS₂-Ag has been performed in the framework of ab initio density functional theory with the PBE^{32,33} (Perdew–Burke–Ernzerhof hybrid) functional and the LANL2DZ basis set. It is generally accepted that the PBE functional exhibits better performance for nanostructured semiconducting clusters and solids.³⁴ For all DFT calculations, we used the Gaussian 09 software package.³⁵ We performed full geometry optimization followed by frequency calculations done for all nanostructured systems to confirm that these geometries are minima on their respective potential energy surface. Single-point energy calculations on PBE0-optimized geometries with the HSEH1PBE functional were also performed at the LANL2DZ level. To reduce the computational complexity involved in the DFT calculations, we have reduced the size of the system to the following: for nanostructured MoS₂, Mo₈S₁₂ is used; for the silver/MoS₂ heterostructure, Ag₄/Mo₈S₁₂; and for the gold/MoS₂ heterostructure, Au₄/Mo₈S₁₂, respectively. The geometric, electronic, and interfacial properties were computed on the optimized structures.

3. RESULTS AND DISCUSSION

In this study, our focus will be on the design of novel nano-heterostructures with tuned optoelectronic properties, formed by the atomically thin nanostructured MoS₂ cluster with silver and gold nanoclusters. To shed light on the molecular, electronic, and interfacial properties of MoS₂-Ag/Au nano-heterostructures, we have performed ab initio DFT calculations using the PBE0 functional and the LANL2DZ basis set. Initially, we have optimized the nanostructured Mo₈S₁₂ cluster and calculated the optoelectronic properties. The Mo–S bond length in the central zones of our optimized structure predicted a value of 2.51 Å, which is in good agreement with the experimental values^{36,37} of 2.41 ± 0.06 and 2.41 Å, respectively. The calculated Mo–Mo bond length value is 3.13 Å, which showed an excellent agreement with the recent estimation of 3.16 Å, obtained from the grazing incidence extended X-ray fine structure value of MoS₂ films.³⁷

To compute the stability of the nano-heterostructures, we calculated the binding energy for the MoS₂-Ag/Au heterostructures defined by the following equation

$$E_{\text{bind}} = E_{\text{MoS}_2\text{-Ag/Au}} - (E_{\text{MoS}_2} + E_{\text{Ag/Au}}) + E_{\text{BSSE}} \quad (1)$$

where E_{bind} is the total binding energy of MoS₂-Ag/Au nano-heterostructures with BSSE³⁸ correction. In eq 1, $E_{\text{MoS}_2\text{-Ag/Au}}$, E_{MoS_2} , and $E_{\text{Ag/Au}}$ are the total energies of the respective optimized structures. The binding energies of Ag₄/Mo₈S₁₂ and Au₄/Mo₈S₁₂ heterostructures were computed to be −4.63 and −3.90 eV, respectively. These negative binding energies indicate that the optimized nano-heterostructures are stable and energy-favorable and also indicate the weak covalent interactions present in the systems. The observed weak covalent interactions between the nanostructures are consistent with that reported in the recent studies,^{26,39} where the TMD-based nanostructures can effectively functionalize through covalent interactions. Moreover, the adsorption of silver and gold clusters on the MoS₂ system leads to the stable nano-heterostructures, and results are in line with previous MoS₂-based studies.^{40–43} In the nano-heterostructures, the computed nearest Ag–Mo distance in Ag₄/Mo₈S₁₂ is found to be 3.27 Å, and Au–Mo distance in Au₄/Mo₈S₁₂ is 3.1 Å; the calculated average Ag–S and Au–S bond lengths are 2.64 and 2.62 Å, respectively. Our calculations reveal that the binding energy of a Ag–MoS₂ heterostructure is higher than the binding energy of a Au–MoS₂ heterostructure.

The electronic properties, chemical bonding nature, and the electronic band gap tunability of MoS₂-Ag/Au nano-heterostructures consisting of atomically thin nanostructured MoS₂ clusters with small silver and gold nanoparticles depend on the electronic energy level alignment between the different nanoclusters. Thus, in such nano-heterostructure interactions, the properties mainly depend on the energetic offsets between the HOMO and LUMO orbitals of the different nano-heterostructures. It is helpful to understand what the HOMO and LUMO levels represent. In individual molecules or nanoclusters, the HOMO energy (minus) corresponds exactly to the amount of energy required to remove an electron from the molecule or nanocluster (vertical ionization potential), while the LUMO energy (minus) level corresponds to the amount of energy required to add an electron to the molecule/cluster (vertical electron affinity). However, in solid-state materials, the large number of involved orbitals leads to the concept of bands, the valence band (VB) and conduction

bands (CB). In general, the formation of solid-state bands (VB or CB) is closely related to HOMO and LUMO levels. Moreover, it was found that both HOMO and LUMO have significant contributions to the formation of the conduction band and valence bands. Thus, heterostructure interactions and properties are closely related to molecular orbital distribution, HOMO/LUMO energy levels, and band gaps (E_g s, difference in energy between HOMO and LUMO). However, the band gaps of TMD-based nanomaterials as obtained from the Kohn–Sham HOMO-LUMO gaps (within the density functional framework) are significantly smaller with respect to experimental fundamental band gaps. This is known as the well-known band gap problem. Over the past decades, there were a lot of approaches to solve the fundamental band gap problem,^{44,45} within the DFT framework, but they are beyond the scope of the present study.

For new nano-heterostructured materials, it is important to study their electronic structures. Here, we study how the structural energies and HOMO-LUMO gaps of MoS₂ clusters are altered by new heterostructures made of silver and gold. Table 1 shows the computed HOMO and LUMO level

Table 1. The Computed HOMO and LUMO Level Energies and the Energy Gap (in eV) for the Studied Systems: MoS₂, Ag-MoS₂, and Au-MoS₂^d

studied systems	HOMO (eV)	LUMO (eV)	E_g (eV)
Mo ₈ S ₁₂	-6.30	-3.82	2.48, 1.1–2.7 ^a , 1.88 ^b , 2.48 ^c
Ag ₄ /Mo ₈ S ₁₂	-5.11	-3.53	1.58
Au ₄ /Mo ₈ S ₁₂	-5.37	-3.76	1.61

^aRef 46, the range of energy gap values obtained with the different DFT functionals. ^bRef 47, obtained from experimental photo-conductivity spectra. ^cRef 12, G₀W₀ calculation. ^dEnergy values are obtained by the DFT-PBE0/LANL2DZ level of theory.

energies and the energy gap, for the studied systems: MoS₂, MoS₂-Ag, and MoS₂-Au. Figure 1a,b presents the optimized structure and HOMO-LUMO plots of nanostructured MoS₂. For the cluster Mo₈S₁₂, we have obtained a HOMO-LUMO gap value of 2.48 eV from DFT-PBE0/LANL2DZ calculation (a value of 1.74 eV obtained via single-point calculation with the HSEH1PBE/LANL2DZ level of theory). This result is in

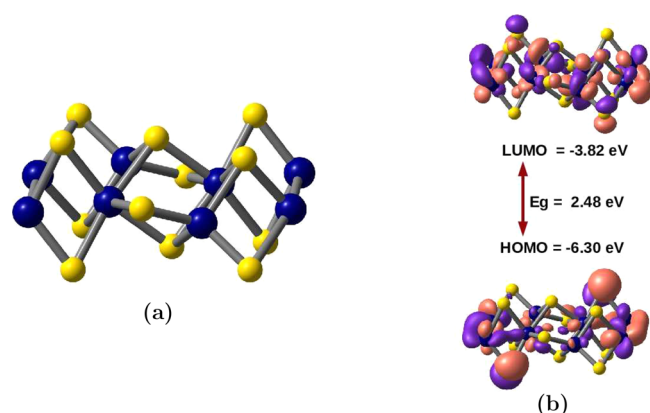


Figure 1. (a) DFT-PBE0/LANL2DZ-optimized model structure of monolayer MoS₂ and (b) energies, electronic band gap (E_g), and HOMO and LUMO orbitals of the MoS₂ cluster calculated at the DFT-PBE0/LANL2DZ level of theory.

good agreement with the recent theoretical estimate of Wang et al.,⁴⁶ who have obtained a range of HOMO-LUMO gap values, 1.1–2.7 eV, with the different DFT functional (B3LYP and PW91) calculations for various nanostructured MoS₂-based clusters. Similarly, our result is in reasonable agreement with the band gap value of 1.88 eV, derived from photo-conductivity spectra reported for a large MoS₂ nanostructured sheet by Mak et al.⁴⁷ Our result is also in good agreement with the theoretical band gap prediction of 2.48 eV from a G₀W₀ calculation⁴⁸ and 2.02 eV from an HSE theoretical estimate.¹²

Figure 2a,b presents the minimum energy structure and HOMO-LUMO plots of the MoS₂-Ag heterostructure. Figure

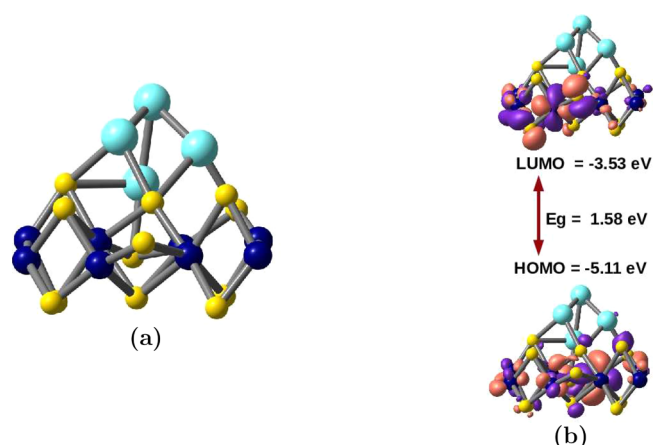


Figure 2. (a) DFT-PBE0/LANL2DZ-optimized model structure of the Ag-MoS₂ nanostructure and (b) frontier orbitals, the orbital energies, and electronic band gap (E_g) of the corresponding structure.

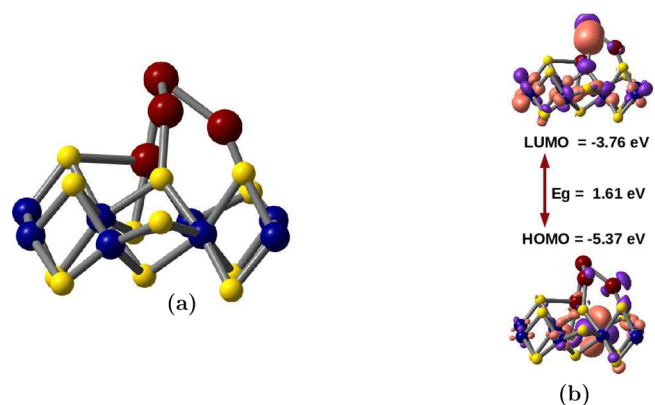


Figure 3. (a) DFT-PBE0/LANL2DZ-optimized model structure of the Au-MoS₂ nanostructure and (b) orbital energies, electronic band gap (E_g), and HOMO and LUMO orbitals of the Au-MoS₂ calculated at the DFT-PBE0/LANL2DZ level of theory.

3a,b presents the optimized structure and HOMO-LUMO plots of the MoS₂-Au heterostructure. Our calculations show that the electronic band gap highly depends on the HOMO-LUMO gap of the heterostructure system. For example, the electronic band gap of the Mo₈S₁₂ nanostructured cluster can be changed from 2.48 eV to even a low value of 1.58 eV by Ag₄/Mo₈S₁₂ and 1.61 eV by Au₄/Mo₈S₁₂ hetero-nanostructures, respectively. Values of 0.9 and 0.92 eV have also been obtained via single-point calculations with the HSEH1PBE/

LANL2DZ level of theory. The formation of weak covalent interactions between the nanostructures reduces the molecular HOMO-LUMO gap significantly. The range of tunable band gap values obtained in this study is 0.9 and 0.87 eV, respectively. Thus, the tunable electronic band gap results show an excellent agreement with an experimental⁴⁹ estimate of 0.85 eV by Huang et al., from an unexpected band gap tunability obtained with distance against the single layer MoS₂ grain boundary. The density of state (DOS) calculations for nanostructured MoS₂, the silver/MoS₂ heterostructure, and the gold/MoS₂ heterostructure are given in the Supporting Information.

For the application prospect, we have used density functional theory to investigate the adsorption of molecular hydrogen on both the nano-heterostructures (based on the optimized nano-heterostructures) within the framework of the DFT-PBE0/LANL2DZ method. Herein, we are particularly interested in understanding the binding energy of the hydrogen adsorption process (however, in this preliminary study, other important parameters like orientation, different adsorption sites, etc. are not included). The adsorption energy (E_{ads}) is calculated by the following equation

$$E_{\text{ads}} = E_{(\text{heterostructure}+\text{H}_2)} - E_{\text{heterostructure}} - E_{\text{H}_2} \quad (2)$$

The calculations give the adsorption values of MoS₂-Au and MoS₂-Ag nano-heterostructures, which are -0.1 and -0.11 eV, respectively, and are in good agreement with the most acceptable energy limits of 0.1–0.2 eV for the hydrogen adsorption values predicted previously.^{50,51} It can be seen that the adsorption energies (E_{ads}) obtained are negative; this indicates stable adsorption (a positive value indicates instability) and predicted a lower adsorption energy theoretically. It is found that hydrogen molecule adsorption on the heterostructures originates from the vdW interactions. Based on DFT calculations, we found that Ag and Au NPs bind strongly with nanostructured MoS₂ and further serve as a binding center for H₂ molecules with a good adsorption energy lying between the accepted energy range reported previously.^{50,51}

Thus, the results suggest that the MoS₂-Ag and MoS₂-Au nano-heterostructures are beneficial to improve the application of nanostructured MoS₂ and make it interesting for different optoelectronic device applications through the tunable band gap.^{1–3,52,53} Moreover, our first-principles density functional theory calculation results can provide guidance for discovering and designing new nanostructured dichalcogenide-based heterostructures.

4. CONCLUSIONS

In summary, we have performed ab initio DFT calculation to study the structural, electronic, and interfacial properties of MoS₂-Ag/Au nano-heterostructures. The higher binding energy calculated at the optimized nano-heterostructures and the average bond lengths (Ag–S and Au–S) indicate that both the nano-heterostructures are stable. The electronic band gap of atomically thin nanostructured MoS₂ clusters shows tunability with forming heterostructures with silver and gold. Most interestingly, our DFT calculations show that the band gap of nanostructured MoS₂ clusters can be tuned from 2.48 to 1.58 and 1.61 eV with silver and gold heterostructures, respectively. Moreover, our findings showed that H₂ molecules can be adsorbed on nano-heterostructures through an appropriate range of adsorption energy. In this work, our

results based on DFT calculations and the electronic structures of nanostructured MoS₂ clusters as well as MoS₂-Ag/Au nano-heterostructures serve as models for nanostructured MoS₂ and MoS₂-based heterostructures and provide a new way for designing and applications in future MoS₂-based nanodevices with controllable band gaps.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c05274>.

Density of state (DOS) calculations of the nanostructured structures: (Figure S1) MoS₂, (Figure S2) silver/MoS₂ heterostructure, and (Figure S3) gold/MoS₂ heterostructure (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All the authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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