

PHOTO-SWITCHABLE OPTICAL PROPERTY OF TWO-DIMENSIONAL TRANSITION METAL DICHALCOGENIDES

Connor Cunningham¹, Srajan Pillai¹, Jeong Ho You¹, Jaehoon Ji², Jong Hyun Choi²

¹ Department of Mechanical Engineering, University of St. Thomas, St. Paul, MN 55105, USA

² School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907, USA

ABSTRACT

Transition metal dichalcogenides (TMDCs) have received much attention for optoelectronic applications because of their band gap transition from indirect to direct as they decrease from multilayer to monolayer. Recent studies have experimented with the use of photochromic molecules to optically control the charge transport of two-dimensional (2D) TMDCs. In this work, a numerical study using density functional theory has been performed to test the possibility to control the optical property of 2D TMDC monolayers with various photochromic molecules. When the photochromic molecule's highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) energy levels are within the band gap of 2D TMDC

monolayers, holes or electrons will transport to the photochromic molecules, resulting in the reduction of excitons in the 2D TMDC monolayers. The reduced optical response can be recovered by going through reverse isomerization of the photochromic molecules. Molybdenum disulfide (MoS₂) and tungsten diselenide (WSe₂) monolayers were tested with various photochromic molecules including azobenzene, spiropyran, and diarylethenes (DAE 2 ethyl, DAE 5 ethyl, DAE 5 methyl). The systematic study presented in this work displays that MoS₂-Spiropyran and every diarylethene derivative used in this study except MoS₂-DAE 5 methyl exhibited photo-switchable behavior.

Keywords: Transition metal dichalcogenides; two-dimensional monolayers; photochromic isomerization; density functional theory

1. INTRODUCTION

While graphene is well known for its many fascinating properties such as high hardness and electrical conductivity, the search for two-dimensional materials with semiconducting properties has been sparked by graphene's lack of an electronic band gap [1]. Transition metal dichalcogenides (TMDCs) represent an intriguing alternative to graphene due to their potential to have an electronic band gap. TMDCs are identified by the formula MX₂, where M is a transition metal atom and X is a chalcogen atom. MX₂ has a layer structure consisting of three atomic stacks as chalcogen-transition metal-chalcogen as shown in Fig. 1. For multilayers, the in-plane position of M atoms in one layer are aligned with one of X atoms in the adjacent layer [2]. Layers in TMDCs are bound together by van der Waals forces while the M-X atoms in a layer are covalently bound.

The TMDC family contains semiconductors (such as MoS₂, WSe₂), metals (such as MoTe₂), and superconductors (such as NbS₂, NbSe₂) due to the abundant atomic combinations and rich phases including trigonal symmetry, hexagonal symmetry, and rhombohedral symmetry. Semiconducting molybdenum and tungsten TMDCs are particularly intriguing prospects for electrical and optoelectronic applications because their band gap energies span the visible and near-infrared regions of the electromagnetic spectrum [3,4]. For example, TMDCs make excellent candidates for solar cells, photodetectors, light-emitting diodes, and phototransistors [5]. Additionally, they can be used for special applications such as flexible devices, tunneling devices, and valley and spin electronics [6]. Multifunctional devices are also being created from 2D materials and related hybrid systems [7].

The characteristic of band gap of TMDCs depends on the number of layers. Bulk TMDCs typically have an indirect

band gap, while a TMDC monolayer has a direct band gap. For example, bulk MoS₂ has an indirect band gap of ~1.2 eV. The indirect band gap is between the valence band maximum (VBM) at the Γ point and the conduction band minimum (CBM) between Γ -K. A monolayer of MoS₂ has a direct band gap of ~1.8 eV with both VBM and CBM at the K point [8,9]. Due to the direct band gap, the high light emitting efficiency makes TMDC monolayers promising for new optoelectronic device applications [10].

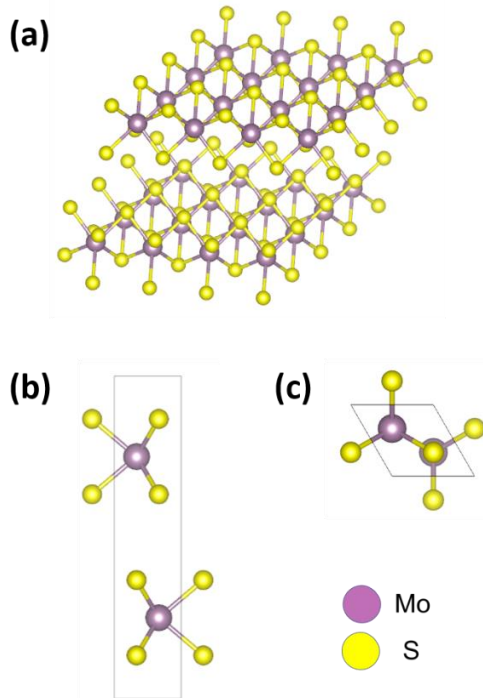


FIGURE 1: ATOMIC STRUCTURE OF MoS₂. (A) PERSPECTIVE VIEW (B) SIDE VIEW AND (C) TOP VIEW.

Photochromism is a phenomenon that describes when a chemical species undergoes a reversible photo transformation into two separate forms with distinct absorption spectra. Photochromic processes are often unimolecular or bimolecular in nature [11]. Therefore, photochromic molecules switch between isomers with distinct energy levels when irradiated with ultraviolet (UV) or visible light. These photoinduced and reversible changes in molecular properties result in considerable changes in macroscopic features. For instance, the photoinduced interconversion of one state of a photochromic material into another is typically accompanied by significant structural alterations. In fact, the interconversion of a photochromic system within a liquid solution or a rigid polymer or a crystal could change the color and refractive index of the overall material. As a result, photonic materials with distinct behavior can be developed based on the photo-responsive features of photochromic compounds [12]. Many photonic devices, such as erasable optical memory and photo optical switch components, can benefit from these molecular property changes [11].

Figure 2 shows the structural change of spiropyran involved with the photochromism phenomenon. When exposed to UV light, the spiropyran ring unfolds its closed ring structure (Fig. 2a) and becomes an open ring structure (Fig. 2b). The open ring isomer is thermally unstable and will revert back to the original closed ring even without visible light irradiation [11].

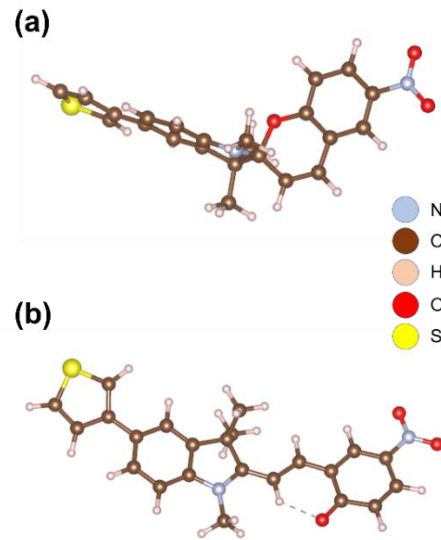


FIGURE 2: ATOMIC STRUCTURE OF SPIROPYRAN. (A) CLOSED ISOMER (VISIBLE LIGHT IRRADIATION) (B) OPEN ISOMER (UV LIGHT IRRADIATION).

Comparatively, when exposed to ultraviolet light, the open diarylethene (DAE) ring transforms to its closed isomer. Photoinduced cis/trans isomerization, as an alternative to ring opening and shutting processes, can also be used to implement photochromic changes. For example, when exposed to ultraviolet light, trans-azobenzene converts to the cis isomer.

In addition to structural changes, photochromism initiates significant alterations of electronic states of molecules. Placing photochromic molecules on 2D semiconductors has demonstrated the feasibility of photo-induced charge modulation in the semiconductors via tuning the electronic energy levels of molecules [13].

In this study, we present computational work for hybrid devices containing a TMDC monolayer and a photochromic molecule to test the controllability of optical response through photo-induced charge transfer. To be able to modulate the charge transfer in the TMDC monolayer, the switchable energy levels of photochromic molecules with respect to the CBM and VBM is critical. This systematic study with various TMDC monolayers and photochromic molecules will provide a material selection guide for hybrid devices with photo-switchable optical properties.

2. METHODS

Although many photochromic molecules exist, three of the most popular families were chosen in order to see their varying effects with the TMDC monolayers. Two of the families, azobenzene and spiropyran, can undergo isomerization due to either thermal or optical stimuli. The third family, diarylethene, is not affected by thermal fluctuations, making them more preferred for optoelectronic applications [11]. For this reason, more molecules in the diarylethene family were selected to be part of this study.

To investigate the feasibility of photo-switchable optical properties in hybrid devices, density functional theory (DFT) calculations were performed using Vienna Ab initio Simulation Package (VASP) [14,15]. All DFT calculations were carried out with the generalized gradient approximation in the form of Perdew-Burke-Ernzerhof (PBE) functional, and projector augmented wave (PAW) potentials [16]. The van der Waals force between TMDCs and photochromic molecules was included [17]. All ionic positions were relaxed until all Hellmann-Feynman forces were smaller than 10 mV/Å.

3. RESULTS AND DISCUSSION

Five different photochromic molecules were used for this study: Azobenzene, Spiropyran, 1,2-bis(2-ethyl-5-phenyl-3-thienyl) perfluorocyclopentene (DAE 2 ethyl), 1,2-bis(5-ethyl-2-phenyl-4-thiazolyl) perfluorocyclopentene (DAE 5 ethyl), and 1,2-bis(5-methyl-2-phenyl-4-thiazolyl) perfluorocyclopentene (DAE 5 methyl) [11]. All these molecules in open chain and closed chain forms were paired with a monolayer of MoS₂ and WSe₂. The photochromic molecule was overlaid over the 2D TMDC monolayer as shown in Fig. 3.

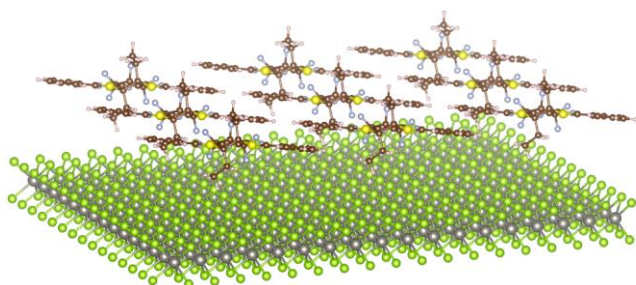


FIGURE 3: TWO-DIMENSIONAL WSe₂ MONOLAYER AND PHOTOCHROMIC DAE 5 ETHYL IN A CLOSED FORM.

The possibility to control the optical properties relies on the relative energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the photochromic molecule isomer in relation to the VBM and CBM of the 2D TMDC monolayer. As illustrated in Fig. 4(a), when the HOMO is above the VBM, holes from the TMDC transfer to the photochromic molecule. This reduces the hole concentration in the TMDC, which in turn reduces the exciton density and photoluminescence (PL) intensity. Similarly, if the LUMO is below the CBM, electrons from the TMDC jump to

the photochromic molecule, reducing the electron concentration and thus PL intensity of the TMDC (Fig. 4b). If both the HOMO and LUMO are between the VBM and CBM, there is a large reduction in the exciton density and PL intensity of the TMDC (Fig. 4c). However, if neither the HOMO nor LUMO are between the CBM and VBM, the excitation of holes and electrons across the TMDC's band gap is not affected (Fig. 4d). Thus, there is no change in the optical properties of the TMDC in this case. Given these situations, in order for a TMDC monolayer-photochromic molecule pair to exhibit successful photo-switchable properties, the response of one photochromic isomer should resemble Fig. 4(a)/4(b)/4(c) whereas the response of the other photochromic isomer should resemble Fig. 4(d).

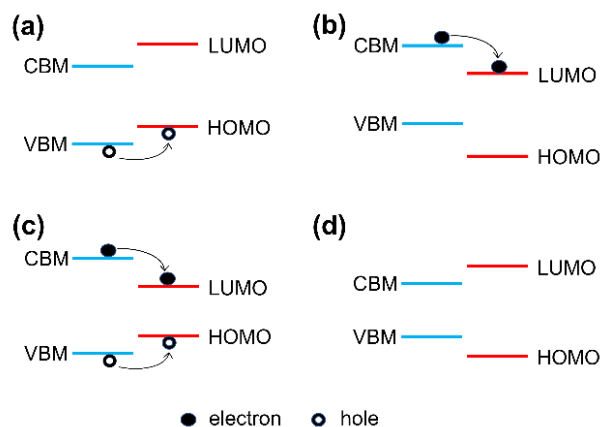


FIGURE 4: SCHEMATIC OF ELECTRON AND HOLE TRANSFER FROM TMDC TO MOLECULE. (A) HOLE, (B) ELECTRON, AND (C) BOTH HOLE AND ELECTRON TRANSFER TO MOLECULE. (D) NO CARRIERS TRANSFER.

If the HOMO or LUMO of both isomers of the photochromic molecule share the same relationship with respect to the band edges of the 2D TMDC monolayer, either between or outside the band gap, then there is no change in the optical response. A representation of this situation is shown in Fig. 5 with the MoS₂ monolayer and azobenzene. As can be seen in Fig. 5(a), the HOMO of trans-Azobenzene is above the VBM of MoS₂. The same is true when it is irradiated with UV light and becomes cis-Azobenzene (Fig. 5b). The HOMO of the cis-Azobenzene is still above the VBM of the MoS₂ monolayer. Since the HOMO stays above the VBM for both isomers, there is no change in the exciton density, and, thus, the optical properties of the MoS₂ monolayer.

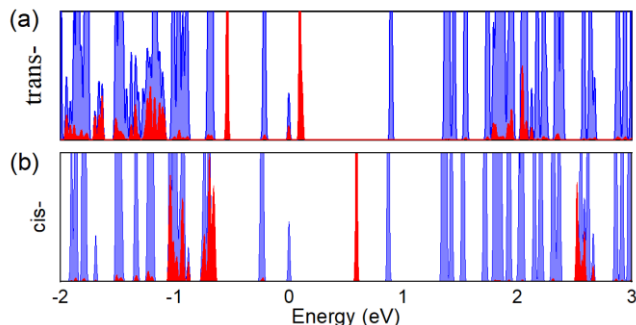


FIGURE 5: DENSITY OF STATES OF MoS2 MONOLAYER WITH AZOBENZENE AS EXAMPLE OF NON-PHOTO-SWITCHABLE BEHAVIOR. (A) MoS2 MONOLAYER (BLUE) WITH TRANS-AZOBENZENE (RED), (B) MoS2 MONOLAYER (BLUE) WITH CIS-AZOBENZENE (RED).

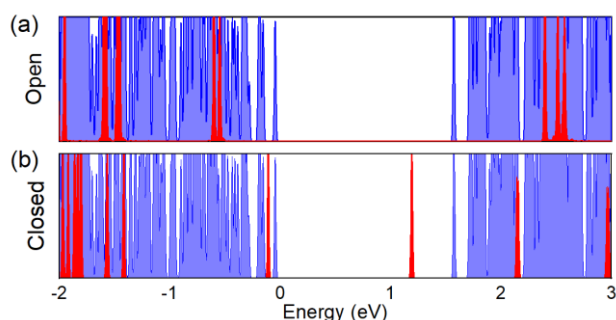


FIGURE 6: DENSITY OF STATES OF WSe2 MONOLAYER WITH DAE 5 ETHYL AS EXAMPLE OF PHOTO-SWITCHABLE BEHAVIOR BY ELECTRON TRANSFER. (A) WSe2 MONOLAYER (BLUE) WITH OPEN-DAE 5 ETHYL (RED), (B) WSe2 MONOLAYER (BLUE) WITH CLOSED-DAE 5 ETHYL (RED).

Comparatively, if the relative energy levels of the HOMO (LUMO) with respect to the VBM (CBM) of the 2D TMDC monolayer changes between isomers, there is a reduction in the optical response due to excitons in the TMDC monolayer transferring to the photochromic molecule. One representation of this situation is shown in Fig. 6.

As can be seen in Fig. 6(a), neither the HOMO nor LUMO of open DAE 5 ethyl fall between the band gap of WSe₂. However, there is a shift of the LUMO when the molecule is irradiated with UV light and becomes the closed isomer. Figure 6(b) shows the LUMO of the DAE 5 ethyl isomer (closed DAE 5 ethyl) below the CBM of WSe₂. Since the LUMO energy level of the closed DAE 5 ethyl is lower than the CBM, electrons from the WSe₂ monolayer travel to the photochromic molecule. As a result, the concentration of electrons in the WSe₂ monolayer decreases, and the optical response reduces due to the lower exciton density.

Another representation of successful photo-switchable behavior is shown in Fig. 7. As can be seen in Fig. 7(a), neither the HOMO nor LUMO of open DAE 2 ethyl fall between the band gap of WSe₂. However, when DAE 2 ethyl is irradiated with UV light, the HOMO of closed DAE 2 ethyl lies above the VBM of the WSe₂ monolayer. Consequently, holes transfer from the WSe₂ monolayer to closed DAE 2 ethyl, lowering the exciton density and decreasing PL intensity.

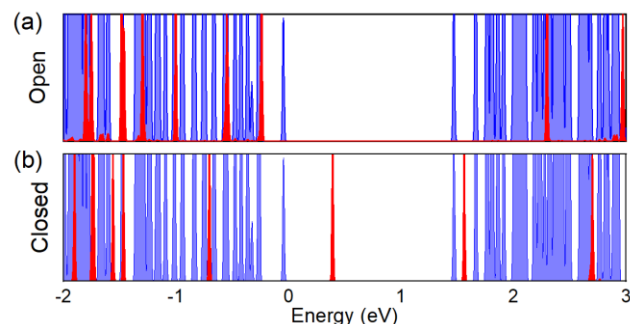


FIGURE 7: DENSITY OF STATES OF WSe2 MONOLAYER WITH DAE 2 ETHYL AS EXAMPLE OF PHOTO-SWITCHABLE BEHAVIOR BY HOLE TRANSFER. (A) WSe2 MONOLAYER (BLUE) WITH OPEN-DAE 2 ETHYL (RED), (B) WSe2 MONOLAYER (BLUE) WITH CLOSED-DAE 2 ETHYL (RED).

In some cases, a photochromic isomer has its HOMO while the other isomer has its LUMO in between the band gap of the 2D TMDC monolayer. Both isomers reduce the exciton density in the 2D TMDC. One decreases the concentration of holes, while the other decreases the concentration of electrons. Despite this switch, the optical response of the 2D TMDC would be reduced in both cases. However, if the HOMO (LUMO) for one isomer is close to the VBM (CBM) of the 2D TMDC, the likelihood of holes (electrons) transporting to the photochromic molecule is less likely. The small difference between energy levels is weaker at attracting the carriers to a slightly more relaxed energy state. This phenomenon is shown in Fig. 8. As can be seen in Fig. 8(a), the LUMO of open spiropyran is within the band gap of the WSe₂ monolayer, although it is close to the CBM. Conversely, in Fig. 8(b), the HOMO of closed spiropyran is within the band gap of the WSe₂ monolayer and clearly at a higher energy than the VBM. Therefore, the reduction of holes in the closed isomer would be more significant than the reduction of electrons in the open isomer. Due to this, the PL intensity of the closed isomer is expected to be less than that of the open isomer.

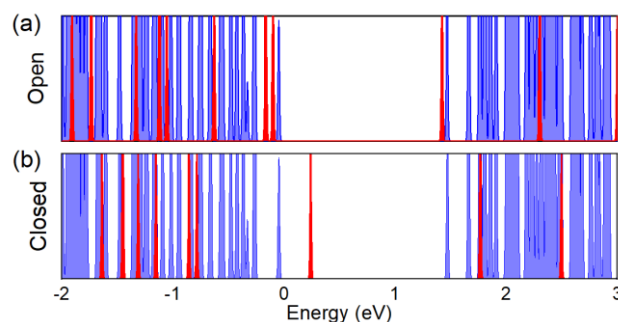


FIGURE 8: DENSITY OF STATES OF WSe2 MONOLAYER WITH SPIROPYRAN AS EXAMPLE OF PHOTO-SWITCHABLE BEHAVIOR FROM ELECTRON TRANSFER TO HOLE TRANSFER. (A) WSe2 MONOLAYER (BLUE) WITH OPEN SPIROPYRAN (RED), (B) WSe2 MONOLAYER (BLUE) WITH CLOSED SPIROPYRAN (RED).

All possible combinations of MoS₂ and WSe₂ based hybrid devices with the five photochromic molecules have been tested and tabulated in Table 1. The combinations with the LUMO level switching across the CBM through isomerization are photo-switchable by electron transfer to the photochromic molecule. Those with the HOMO level switching across the VBM are photo-switchable due to hole transfer.

There are six combinations that exhibit a strong controllability of exciton density via irradiation with UV or visible light. These successful hybrid devices include MoS₂-Spiropyran and every diarylethene derivative except MoS₂-DAE 5 methyl. As mentioned above, WSe₂-Spiropyran has the potential to exhibit photo-switchable behavior, although not to as great of a degree, because the LUMO of open spiropyran is only slightly lower than the CBM of WSe₂ (Fig. 8)

TABLE 1: CARRIER TRANSFER BETWEEN 2D TMDC MONOLAYERS AND PHOTOCHROMIC ISOMERS.

Hybrid combination	Isomers	Relative Energy Level	Photo-Switchability
WSe ₂ -Azobenzene	Trans-	LUMO between VBM & CBM	Not photo-switchable
	Cis-	HOMO between VBM & CBM	
MoS ₂ -Azobenzene	Trans-	HOMO between VBM & CBM	Not photo-switchable
	Cis-	HOMO between VBM & CBM	
WSe ₂ -Spiropyran	Closed	HOMO between VBM & CBM	Potentially photo-switchable (see Fig. 8)
	Open	LUMO between VBM & CBM	
MoS ₂ -Spiropyran	Closed	Outside VBM & CBM	Photo-switchable (hole transfer)
	Open	HOMO between VBM & CBM	
WSe ₂ -DAE 2 ethyl	Open	Outside VBM & CBM	Photo-switchable (hole transfer)
	Closed	HOMO between VBM & CBM	
MoS ₂ -DAE 2 ethyl	Open	HOMO between VBM & CBM	Photo-switchable (hole transfer)
	Closed	Outside VBM & CBM	
WSe ₂ -DAE 5 ethyl	Open	Outside VBM & CBM	Photo-switchable (electron transfer)
	Closed	LUMO between VBM & CBM	
MoS ₂ -DAE 5 ethyl	Open	Outside VBM & CBM	Photo-switchable (hole transfer)
	Closed	HOMO between VBM & CBM	
WSe ₂ -DAE 5 methyl	Open	Outside VBM & CBM	Photo-switchable (electron transfer)
	Closed	LUMO between VBM & CBM	
MoS ₂ -DAE 5 methyl	Open	HOMO between VBM & CBM	Not photo-switchable
	Closed	HOMO between VBM & CBM	

4. CONCLUSION

A numerical study has been performed to test the possibility to control the optical property of 2D TMDC monolayers with photochromic molecules. It has been found that MoS₂-Spiropyran and every diarylethene derivative except MoS₂-DAE 5 methyl exhibit photo-switchable behavior. WSe₂-Spiropyran could exhibit photo-switchable behavior, but it would be weak. This result provides the list of possible combinations that can be used in the development of photo-switchable optoelectronic devices.

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