Changes in electronic and optical characteristics of halogen–alkali adsorbed WSe$_2$ monolayer

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ABSTRACT

Adsorbing halogen and alkali metals atoms modify the optical and electrical characteristics of WSe$_2$ monolayer (2D). The electrical and optical characteristics of the Wse$_2$ monolayer, alkali and halogen atoms adsorbed WSe$_2$ structures are investigated through density functional theory (DFT) simulations. The pristine WSe$_2$ monolayer has insignificant absorption in the infrared and most parts of the visible region, and substantial absorption in the ultraviolet (UV) region (λ < 410 nm) as well as in a small section of the visible spectrum. The absorption coefficient of alkali–halogen adsorbed structures of WSe$_2$ seems to expand with wavelength, and absorption peaks move toward the higher energy region of the optical spectrum, resulting in redshift effect. Significant absorption is observed in the entire visible spectrum (≈ 410 to 780 nm) for both alkali and halogen adsorbed WSe$_2$ nanostructures. The chlorine, bromine, and iodine adsorbed WSe$_2$ structure shows larger absorption in the entire visible region among all other adsorbed structures. Presence of absorption peaks in the visible range of wavelengths rather than in the UV region, is beneficial for optoelectronic applications such as LEDs, CRTs, solar cells, and sensors. Trends in computed dielectric constant and refractive index values are also found to be compatible with trends in absorption coefficient values.

1 Introduction

Researchers are particularly interested in two-dimensional (2D) monolayer graphene because it has unique and outstanding properties that may be used in a broad range of applications, including optoelectronics and nanoelectronics [1]. Researchers have investigated transition metal dichalcogenides (TMDCs) and other 2D materials with unique properties since then. For decades, TMDCs have been considered among the most potential material for a wide range of applications [2, 3], as their electrical and optical characteristics are particularly promising for a wide variety of applications due to their remarkable performance at monolayer thickness. The first-row transition metal chalcogenides (Molybdenum) has already emerged as a critical material for researchers due to their unique characteristics that differ from graphene and their elemental abundance. Second-row transition metal chalcogenides
(tungsten) have also shown remarkable characteristics in the chalcogenides structure, although heavier transition metal dichalcogenides have garnered less attention so far. Selenium (Se) is an emerging star in the chalcogen family because of its low cost and excellent electrical conductivity. The interaction energies of heavier chalcogens are lower since the distance between the metal atoms is longer. Heavier transition metals allow for further manipulation of the 2D structure to influence material characteristics [4]. The greater W (tungsten) size of tungsten dichalcogenides has lately attracted a lot of attention because it can change the 2D structure. Despite being a heavier metal, W has a natural abundance which is comparable to Mo [5].

The inorganic compound tungsten diselenide (WSe2) relates to the group VI TMDCs and is a stable semiconductor. Similar to molybdenum disulfide (MoS2), it has a hexagonal crystalline structure. As in a trigonal prismatic coordination sphere, a tungsten atom is covalently bound to six selenium ligands, whereas three tungsten atoms are covalently bonded to a selenium ligand as in a pyramidal geometry.

A WSe2 monolayer is made up of a tightly bonded Se-W-Se pack that is stacked weakly with adjacent layers. The WSe2 has absorption peaks at the value of 1.592 eV of photon energy and in visible frequency spectrum. It has the potential to be a contender in emerging valleytronics, spintronics, and optical devices due to its ability to isolate carriers in spin-valley linked systems. At the monolayer and bulk levels, the WSe2 has distinct characteristics. Bulk WSe2 exhibits an indirect bandgap, which widens as the monolayer thickness increases [6].

The electronic characteristics of monolayer WSe2 differ from those of graphene, which have a wide insulator type bandgap. Due to wide bandgap in graphene, it is seldom utilized in optoelectronic applications, whereas TMDCs are an excellent material for optoelectronic applications since monolayers of all transition metal dichalcogenides have direct as well as indirect bandgaps which may be changed by varying the number of layers and size [7–10].

In many applications, WSe2 and MoSe2 offer significant benefits, while WSe2 as a comparable option has received less attention. The electronic structure and preference of WSe2 are its most distinguishing characteristics when compared to other TMDCs [11, 12]. WSe2 monolayer photoelectrodes can be exploited in electrochemical solar cells because they are adaptable in both acidic and basic environments [13–15]. WSe2 has also demonstrated good photocatalytic capabilities [16], an n-type WSe2 photoelectrode to electrolyze HI, forming H2 and HI3 [17]. Tungsten dichalcogenide (WSe2) is a rising star in the TMDC family, and has been effectively used in a range of applications such as photodetectors [18–20] and field-effect transistors (FETs) [21–27].

Alkali-metal and halogen adsorbed semiconductors have piqued the curiosity of researchers for decades [28–39] as essential building blocks for semiconductors with adjustable optical characteristics. On adsorbing alkali and halogens, optical characteristics change in tandem with electronic properties. It’s crucial to look at the changes in WSe2 optical characteristics on alkali and halogen.

Adsorption of halogen atoms like Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), Astatine (At), and Alkali metal atoms like Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Ru), and Cesium (Cs) on monolayer WSe2 have been found to modify its electronic and optical characteristics. Density-functional theory (DFT) has been accustomed to investigate the optical and electronic characteristics of pristine monolayer WSe2 and alkali–halogen adsorbed monolayer WSe2 structures.

2 Computational details

Using ab initio estimation based on DFT, the optical and electrical characteristics of suggested nanostructures have been evaluated. This is used to estimate the lattice structure, molecules, surfaces, crystal representations, and their potential interactions.

The Perdew–Burke–Ernzerhof (PBE) function is utilized to quantify the exchange–correlation energy in DFT calculations [40, 41]. To optimize the geometry, generalized gradient approximation (GGA) and Monkhorst–Pack were used to sample 15 × 15 × 1 K points with cutoff mesh energy fixed at 120 Rydberg [42]. The DFT and meta-GGA [43] are used to predict electronic bandgap structure, dielectric, and optical absorption characteristics using the Atomistic Tool Kit (ATK) software [44]. The information regarding homogeneity of the density gradient and the electron density is included in the exchange–correlation functional associated with the GGA. Figure 1 illustrates all optimized geometries investigated, while
Table 1 lists the average bond length. To investigate the bandgap, we described 95 spots per section, with an optical spectrum widening value of 0.01 eV.

The susceptibility tensor, $\chi(\omega)$, is computed by using the Kubo–Greenwood formalism [45, 46] as:

$$
\chi_{ij}(\omega) = -\frac{e^2 \hbar^4}{\epsilon_0 m^2 \omega^2 V} \sum_{nm} \frac{f(E_m) - f(E_n)}{E_{nm} - \hbar \omega - i \Gamma_{nm} \pi_{nm}}
$$
where $\Gamma$, $V$ and $f$ are the broadening, volume and Fermi function, and $\pi_{mn}^i$ is the $i$th element of the dipole matrix constituent within states $m$ and $n$.

Susceptibility is related to polarizability, $\alpha$, and relative dielectric constant, $\varepsilon_r$, expressed as:

$$\chi(\omega) = V\varepsilon_0 \chi(\omega),$$

$$\varepsilon_r(\omega) = (1 + \chi(\omega)),$$

The optical conductivity, $\sigma$ is expressed as [47]:

$$\sigma(\omega) = -i\omega\chi(\omega)$$

As a function of the refractive index, $\eta$, and extinction coefficient, $\kappa$, the relative dielectric constant, $\varepsilon_r$, is calculated:

$$\eta + i\kappa = \sqrt{\varepsilon_r}$$

The refractive index, $\eta$, and the extinction coefficient, $\kappa$, are functions of the dielectric constants' real, $\varepsilon_1$, and imaginary, $\varepsilon_2$, parts, which are given as:

$$\kappa = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}}$$

$$\eta = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}{2}}$$

The optical absorption coefficient, $\alpha$, is directly related to the extinction coefficient, $\kappa$, as follows [48]:

$$\alpha = \frac{2\omega\kappa}{c}$$

where $\omega$ and $c$ represent frequency and speed of light, respectively.

In order to implement effectual and suitable nanostructures within the context of proposed study, the structural properties of base pristine WSe$_2$ and halogen–alkali atoms adsorbed WSe$_2$ nanostructures are investigated. Figure 1 depicts optimized super-cell geometries of a $3 \times 1 \times 1$ of adsorbed nanostructures.

The in-plane lattice parameters of pristine WSe$_2$ monolayer with lattice constant $\sim 3.205$ Å, and the average bond length $\sim 2.526$ Å are consistent with previous findings [49, 50]. The results of the investigation on adsorbed WSe$_2$ structures with all possible Alkali and Halogen elements are presented, along with results of binding energy computations for experimental monolayer stability, dielectric constant, refractive index, absorption index estimation for optical properties and band structure assessment for electronic properties (see Figs. 2, 3, 4 and 5).

### Results and discussion

As shown in Fig. 1, each proposed structure has been relaxed using the LBFGS geometry optimization algorithm [51] while ensuring that each atom has a residual force less than the value of 0.05 eV/Å. The average bond lengths of the optimized structures are shown in Table 1.

The imaginary dielectric constant and refractive index are plotted with relation to energy in Figs. 3 and 5, whereas the absorption coefficient plotted against wavelength and energy is shown in Fig. 4 for each pristine and adsorbed WSe$_2$ nanostructure. Analyzing optical transmission data yielded the optical absorption coefficient spectra. Figure 4 shows a plot of the absorption coefficient for adsorbed WSe$_2$ nanostructures, indicating that the optical absorption spans across the entire visible spectrum.

| Structures         | Average bond distance with W(Å) | Average bond distance with Se(Å) |
|--------------------|---------------------------------|---------------------------------|
| WSe$_2$ monolayer  | 2.5261                          | 2.5261                          |
| Li adsorbed WSe$_2$| 2.6619                          | 2.2031                          |
| Na adsorbed WSe$_2$| 2.1799                          | 2.3560                          |
| K adsorbed WSe$_2$ | 1.8760                          | 2.4035                          |
| Rb adsorbed WSe$_2$| 3.7642                          | 2.4698                          |
| Cs adsorbed WSe$_2$| 3.6684                          | 2.3745                          |
| F adsorbed WSe$_2$ | 1.8986                          |                                  |
| Cl adsorbed WSe$_2$| 2.0364                          | 2.1042                          |
| Br adsorbed WSe$_2$| 2.0657                          | 2.4328                          |
| I adsorbed WSe$_2$ | 2.1160                          | 2.1582                          |
| At adsorbed WSe$_2$| 2.1616                          | 2.3784                          |
We calculated the binding energies (B.E.) of alkali–halogen atoms adsorbed WSe₂ nanostructures to test their stability which are characterized by $E_B = \frac{(E_{\text{adsorbed}} - (E_{\text{Pristine monolayer}} + E_{\text{alkali/halogen}}))}{N}$, where $E_{\text{adsorbed}}$, $E_{\text{Pristine monolayer}}$ and $E_{\text{alkali/halogen}}$ represents the total energies of adsorbed nanostructure, pristine WSe₂ monolayer and halogens/alkali atoms, respectively, and $N$ represents how many atoms are in an adsorbed nanostructure. For stable adsorbed structure, the binding energies should be as low as possible. The calculated binding energies per atom for Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), and Astatine (At) atoms adsorbed WSe₂ are 123 eV, 197 eV, 120 eV, 122 eV, 130 eV, 438 eV, 343 eV, 360 eV, 266 eV, and 1451.62 eV, respectively. All structures attained negative binding energies during the experiment, demonstrating structural stability. Based on the amount of negative energy, it follows that the resulting adsorbed structures have high Vander-Waals-forces of molecular attraction.

### 3.1 Electronic properties

Figure 2 depicts the electronic band structure of a pristine WSe₂ monolayer. The Brillouin-zone route is represented as A–C–B–Γ–Y–X–Z–L as a representation of the unit cell’s symmetrical points. At the Γ’–Γ’ point, the conduction band minimum (CBM) and valence band maximum (VBM) are located, which indicates a direct bandgap of 1.769 eV as well as an indirect bandgap of 1.589 eV, which is in consistent with our results reported in [6]. Dielectric values presented in Fig. 3 demonstrate that the bandgap in alkali–halogen adsorption monolayer has metallic features with negligible bandgaps. A low conduction band minimum (CBM) and a high valence band maximum (VBM) distinguish n-type (Alkali) adsorption for WSe₂ from p-type (Halogen) adsorption. Optical absorption is determined by inter-band electronic transitions. The electronic inter-band transition between occupied and unoccupied states in semiconductor occurs as a result of photon-electron interaction. Electrons enter the conduction band of semiconductors with high absorption coefficients following the absorption of photons.

### 3.2 Optical properties

There are two parts of the dielectric constant: a real and an imaginary portion (see Fig. 3). The dielectric constant illustrates a dielectric material’s efficiency in terms of energy storage. When light passes through a structure, its dielectric constant describes how it interacts with it. A dielectric constant’s imaginary part ($\varepsilon_2$) is utilized to calculate charge excitation-based energy absorption in nanostructures, while the real part ($\varepsilon_1$) is used to resolve anomalous dispersion and polarization effects.

It is crucial to estimate the optical absorption of 2D structure from the imaginary components of the observed dielectric function displayed along with $xx$, $yy$, and $zz$ directions of structures as illustrated in Fig. 3 [35]. Consequently, only $xx$-dimensional plots of imaginary components are examined, from which results for the other two directions can also be obtained. For pristine monolayer WSe₂, absorption threshold at 1.75 eV and a peak is obtained between 2 and 3 eV with the strongest one at ~ 2.56 eV, as shown in Fig. 4a. The dielectric peaks can be analyzed similarly for other adsorbed nanostructures as shown in Fig. 3. The majority of adsorbed structures have dielectric peaks between 0 and 1 eV. Combined with the decrease in binding energies of excitons in the system, the dielectric function peaks indicate that absorption may take place in the system. Alkali metals and halogen adsorbed WSe₂ nanostructures.
Fig. 3  Plot of imaginary dielectric function ($\varepsilon_2$) for adsorbed WSe$_2$ with atoms of
a Pristine WSe$_2$, b lithium, c sodium, d potassium, e rubidium, f cesium, g fluorine, h chlorine,
i bromine, j iodine, k astatine
Fig. 4 Plot of absorption coefficient ($\alpha$) w.r.t. energy and wavelength for adsorbed WSe$_2$ with atoms of a Pristine WSe$_2$, b lithium, c sodium, d potassium, e rubidium, f cesium, g fluorine, h chlorine, i bromine, j iodine, k astatine
Fig. 5 Plot of Refractive Index w.r.t. energy across the $xx$, $yy$ as well as $zz$ tensors for adsorbed WSe$_2$ with atoms of
a Pristine WSe$_2$, b lithium, c sodium, d potassium, e rubidium, f cesium, g fluorine, h chlorine, i bromine, j iodine, k astatine
were studied as functions of energy and wavelength. The electronic bandgap structure, dielectric function, absorption coefficient and refractive index were calculated and are plotted in Figs. 2, 3, 4 and 5, respectively. We obtained the optical absorption coefficient spectrum by analyzing optical transmission measurements. According to Fig. 4, the absorption coefficient for both halogen-adsorbed WSe₂ nanostructures and alkali metal-adsorbed WSe₂ nanostructures expands over the entire visible spectrum.

The photon energy and the dielectric constant define the absorption coefficient. Photons are absorbed by semiconductors with a high absorption coefficient, causing electrons to enter the conduction band.

The absorption threshold for Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), and Astatine (At) atoms adsorbed WSe₂ is shown in Fig. 4, which begins at ~ 0 eV and reaches its maximum value at 2.952 eV, 3.082 eV, 2.923 eV, 2.662 eV, 3.12 eV, 2.652 eV, 1.75 eV, 2.56 eV, 1.95 eV and 2.09 eV, respectively. Alkali-adsorbed WSe₂ monolayers exhibit a higher value of absorption coefficient at lower photonic energies, whereas halogen-adsorbed WSe₂ monolayers exhibit comparatively low value of absorption coefficient at higher photonic energy.

Pristine WSe₂ monolayers absorb strongly over the entire UV region as well as the blue region of the visible spectrum, and weakly in another area of the visible spectrum as well as the entire IR region. Figure 4a shows that the absorption coefficient of WSe₂ monolayer has negligible change in the range 0–1.8 eV of energy, and then starts to increase with increasing photon energy within window of 1.8–5 eV and achieve peak within the range 3–3.2 eV of energy.

The K, F, Cl, Br, I, and At adsorbed structures displayed a shift in the absorption peak toward the higher energy of the spectrum as seen in the plot for absorption coefficient in Fig. 4, whereas the remaining structures showed peaks at lower energies. Blueshifts occur in structures adsorbing Li, Na, and Cs atoms, with absorption peaks shifting toward lower energies, whereas redshifts occur in remaining adsorbed structures with absorption peaks shifting toward higher energies in the absorption spectrum.

The adsorbed WSe₂ structures with chlorine, bromine, and iodine have a much wider spectrum range indicating stable absorption in the visible part of the spectrum as represented in Fig. 4h–j, respectively. The optical absorption peaks in all adsorbed nanostructures are lower than that in pristine WSe₂, although it is significant to mention that the absorption is dispersed over the whole visible region, which is needed for optoelectronics applications. For adsorbed WSe₂ structures with sodium and cesium, the absorption remains almost the same as in pristine WSe₂ as shown in Fig. 4c and f.

Additionally, the xx and yy tensors in K, Cs, Cl, Br, I, and At adsorbed WSe₂ structures nearly overlap, with zz remaining distinct. This validates the isotropic/anisotropic property of these adsorbed structures [52]. The dielectric constants (ε₁, ε₂) have been used to determine the refractive index as in given Eq. (6) for all pristine and adsorbed structures considered. As presented in Fig. 5, the refractive index (η) is computed with respect to the photon energy for all structures along with the xx, yy, and zz direction. For pristine WSe₂ monolayer, the refractive index increases with energy between 0 and 2.1 eV. The adsorbed WSe₂ structures have a peak value of refractive index peaks in the range of 0–0.5 eV. There is a correlation between the peak value of refractive index and the dielectric constant (as shown in Figs. 3 and 5) indicating that the refractive index follows patterns in the dielectric constant as well as the absorption coefficient. Large absorption would be stimulated in regions with high refractive indices, implying that light would be confined for a significantly longer amount of time, which in turn would enhance photon absorption in that spectral range.

A lower absorption would lead to a lower refractive index, as would be predicted by the dielectric function (ε₂). The deterioration in the value of refractive index with photon energy indicates that the adsorbed WSe₂ structures are dispersed normally.

### 4 Conclusion

DFT simulations have been used to explore electronic structure and optical characteristics for WSe₂ monolayer adsorbed with alkali metal (Lithium, Sodium, Potassium, Rubidium, and Cesium) and halogen atoms (Fluorine, Chlorine, Bromine, Iodine, and Astatine). The adsorbed WSe₂ structures exhibit...
optical absorption heights that move significantly toward the visible spectrum region. By adding alkali metal atoms and halogen atoms, the optical absorption peak of WSe$_2$ monolayer adjusted toward the visible range and opening wide applications in optoelectronic devices.

**Author contributions**

MT was involved in formal analysis, writing original draft, developed the theoretical formalism and performed the analytic calculations and the numerical simulations. SC was involved in supervision. Both authors discussed the results and commented on the manuscript and contributed to the final version of the manuscript.

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**Data availability**

All data generated and analyzed during this study are included in this published article in the form of plots and its supplementary information files. The raw/detailed datasets generated during the current study are available from the corresponding author on request.

**Declarations**

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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